

**Development and Evaluation of Cathodic Arc Physical
Vapor Deposition (PVD) Coated Friction Stir Welding
(FSW) Tools**

BY

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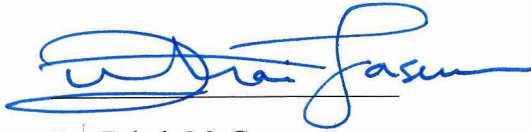
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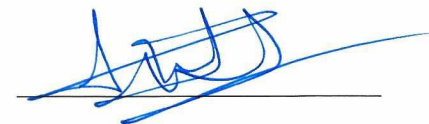
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DEDICATION

قُلْ إِنِّي هَدَانِي رَبِّي إِلَى صِرَاطٍ مُسْتَقِيمٍ دِينًا قِيَمًا مِلَّةَ إِبْرَاهِيمَ حَنِيفًا ۚ وَمَا كَانَ

مِنَ الْمُشْرِكِينَ ﴿١٦١﴾

قُلْ إِنَّ صَلَاتِي وَنُسُكِي وَمَحْيَايَ وَمَمَاتِي لِلَّهِ رَبِّ الْعَالَمِينَ ﴿١٦٢﴾

لَا شَرِيكَ لَهُ ۚ وَبِذَلِكَ أُمِرْتُ وَأَنَا أَوَّلُ الْمُسْلِمِينَ ﴿١٦٣﴾

(161) Say (O Muhammad صلى الله عليه وسلم): "Truly, my Lord has guided me to a Straight Path, a right religion, the religion of Ibrahim (Abraham), Hanifa [i.e. the true Islamic Monotheism - to believe in One God (Allah i.e. to worship none but Allah, Alone)] and he was not of Al-Mushrikun."

(162) Say (O Muhammad صلى الله عليه وسلم): "Verily, my Salat (prayer), my sacrifice, my living, and my dying are for Allah, the Lord of the 'Alamin (mankind, jinn and all that exists).

(163) "He has no partner. And of this I have been commanded, and I am the first of the Muslims."

Sooratul-An'aam, 161 – 163

Translation: Taqi-ud-Din Al-Hilali & Muhsin Khan

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LIST OF ABBREVIATIONS

AAC: Aluminum Alloys and Composites	AEGD: Arc-Enhanced Glow Discharge
AE: Acoustic Emission	APA: Arc Assisted Plasma
AFM: Atomic Force Microscope	AlCrN: Aluminum Chromium Nitride
AlTiN: Aluminum Titanium Nitride	Al: Aluminum CA: Cathodic Arc
COF: Coefficient of Friction	Co: Cobalt
Cr: Chromium	CrN: Chromium Nitride
CrAlN: Chromium Aluminum Nitride	CVD: Chemical Vapor Deposition
CRPs: Scratch Crack Propagation Resistance	E: Elastic Modulus
EDS: Energy Dispersive Spectroscopy	H: Hardness
EIS: Electrochemical Impedance Spectroscopy	HAZ: Heat Affected Zone
FSW: Friction Stir welding	HSS: High Speed Steel
HfC: Hafnium Carbide	<i>L_{c1}</i>: Lower Critical Load
HIP: Hot Isostatic Press	<i>L_{c2}</i>: Upper Critical Load
LPR: Linear Polarization Resistance	MMC: Metal Matrix Composites
MA: Mechanical Alloying	N: Nitrogen
PDP: Potentiodynamic Polarization	PVD: Physical Vapor Deposition
OCP: Open Circle Potential	Re: Rhenium
RPM: Revolution Per Minute	Si: Silicon
SiC: Silicon carbide	SEM: Electron Scanning Microscope
SPS: Spark Plasma Sintering	Ti: Titanium
TiN: Titanium Nitride	TiAlN: Titanium Aluminum Nitride
THAZ: Thermomechanically Heat Affected Zone	W: Tungsten
WC: Tungsten Carbide	XRD: X-Ray Diffraction

ABSTRACT

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Thesis Title : [Development and Evaluation of Cathodic Arc Physical Vapor Deposition (PVD) Coated Friction Stir Welding (FSW) Tool]

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Because of the combined effect of high frictional heat generated and extensive plastic deformation required to create the weld during friction stir welding (FSW) process, the tool is subjected to severe wear and deformation. This often leads to severe wear and tool failure and thus high production cost. Efforts have been exerted to develop tools with enhanced properties especially for FSW of engineering alloys and composites where the tool wear and deformation are extremely high. However, wear and chemical dissolution of the tool into the joint as well as the high cost have limited their use. Coating of FSW tool has been considered as a viable and more economical approach. This dissertation aimed to develop and to evaluate the performance of nitride-based cathodic arc physical vapor deposited (PVD) coatings on the wear resistance of FSW tool during welding of a commercial aluminum alloy and a particulate-reinforced aluminum composite. State-of-the-art cathodic arc PVD machine was employed to deposit micro-alloyed nitride-based (TiN, CrN, AlCrN, TiAlN) coatings. Characterization techniques including X-ray diffraction, scanning electron microscope, energy dispersive spectroscopy, mechanical, tribological and corrosion analysis tests were used to evaluate and study the properties of these coatings. Promising cathodic-arc PVD coatings were then selected for coating FSW tools.

The coated tools were employed in RM-1 friction stir welder for joining 6061-T6 aluminum alloy and AA 2124-17% SiC composite.

Characterization and test results showed that all applied coatings enhanced the surface properties of their respective substrate. However, ternary coatings (AlCrN and TiAlN) exhibited markedly improved mechanical and tribological properties compared to the binary (TiN and CrN) coatings. In-situ isothermal oxidation test in air at different temperatures (800 – 1000 °C) revealed that the ternary coatings displayed higher thermal stability and the oxidation rates were in the order of $\text{TiN} > \text{CrN} > \text{TiAlN} > \text{AlCrN}$.

The ternary coatings were applied on specially designed and fabricated FSW tools using 4140 steel alloy for the welding process of 6 mm thick 6061-T6 aluminum alloy. The results revealed that the AlCrN coated FSW tool improved the dimension stability of the pin due to improved surface properties. About 10% variation in pin length was observed for the uncoated FSW tool as compared to the coated tool with negligible pin length variation. Furthermore, AlCrN and TiAlN cathodic arc PVD coatings were deposited on hardened H13 tool steel for FSW of 8 mm thick A2124/SiC/17p MMC. Significant improvement in the wear resistance of coated FSW tools was observed. AlCrN and TiAlN coated H13 tools demonstrated about 92% and 80% reduction in the wear rate, respectively, compared to bare H13 tool. The dominant wear mechanisms observed in AlCrN and TiAlN coated tools were abrasive erosion and chipping-off of the coating by sharp hard SiC particles. Severe striation characterized the wear mechanism of the bare H13 tool.

This study has shown the contribution of the use of ternary nitride coatings in enhancing the performance of FSW tools, weld quality, and tool life in joining an aluminum alloy and

an aluminum composite using an experimental scale FSW process. Further study is needed to investigate the economic benefits of coating FSW tools employed at a commercial scale.

ملخص الرسالة

بسبب التأثير المشترك للحرارة العالية الناتجة عن الاحتكاك والتشوه البلاستيكي الكبير اللازم لإجراء عملية اللحام بطريقة الاحتكاك التحركي (FSW)، فإن الأدوات المستخدمة تخضع للتآكل الشديد والتشوه مما يؤدي إلى تدهور قدرتها لصنع وصلات اللحام وارتفاع تكاليف الإنتاج. بذلت جهود عديدة لتطوير أدوات من مواد ذات خصائص معززة خاصة لتطبيقات اللحام بالاحتكاك والتحرك من السبائك الصلبة والمواد المركبة ولكن اهتراء الأداة وتحللها الكيميائي في وصلات اللحام والكلفة العالية قد حد من استخدامها على نطاق واسع. هناك محاولات معدودة لاستخدام طلاءات شديدة القساوة لحماية أدوات اللحام بالاحتكاك والتحرك مما يعتبر خياراً أكثر اقتصادياً. تهدف هذه الأطروحة إلى تطوير وتقييم أداء طلاءات الغاز الفيزيائي الكاثودي الرسوبي (PVD) على مقاومة التآكل لأداة اللحام بالاحتكاك والتحرك أثناء لحام سبائك الألومنيوم المركبة. تم استخدام آلة PVD القوسية الكاثودية الحديثة لتغليف طلاءات من مركبات النيتريد (TiN، CrN، AlCrN، TiAlN). تم استخدام عدة طرق تحليلية، مثل حيود الأشعة السينية، ومجهر المسح الإلكتروني، والتحليل الطيفي المشتت للطاقة، والاختبارات الميكانيكية، والاحتكاك، والتآكل، لتقييم ودراسة خصائص هذه الطلاءات. تم استخدام الأدوات المغلفة في لحام سبائك الألومنيوم T6-6061 ومركب 17% SiC 2124-A باستخدام آلة اللحام بالاحتكاك والتحرك RM-1. أظهرت نتائج الاختبارات أن جميع الطلاءات عززت خصائص سطوح العينات كما أظهرت الطلاءات الثلاثية (TiAlN و AlCrN) خصائص ميكانيكية وخصائص محسنة مقارنةً بالطلاءات الثنائية (TiN و CrN). كما أظهر اختبار الأكسدة الحرارية عند درجات حرارة مختلفة أن الطلاء الثلاثي يمتلك ثباتاً حرارياً أعلى وأن معدل الأكسدة يكون في الترتيب التالي من الأقل إلى الأعلى: TiN > CrN > TiAlN > AlCrN. تم اختيار الطلاءات الثلاثية على أدوات اللحام بالاحتكاك والتحرك في لحام سبائك الألومنيوم T6-6061 بسماكة 6 مم وكشفت أن الأداة المغلفة ب AlCrN تمتلك مقاومة معززة للتشوه والاهتراء بسبب الخصائص السطحية المحسنة. تم تحقيق انخفاض حوالي 55 ٪ في التآكل والتشوه مع استخدام الأداة المغلفة بالمقارنة مع الأداة غير المطلية والمصنوعة من سبائك الفولاذ 4140. علاوة على ذلك، أظهرت الأدوات المصنوعة من سبائك الفولاذ H13 والمغلفة ب

TiAlN و AlCrN انخفاض في معدل التآكل حوالي 92 ٪ و 80 ٪ ، على التوالي عند لحام سبائك الألومنيوم المدعمة ب جزئيات كربيد السليكون A2124 / SiC / 17p MM بسمك 8 مم بالمقارنة بالأداة الغير مطلية. ان آليات التآكل المهيمنة على أدوات المغلفة ب AlCrN و TiAlN هي التآكل الكاشطة والتقطيع و ذلك بسبب جسيمات صلبة حادة من SiC، في حين الاهتراء الحاد للأداة الغير مغلفة ظهر بشكل أخايد.

أظهرت هذه الدراسة مساهمة الطلاء الثلاثي في تعزيز أداء أدوات FSW وجودة اللحام لسبائك الألومنيوم ومولف الألومنيوم باستخدام عملية FSW تجريبية. هناك حاجة إلى مزيد من الدراسة للتحقيق في الفوائد الاقتصادية من طلاء أدوات FSW المستخدمة على نطاق تجاري.

CHAPTER 1

INTRODUCTION

This chapter provides the background to this dissertation. It briefly introduces physical vapor deposition and friction stir welding processes. The tool wear challenge faced by FSW tools and the potential of hard protective PVD coatings in abating this problem are briefly described.

1.1 Physical Vapor Deposition

Physical vapor deposition (PVD) is a process of depositing coating under vacuum by condensation from the flux of neutral or ionized atoms of metals, also referred to as plasma. The atoms of the metal are physically removed from a target source through evaporation, sputtering of the target or a combination of both. These atoms are then transported energetically towards the substrate where they condense as a film on the surface of the substrate. Reactive gases such as nitrogen, oxygen, hydrocarbons etc. are usually introduced into the vacuum chamber to react with the target material to form a compound coating. PVD is broadly divided into sputtering, evaporation and hybrid PVD processes. Sputtering is a non-thermal process where vaporization of atoms is achieved by physical bombardment of the target using highly energetic gaseous ions or plasma. This can be achieved by ion beam or magnetron (either by direct current or radio frequency) process. Evaporation is subdivided into resistive, induction, electron beam, or arc (anodic or cathodic, DC or AC mode) depending on the means used in evaporating the target. Arc evaporation is a thermal vaporization process where the atoms are ejected by heating the

cathode target (as in cathodic arc) with a high energy arc that moves rapidly over the cathodic surface [1,2]. Both arc evaporation and sputtering processes (schematized in Figure 1) enable vaporization of metals with different melting temperatures, however, in arc evaporation the plasma produced is highly ionized and are of supersonic velocity corresponding to around 20 and 200 eV for light and heavy metals, respectively [3,4]. The focus of this study will be on cathodic arc PVD (CA-PVD) technique since it was utilized in the deposition of the coatings under consideration.

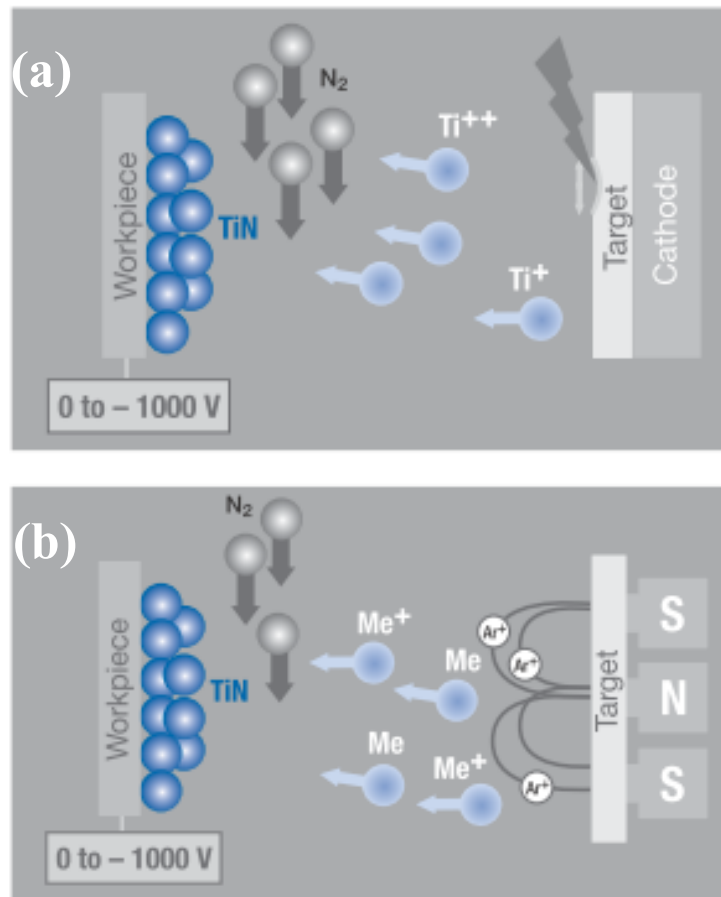


Figure 1-1: Schematic view of PVD (a) arc and (b) sputtering processes [5].

1.2 Cathodic Arc PVD Technique

Cathodic arc PVD technique is among the most versatile deposition techniques which have been used increasingly in a wide range of applications for depositing tribologically enhanced hard coatings [6]. The history of cathodic arc is dated to the 18th century and detailed development of the process can be found in the literature [2,7,8]. Sequel to the potentials of the process, significant development of the process and research have been conducted to further avail its merits. In coating technology, the deposition process is principal to the coating properties. In cathodic arc PVD, the arc is created by means of a high current and low voltage ignition plasma between the cathode (target material) and the anode (sometimes chamber wall). Interrupted arc, laser evaporation or high-voltage flashover arc among other methods are used in generating the ignition plasma [5], however, physical intermittent contact with the cathode by a mechanically triggered electrode held at anode potential is commonly utilized [2,3]. This generates a stream of electrons of 10 - 100 A which flows through the surface of the cathode thus locally melting the surface. The evaporated material of the cathode is a plasma of high ionization between 20 to 100 % depending on the melting temperature of the target. The atoms and ions are emitted alongside with droplets which are tiny globules of the target material between 100 nm and 10 μm in size [5]. The emitted cathode material leaves a crater on the surface of the cathode as shown in Figure 1-2. The tendency of the arc to conduct current makes it possible for the cathode spot to be influenced by applying an electromagnetic field to rapidly move the arc over the entire surface of the cathode in order to achieve uniform depletion with time. A typical configuration for a cathodic arc deposition system is shown in Figure 1-3. The high-

power density of the arc results in the highly ionized, multiple charged ions, atoms and macro particles.

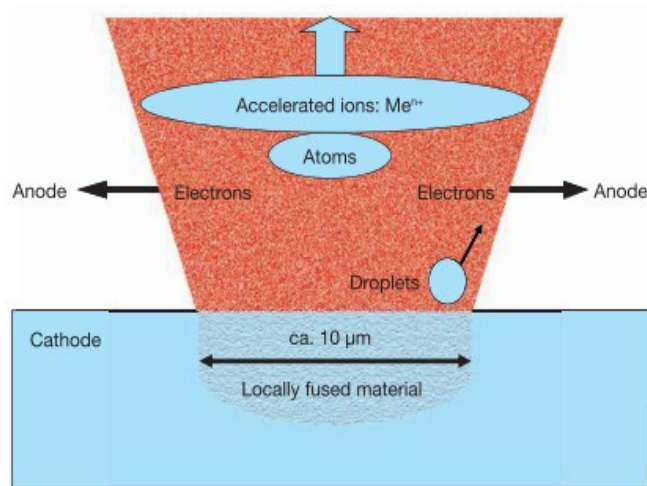


Figure 1-2: Schematic view of the Arc PVD process at the cathode showing the crater [5].

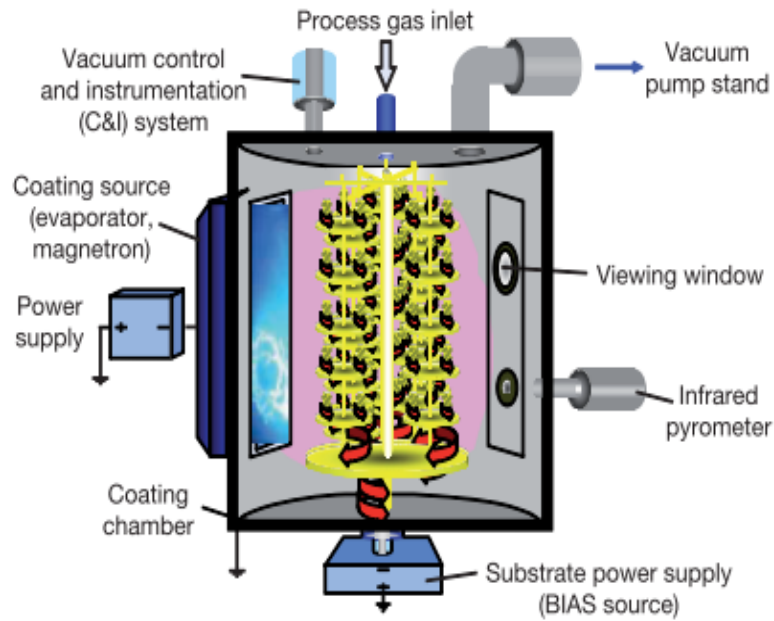


Figure 1-3: Cathodic arc evaporation system [5].

The ionized species are accelerated in the electric field to velocities ranging from few 10^4 to a few 10^5 m/s and frequently manifest multiple ionization (Me^{n+} , in which $n = 1, 2, 3$ etc.) towards the negatively biased substrate. The energetic condensation, due to the current density of the cathode spots and the supersonic acceleration of the highly ionized plasma, leads to the deposition of highly dense and an adherent coating which confers superior properties to CA-PVD coatings and makes them more desirable as compared to other PVD processes.

1.3 Applications of Cathodic Arc PVD Coatings

Of the various coating deposition technologies available, physical vapor deposition (PVD) technique stands out and has received widespread adoption and increased industrial application since it was first introduced in the early 1980s. Its acceptability is due to the excellent properties of its coatings as well as been an environmentally clean process [9]. Besides, such coatings provide an excellent means to enhance tool durability, improve wear resistance and prevent sticking by reducing adhesion between tools and workpiece.

Generally, cathodic arc PVD is capable of evaporating wide of range metallic targets and their alloys, examples include Ti, Al, Cr, AlTi, CrAl etc. Respective reactive gases are introduced during the coating process to deposit nitride, oxides, carbides, and its mixtures and layers. Thus, an enormous range of coatings can be deposited. The first generation of cathodic arc PVD coatings TiN and CrN were developed in the 1980s for their excellent wear and corrosion resistance for applications in the cutting tool industries. CrN which was developed after TiN was found to exhibit a low coefficient of friction and higher oxidation resistance. By the late 90s, several binary coatings such as HfN, ZrN, TiC etc. were

produced. Due to advancement in the cutting tool industries, TiN and CrN could not withstand the very high cutting temperature at the cutting edge due to high cutting speed and the harsh machining condition resulting in high tool wear, hence, the need for improved coatings with high oxidation and wear resistance. In addition, with the evolution of new technologies and advancement in various fields requiring hard protective coatings which can withstand severe conditions, the desire for enhanced coatings became imperative and thus remains a field of intense research up to date. Hence, several coatings have been developed and are continuously been developed for various applications such as wear resistance, decorative, optical, transparent conductor, solar energy, electronics and photocatalytic applications [6]. Other applications include field emission, metallization, and biomedical applications. Table 1-1 summarizes the most common applications for typical coatings. Among the aforementioned applications, wear, corrosion and oxidation resistant application has received significant attention over the past decades due to the associated damage and increase in production and/or operating cost they can cause. Thus, the popularity of hard coatings using cathodic arc (CA) PVD process in a number of industrial coating applications is due to the better adhesion of its coatings and its higher deposition rates [10–12]. Continuous development of the technology has subsequently enabled deposition of coatings with better interfacial adhesion, increased layer density, providing thin, smooth and dense coatings while reducing growth failure and droplets emission significantly [13]. Tool industries (for cutting, shaping and forming), automotive industries (in piston ring, power-train components), turbine and compressor engine industries (compressor blades) and biomedical industries (medical tools and instruments e.g. bone punches) have recorded considerable success in the use of these hard coatings,

such as TiN, CrN, TiC, (TiAl)N, Al(CrN), to elongate life, reduce cost and to protect components and equipment [6]. Hence, engineers and researchers have utilized and are still utilizing them in various applications ranging from corrosion protection, wear resistance, thermal barrier, oxidation resistance and reduction in friction. However, modern technologies such as friction stir welding (FSW) where wear of the tool is of significant importance to the integrity of the process is yet to utilize the advantages of these hard-protective coatings.

Table 1-1: Some commercial application and typical materials of cathodic arc coatings
(modified from reference [6]).

Category	Application	Typical coating material
Hard coatings	Cutting tools	TiN, TiAlN, TiCN, TiAlYN, Multilayers
	Corrosion and wear resistance	TiN, CrN, TiC, TiAlN, CrAlN, AlCrN
	Oxidation protection	TiAlN, AlCrN, CrAlN, TiAlSiN, CrAlSiN
Hard coatings with solid lubrication layer	Forming dies and punches	CrN, multilayers TiAlN/W-C:H, TiAlN/WC/C, TiAlN/MoS ₂
	Cutting tools	
Decorative and protective coatings	Forming dies and punches	CrN, CrN, TiAlN
	Faucets, shower heads, etc.	
Functional coatings	Door hardware	ZrN
	watch housing and wrist bands	ZrN, TiN, Au, TiAlN
	jewelry	
	Engine parts	CrN (piston)
	Fuel injections	Metal-containing ta-C
	Automotive interior parts	Metal-containing ta-C, AlSn, CrN
	Textile	TiCN, Metal containing DLC
	Bio-compatible surfaces for medical tools and implants	Ti, ta-C, TiN, TiCN, ZrN and CrN, Ag, Au, Pt
	Metallization and diffusion barrier layers for semiconductors	Ta, TaN, TiN, Cu
	Protection of magnetic disk and read-wire heads	Ultrathin diamond-like carbon

1.4 Friction Stir Welding (FSW) Process

Friction stir welding (FSW) is a recent innovation in the solid state joining process invented in 1991 by The Welding Institute (TWI) [14,15]. Within the past two decades, FSW has rapidly developed from experimentation stage into advanced technology which has been deployed in aerospace, automotive, shipbuilding and defense industries with huge research and development (R&D) investment [16,17]. The manner by which the joint is produced, and the resulting excellent properties of the joint have been the major grounds for its successful and continuous acceptance in the industries. Among its merits are; it is environmentally benign welding technology due to its low energy requirement and it does not require consumables and shielding gas. Also, common defects such as hot cracking and porosity associated with conventional fusion welding processes of lightweight metals are eliminated in FSW because there is no bulk melting of the material. Detailed advantages of FSW process have been outlined in many literatures [16–20]. Figure 1-4 shows the schematics of the FSW process. The process involves: (i) inserting a non-consumable rotating tool made of a pin and shoulder into the joint configuration of the plates to be welded (called the plunge and dwell stage) (ii) subsequently translating the rotating tool along the joint (called the traverse stage) (iii) finally withdrawing the tool from the plates (called the retract stage). Typically, the tool pin dimension is 0.85 – 0.95 of the workpiece thickness in length while its diameter is typically between 0.3 – 0.4 the tool shoulder diameter to avoid lack of penetration through the joint and ensure sufficient friction heat generation and proper stirring between workpiece materials.

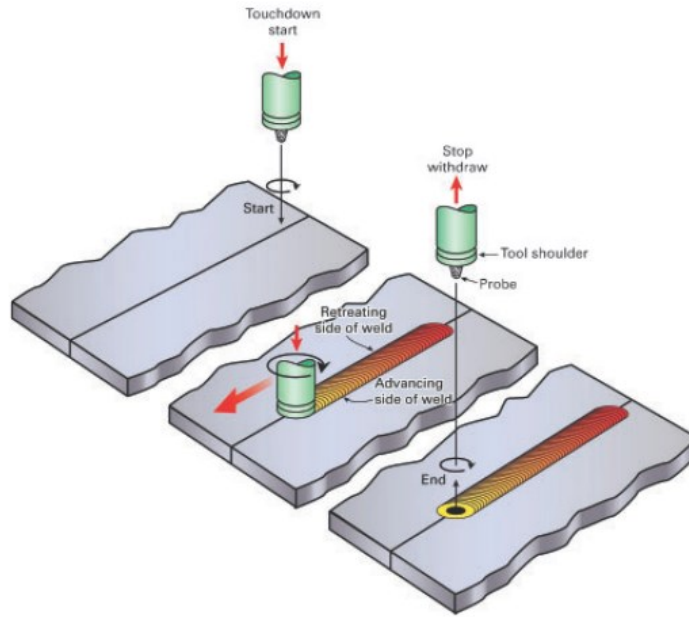


Figure 1-4: Schematics of Friction Stir Welding Process [17].

Since FSW does not involve melting, a relatively low amount of heat is required for the process. This is generated by the high contact pressure and shearing action (caused by the rotation of the tool) between the shoulder and surface of the workpiece. Thus, the tool is responsible for: (a) heat generation, (b) material movement and mixing to produce the joint and (c) constraining the soften metal at the interface between the workpiece and tool shoulder. As the rotating tool is pressed against the workpiece, the localized heating softens the workpiece material in the vicinity of the pin. The combined effect of the rotation and translation of the tool results in the material been mechanical moved from the advancing side to the retreating side by a severe plastic deformation, this eventually leads to the formation of a solid-state joint [18,21]. Due to the frictional heat generated at the tool shoulder/workpiece surface interface and at the pin/workpiece material interface, the deformation occurring during FSW are summarized as (a) deformation due to the tool

shoulder and workpiece interaction and (b) deformation at the tool pin and workpiece interface, respectively [18]. Besides these deformations, the plunge and dwell stage of the FSW process is challenging since the tool and the workpiece material are cold thus require a large plunge force. From the aforementioned, FSW tool is critical to the process as well as to the weld quality as it affects both the tool life and the weld characteristics [22]. Strength at ambient and working temperatures, excellent fracture toughness, thermal and chemical stability at working temperatures, fatigue and wear resistance are properties that are required for any FSW tool material. These properties are necessary due to the severe stress, deformation and elevated temperatures which the tool encounters during FSW process. Wear is of particular interest due to the limitation it poses in the development of FSW for welding of hard alloys. Besides, tool wear is also possible during FSW of soft materials especially during long runs of several hundreds of meters that characterizes industrial settings or via other wear mechanisms. Wear becomes more challenging when it involves the chemical reaction of tool material with the workpiece or with the environment leading to oxidation of the tool. Diffusion, adhesion, abrasion, and oxidation at high temperature are also common wear mechanisms [23].

1.5 Friction Stir Welding of Aluminum Alloys and Composites

Joining aluminum alloys and composites (AAC) by conventional fusion welding methods are susceptible to various problems induced by the high heat input of fusion welding processes. These traditional welding processes often deteriorate the joint mechanical properties due to the formation of a highly heterogeneous weld, solidification shrinkages, susceptibility to porosity, initiation of brittle intermetallic phases from interfacial chemical reactions between matrix and particulates and the different thermal expansion coefficients

as well as segregation [24–27]. These have hampered meeting the increasing demand of AAC in the industries despite their excellent properties. The high strength to weight ratio at a wide range of temperatures, improved creep and wear resistance, thermal and chemical stability, and improved fatigue and high formability properties have made AAC eligible and attractive in a wide range of applications most importantly in the aerospace, automotive and marine industries. Thus, among the alternative solid-state welding processes, friction stir welding (FSW) process for joining AAC has been found to possess meritorious potency to overcome challenges associated with fusion welding of AAC [26].

The FSW process induces dynamic recrystallization in the weld zone which results in fine equiaxed microstructure with improved joint properties [28,29]. Sequel to the low heat input, problems of segregation of ceramic reinforcement in the AAC, the formation of shrinkages and thermal stresses due to the large difference in the coefficient of expansion can be avoided in addition to the characteristic refined microstructures formed [28,30,31]. Hence, welding AAC using FSW have appealed to the interest of several researchers and engineers from the industries as evident from the large volume of literatures [24–33] published within the last two decades after the invention of FSW process in 1991 [14,15].

1.6 Hard Protective PVD Coating for FSW Tools

It is generally known that hard protective coatings play a significant role in improving the performance and prolonging the life of tools and equipment [34,35] and recently it has also been considered for protecting FSW tools against wear [18]. Protecting FSW tool with hard protective coatings is a viable option and a suitable alternative to hard and wear resistance tool materials which are very expensive. Among the options that are considered for

reducing tool wear in FSW, surface modification of the tool with hard coatings is of central attraction. Hard coatings have positively and significantly impacted the cutting tool industries. With the use of hard coatings, difficult-to-machine materials are now machined at relatively low cost while dry machining is being adopted with relative ease [6,36,37]. Based on the success recorded in the cutting tool industries, it is possible to avail the properties of specifically designed coatings to improve the mechanical, wear resistance and thermal properties of FSW tools. Also considering the similarity between machining and FSW process, it is expected that hard coatings can abate the problem of FSW tool wear and reduce the high cost of newly developed tools [18,21,22] especially in FSW of metal matrix composites (MMC), steels and titanium alloys. |

CHAPTER 2

LITERATURE REVIEW

This chapter presents the review of literatures related to; (i) characterization and testing of PVD coatings with a focus on cathodic arc PVD binary and ternary nitride-based coatings, (ii) materials and wear of FSW tools and (iii) PVD coatings of FSW tools. The mechanical properties, wear resistance, corrosion resistance, high-temperature oxidation resistance and thermal stability properties of PVD coatings are reviewed in the first three sections. The review of FSW tools; design, materials and wear, is presented in the fourth section while the literature review of PVD coated FSW tools is presented in the fifth section.

2.1 Mechanical and Wear Resistance Properties of PVD Coatings

The first generation of PVD coatings developed in the 80's were the binary coatings with TiN coating being the first to be deployed and used in the industries. CrN coatings were developed later to improve the wear and corrosion resistance properties of PVD coatings. However, industries quest for increased productivity and advent of new advanced materials which require hard machining conditions necessitate the need for improved coating properties. Consequently, further improvement or an alternative coating became necessary since the binary coatings were unable to meet these industrial requirements. With recent progress in nitride-based PVD coatings, involving the addition of aluminum, aimed at improving the properties of the TiN and CrN coatings over the conventional binary coatings has attracted the interest of researchers and engineers [38,39]. Among such coatings, (Ti, Al, N) and (Cr, Al, N) are widely known for their enhanced tribological and

mechanical properties. The incorporation of Al has been observed to enhance the mechanical, thermal, and corrosion and oxidation resistance properties of these coatings [40–43]. Numerous studies evaluated the tribological properties of both binary and ternary nitride-based coatings deposited by magnetron sputtering and arc evaporation PVD techniques [41–46]. Comparative evaluation of tribological properties of TiN, TiAlN, TiCN and CrN PVD coatings shows that the coatings considerably reduced both adhesive and abrasive wear, seizure as well as friction [47]. However, TiAlN coating exhibited the most stable and the best properties compared with TiN, TiCN, and CrN under dry testing conditions [47]. In another study, a comparative evaluation of the tribological properties of AlCrN and TiAlN monolayer coatings deposited using PVD process were conducted [39]. These commercial ternary coatings were evaluated with respect to the wear mechanism and coefficient of friction (COF) under reciprocating sliding and ball-on-disc tribological tests. It was found that AlCrN coating had excellent anti-abrasion properties. Both the normal load of the reciprocating sliding test and the sliding velocity of the ball-on-disc test had a noteworthy influence on the sliding tribological behavior of AlCrN coating. Nsongo et al. [48] investigated the adhesion behavior of titanium and titanium nitride coatings on metal using scratch test. They made effort to calculate the effective stress that causes the delamination of the coating from the substrate. This stress is made up of the residual stress in the coating and the stress due to the indenter. The adhesion energy was calculated from the van der Waals' interaction model. The wear resistance mechanism of (Ti, Al)N coatings was investigated by indentation and scratch test in a study by Henry et al. [49]. The coating crack initiation resistance was related to the quantities of debris particles generated by friction. It was found that the nature of wear debris, i.e. ductile or brittle, acting as a third

body, has a major influence on the evolution of the thin film damage. Since the 1980s when physical vapor deposition TiN coatings were introduced on a commercial scale, there has been a growing demand for improving their properties. Alongside, CrN coating was developed for improved oxidation and corrosion resistance, and enhanced surface properties for cutting tool application. However, due to an ever-increasing need for more productivity, the necessity for dry machining and the development in high strength materials, nitride-based ternary (Ti, Al)N and (Cr, Al)N PVD coatings were developed. Subsequently, several efforts have been tailored towards enhancing the properties of these coatings. The incorporation of an additional element(s), to increase the lattice distortion [50,51] or for the formation of second phase [52,53], as well as compositional optimization [54,55] and multi-layer coating design [35,56] have been explored for enhancing coating properties. Elements such as aluminum (Al), silicon (Si), boron (B), hafnium (Hf), etc. are usually incorporated into nitride-based binary and ternary coatings so as to improve the mechanical and tribological properties of the coatings [57–59]. Furthermore, due to the significant effect of the deposition process on the coating properties, various deposition techniques have been developed for the purpose of depositing advanced coatings and in recent times hybrid deposition techniques have been explored. Details of the various deposition processes have been well documented in the literature and handbooks [1,60,61].

Several studies have been conducted on the evaluation of the tribological properties of both binary and ternary nitride-based coatings deposited by various PVD techniques [44]. However, most studies have evaluated the coatings at relatively low load-bearing conditions [45,62]. For example, Mo et al. [63] compared the tribological properties of AlCrN and TiAlN coated cemented carbides at 5 N normal load for a sliding distance of

300 m. In another study, Mo et al. [64] evaluated the tribological behavior of CrN, AlCrN and AlTiN deposited by multi-arc ion plating technique using 5 N normal load. In both studies, AlCrN exhibited better wear resistance than AlTiN coating, though they found that CrN coating possessed a higher wear resistance despite its low hardness. Also, Aihua et al. [65] used 10 N normal load to compare the wear and friction properties of CA-PVD TiN, TiAlN, AlTiN and CrAlN coatings. They found that the TiAlN coating possessed the best wear resistance due to improved mechanical properties. However, the wear behavior of ceramic coatings also depends on the load-bearing capacity besides the internal stresses, coating thickness and hardness [66].

2.2 Corrosion of PVD Coatings

Cathodic arc deposition process is a PVD technique which offers very high deposition rate and produces coatings with excellent adhesion to the substrates [67]. However, defects such as pinholes and micro pores due to nitrides layer columnar growth as well as inclusion from liquid droplets resulting into macro particles within the coating, impair their corrosion resistance behavior [35,68]. This is because defects create a solution path between the coating and the substrate thereby compromising the effectiveness of resistance against charge transfer [69,70]. For this and other reasons, arc and plasma technologies are constantly being improved to ultimately enhance coating properties by reducing macroparticles.

Wen-Jun Chou et al. [71] studied the behavior of TiN coatings on 304 SS in 5% NaCl and 1 M H₂SO₄+ 0.05 M KSCN solutions. Using the standard salt spray and potentiodynamic polarization (PDP) test, they determined the critical coating thickness in the NaCl and

H₂SO₄ solutions to be 0.7 μm and 0.3 μm, respectively. When the coating thickness was smaller than the critical thickness value, corrosion current abruptly increased. Electrochemical impedance spectroscopy (EIS) and PDP were used to evaluate the corrosion resistance of TiN and TiAlN coatings on a martensitic stainless steel in 0.5 mol/l NaCl and 1 mol/l H₂SO₄ solutions by Yang Li et al. [72]. They found that TiAlN coating presented better corrosion resistance stability after 100h immersion than TiN coating, attributing the corrosion mechanism to adhesive failure of the coating. Also, Korablov et al. [73] studied the hydrothermal corrosive behavior of commercial TiAlN and CrN coatings for a range of parameters; temperature up to 1223 K (950 °C), water pressure 100 MPa, exposure time to the tune of 750 h and in various pH solutions. Their findings showed that TiAlN and CrN coatings can sustain a working temperature of 973K (700 °C) and 1073K (800 °C), respectively. A comparative study conducted by Ding et al. [68] on the corrosion resistance of CrAlN and TiAlN coatings deposited using lateral rotating cathodes in 3 wt.% NaCl solution showed that both coatings exhibited good corrosion resistance. However, CrAlN coatings exhibited superior corrosion resistance than TiAlN. This was attributed to the ability of both chromium and aluminum to form protective oxides preventing diffusion through the coating. Cegil et al. [74] have also studied the corrosion resistance of CrAlN and TiAlN coatings deposited on AISI D2 steel by thermos-reactive deposition (TRD) process. They concluded that both coatings possessed good corrosion resistance when compared with the substrate steel at room temperature in 0.5 M NaCl solution.

2.3 Elevated Temperature Evaluation of PVD Coatings

2.3.1 Oxidation resistance

The oxidation resistance of nitride based binary coatings such as TiN, CrN, deposited using various physical vapor deposition techniques have been investigated in the past two decades [54,75–79]. However, their thermal stability and oxidation resistance is currently limiting their application especially in processes that operate at a much higher temperature. Thus, ternary and quaternary coating systems have attracted much attention due to increased demand for sustainable and improved mechanical properties at high temperature and/or aggressive and harsh conditions. Bai et al. [80] investigated the thermal stability of CrTiAlN and TiN coatings on a dry drilling application. The mechanical and microstructural properties of the coatings were evaluated after annealing at different temperatures. CrTiAlN maintained its hardness up to the temperature of 600 °C, then declined gradually. At 900 °C, the wear depth and indentation size increased. It was observed that at 900 °C the Cr₂N and CrN phases found in the coating started to decrease leading to the formation of brittle oxides of Cr, Al, and Fe which result in the coating failure. Noticeable changes to CrTiAlN microstructure and mechanical properties were not observed up to 600 °C for 2h. Zhou et al. [81] also evaluates the high temperature oxidation of CrTiAlN by conducting static oxidation tests in air at different temperatures (500 – 900 °C). CrTiAlN was found to perform better than TiN and TiAlN due to the formation of dense protective oxide layers consisting of Cr₂O₃ and Al₂O₃. It was reported that even at 900 °C, the coating still retained its microstructural, mechanical and tribological properties. Chim et al. [77] compared the oxidation stability of coatings deposited using lateral rotating cathodic arc method. They deposited and characterized TiN, TiAlN, CrN and CrAlN

coatings after annealing for 1 hr at various temperatures (500 – 1000 °C) using energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and nanoindentation test. Findings indicated that TiN and TiAlN coatings showed comparatively low oxidation stability because of coating delamination at 800°C and 1000 °C, respectively. Cr-based coatings commence oxidation at 700°C and they relatively retained their hardness above this temperature. CrAlN oxidation rate was observed to be very low and the coating maintained reasonable hardness of 18.7GPa after being annealed at 1000 °C. Mo et al. [64] studied the tribological oxidation of CrN, AlCrN and AlTiN coatings deposited using PVD multi-arc ion plating technique. They reported that the formation of Cr₂O₃ and TiO₂ layer on AlCrN and AlTiN coatings, respectively, at higher frictional heating was responsible for the improved wear behavior. The formed Cr₂O₃ exhibited better wear resistance properties than TiO₂. Cyclic oxidation method in air at 900°C was used by Chawla et al. [82] to characterize the oxidation resistance properties of nanostructured AlCrN and AlTiN coatings. The cyclic oxidation test was aimed to represent extreme testing condition. Each cycle consisted of heating at 900 °C for 1 hr followed by cooling at room temperature for 20 min. It was observed that the uncoated sample and TiAlN coated steel showed high rate of oxidation at the initial stage and thereafter became constant while AlCrN coated steel exhibit better resistance to oxidation in comparison. After 50 cycles, the cumulative weight gains due to oxidation was 177.24, 203.39, 55.27 mg/cm² for the uncoated, TiAlN and AlCrN coatings, respectively. Thus, TiAlN coating was observed to have failed in protecting the substrate during oxidation. This is attributed to formation of predominantly porous TiO₂ oxides with very little Al₂O₃ oxide formed. The combined effects of both Al₂O₃ and Cr₂O₃ oxides were responsible for the high oxidation resistance of AlCrN.

Lembke et al. [83] evaluated the effects of high speed steel, cemented carbide and stainless steel substrate material on the oxidation resistance of TiAlN/CrN coatings. They investigated the formation of localized oxide defects on the coating and found that the oxidation behavior of the substrate influenced the oxidation stability of the coating. High speed steel exhibited the highest oxidation resistance compared to other substrates. The oxidation of coating on cemented carbide occurred at 800 °C where the substrate material had appeared. However, coated high speed steels showed less pronounced oxide defects and the first defects containing substrate elements occurred at 900°C.

Forsén et al. [84] evaluated the influence of Ti inclusion in $\text{Cr}_{0.4}\text{Al}_{0.6}\text{N}$ coatings on the high temperature and oxidation resistance properties. They found that with the addition of Ti the hardness of the newly formed coating was retained after annealing to 1100°C. The improve thermal stability of the TiCrAlN coating was attributed to age hardening resulting from spinodal decomposition into coherent TiCr- and Al-rich cubic TiCrAlN coatings. In addition, the observed hexagonal AlN precipitates formed near the grain boundaries was suppressed from further growth by the cubic TiCrN also formed in the grain boundary vicinity. Cremer and Neuschütz [85] used combinatorial approach to study the relationship between composition and oxidation resistance of TiAlN hard ternary coatings deposited using reactive magnetron sputtering. The composition was varied from $\text{Ti}_{0.6}\text{Al}_{0.4}\text{N}$ to $(\text{Ti}_{0.1}\text{Al}_{0.9})\text{N}$ and it was found that oxidation resistance of the coating was found to increase linearly with aluminum. Vennemann et al. [86] analyzed the oxidative properties of TiAlSiN coatings deposited by reactive DC magnetron coated on HSS. The influence of the addition of Si was studied by comparing the result with TiAlN coating. Oxidation tests were performed at temperatures between 800 °C and 1000 °C in the presence of oxygen at

partial pressure ranging between 1 and 100 mPa for duration of 1 hr. For test conducted at 1000 °C temperature, 100 mPa partial pressure and for the duration of 1 hr, TiAlN coatings hardness was compromised significantly due to formation of comparatively low hardness aluminum and titanium oxides. Though at 800 °C, its hardness was still retained. This was maintained for TiAlSiN coating and at 800°C oxidation temperature, the hardness increased due to incorporation of oxygen in the lattice sites formerly occupied by nitrogen or between lattice sites related to build-up of strain. Fukumoto et al. [87] synthesized and evaluated the oxidation resistance of monolayer TiAlSiN and multilayer TiAlSiN/CrAlN coatings. The coatings were deposited using cathodic arc ion-plating (AIP) technique and oxidation resistance was studied in the range of 800 to 1000°C. XRD analysis revealed that TiAlSiN annealed at 1000 °C exhibited TiO₂ and Al₂O₃ oxides while the EDX images showed that the oxides observed are mostly Ti-rich oxides (TiO₂). For the TiAlSiN/CrAlN multilayer, the coating has increased Al content which readily formed Al-rich oxides (Al₂O₃) layer at the early stage which prevented inward diffusion of oxygen. In addition, Al and Si-rich oxides (Al_xSi_yO_z) and a multilayer oxide layer which consisted of Ti-rich oxide on top of Al-rich oxide were formed. This led to the improved oxidation resistance of the multilayer coating by preventing the inward and outward diffusion of oxygen and metal (Ti and Cr) ions respectively. Similar improvement of both hardness and oxidation resistance by the incorporation of Si has been reported [88–90] both in single and multilayer coatings. The enhanced hardness was majorly associated to solid solution hardening while the oxidation resistance has been attributed to formation of dense amorphous oxide film [91].

2.3.2 Thermal stability

The thermal stability and oxidation resistance of ternary TiCrBN coatings was investigated by Shtansky et al. [92]. Effect of chromium content on the oxidation resistance of the coating was also evaluated. The coatings were annealed at temperature between 600 °C and 1000 °C in vacuum and air for a period of 1 hr. It was found that Ti-B-N coatings oxidation resistance had improved with the addition of Cr into the coating composition. In addition, increasing the chromium content of the Ti-Cr-B-N coatings showed enhanced adhesion strength and oxidation resistance. The observed Ti-Cr-O rich and Ti-O-B-rich regions at the topmost and underneath layer, respectively, led to the formation of Cr- and B-rich oxide layers on the coating surface, this further increased the oxidation resistance and thermal stability of the coating. Effect of other elements such as yttrium [93,94], boron [95], zirconium [57,96] and tantalum [97] on the oxidation resistance of ternary coatings (thus forming quaternary coating) has been investigated as well. The function and effect of these elemental constituents of metallic coatings are summarized in Table 2-1. Although earlier report had attributed reduction in oxidation resistance by adding Hf to magnetron sputtered TiAlN coating [85], Xu et al. [58] investigated the effect of Hf addition on the thermal stability and oxidation resistance of TiAlN coating deposited by cathodic arc evaporation. Al₂O₃ coated samples were subjected to 800 and 950 °C isothermally for 10h in DSC set up at a heating rate of 10 K/min and cooling at 50 K/min. For further evaluation of the oxidation resistance, samples were heated to 1100 °C with 50 K/min heating rate and cooled immediately. They found that at temperature between 800 and 850 °C, Hf enhanced the thermal stability and oxidation resistance due to the formation of a dense top layer of Al-oxide and a sublayer consisting of mixed Ti-Hf-oxide. Ti-Hf mixed oxides was

beneficial due to its non-porous structure which is as a result of the delay in transformation from anatase to rutile TiO_2 . However, when coated samples were heated to elevated temperature of 1100°C and then immediately cooled, solid solution of Hf in TiO_2 caused increase in the molar volume of the TiO_2 sublayer. This resulted in large molar volume difference between the sublayer oxide and the non-oxidized coating hence cracking of the protective Al_2O_3 top layer. This situation led to the diffusion of porous titanium oxide to the surface causing an increase in the mass gain and thus higher oxidation.

Polcer et al. [30] also studied the thermal stability, oxidation resistance and tribological properties at elevated temperatures of nanostructured quaternary CrAlTiN coating deposited on FeCrAl alloy substrate using cathodic arc evaporation. The coating was subjected to temperatures between 900 and 1050°C and held for 1hr before cooling to room temperature. They observed low mass gain and oxide layer thickness reached $1\text{ }\mu\text{m}$ at 1050°C isothermal temperature. The main mechanism forwarded for the excellent oxidation resistance was that the thick oxide layer formed limited the diffusion process thus acted as a barrier in preventing further oxidation. These oxides, consisting of a combination of Ti and Al oxides, formed by the diffusion of these metallic ions from the coating to the surface and then reacted with oxygen. In addition, chromium oxide, in combination with Al oxide, formed majorly at the interface between bulk and the oxidized coating further enhanced the diffusion limiting the strength of the oxides. Strong peaks of Ti, Al, and O at the surface in the EDX analysis confirmed the mechanism. However, the hardness of the coating measured in situ at around 700°C dropped significantly by over 70%. Feng et al. [98] evaluated the oxidation behavior of AlTiN, AlCrN and AlCrSiWN coatings deposited on cemented carbide by arc evaporation PVD system. Thermal stability

and oxidation resistance tests were carried out using a tube furnace in Ar and ambient atmosphere. Coated samples were heat treated to 700, 800, 900 and 1100 °C at a heating rate of 5 °C/min and held for 2 hr followed by controlled cooling at 5 °C/min to 500 °C, after which the furnace was turned off. Results from both X-ray diffraction and EDS showed that for AlTiN coating, a top thin Al₂O₃ layer followed by a mixed layer of Al₂O₃ and TiO₂ were observed to be 0.15 and 0.6 µm thickness at 700 and 800 °C, respectively. However, AlCrN and AlCrSiWN coatings showed superior oxidation resistance up to 1100 °C due to the formation of WO₃, Al₂O₃ and Cr₂O₃. These oxides, which were formed as a result of synchronous diffusion of Cr and Al to the surface, were noticed at 900°C with 0.1µm thickness. They rapidly increased to 0.8 and 0.5 µm as the temperature increases to 1100 °C for AlCrN and AlCrSiWN, respectively. AlCrSiWN excellent oxidation behavior was attributed to Si addition and the formation of nanocomposite structure in which the grain boundary protracted the diffusion paths of oxygen. In addition, Si addition is known to enhance the formation of Al₂O₃ at high temperature.

Table 2-1: Functions and effects of elements in hard coatings design.

Elemental Constituents	Beneficial Functions	Detrimental Effects	Ref.
Ni	Provides strength	Prone to destructive interaction with sulfur	[99]
Ti	Provides strength and contributes to oxidation resistance and thermal stability		[79]
Co	Provides microstructural stability and strength	Prone to destructive interaction with sulfur	[99]
Al	Major contributor to providing strength. Contributes to oxidation resistance and thermal stability	Large concentration lowers melting point	[96,99]
Cr	Contributes to oxidation resistance Reduces Al requirement for formation of alumina scale. Imparts resistance to hot corrosion	Lowers creep strength	[92,99]
Ta	Enhances hot corrosion and oxidation resistance. Improves strength		[97,99]
Si	Improves oxidation resistance and type II hot corrosion resistance	Large concentration leads to formation of brittle phases	[86,99]
B	Enhances oxidation and thermal stability		[92,100]
Y	Improves oxides adherence and oxidation resistance by retarding diffusion processes at high temperature	Large amount deteriorates the oxidation resistance due to formation of porous oxides	[57,93,94,99]
Zr	Improves strength, thermal stability and oxidation resistance by retarding diffusion processes at high temperature	Strength might reduce at higher temperature	[57]
V		Decreases the oxidation resistance by formation of porous oxides and its outwards diffusion through other protective oxide	[59]
Hf, Y ₂ O ₃ , other reactive oxides	Improves adherence to alumina and chromia scales	Large amount is detrimental due to porous oxide formation especially at high oxidation temperature	[57,58,93,99]
Pt	Improves oxidation and hot corrosion resistance		[99]

2.3.3 Vacuum annealing test

Due to the dependence of the properties of PVD coatings on temperature, several studies have investigated the effect of annealing both in ambient atmosphere and in vacuum in order to evaluate the coating properties [77,92,98,101–103]. In general, vacuum annealing eliminates oxidation which may influence the coating behavior at the treated temperature and thus impact its properties. Vancoille et al. [104] reported that the mechanical properties of arc deposited PVD TiN, TiAlN, TiNbN and TiCN coatings dropped with increasing annealing temperature from 300 to 900 °C in vacuum. The decrease was attributed to stress relief and change in the coating texture. Increases in the adhesion and cohesion strength have also been reported for magnetron sputtered binary TiN and CrN, and ternary TiBN and HfBN coatings after annealing at temperature up to 700 °C [105]. However, other studies have shown that the mechanical properties of PVD ternary coatings can be improved after annealing due to age hardening process [106] and spinodal or isostructural decomposition [107,108]. Koller et al. [109] showed how the hardness of a multilayer TiAlN/TaAlN coating increased from the as-deposited hardness of 30.7 – 34.6 GPa to maximum hardness values of 33.6 – 36.4 GPa after annealing at 800 °C in vacuum. Annealing at 1100 °C, the hardness remained at 33.5 GPa. This increase was reported to be associated with isostructural decomposition of the supersaturated cubic structure of the coating which was greatly influenced by the coating composition.

Similarly, it has also been reported that the corrosion properties of PVD coatings can be improved through appropriate heat treatment procedure [110,111]. Lai and Wu [110] had shown that the corrosion properties of CA-PVD CrN coating in 1 M NaCl solution after annealing under vacuum and N₂ atmosphere at different temperatures from 700 to 1150 °C

were improved. They also reported that the hardness of the coating slightly decreased with increasing annealing temperature and samples annealed in N₂ atmosphere possessed higher hardness compared to vacuum annealed samples. Also, Chen et al. [111] reported the effect of vacuum annealing of AlTiSiN coating at 700, 800 and 900 °C on the corrosion properties in 10 wt.% H₂SO₄ solution. They found that the annealed coatings possessed better corrosion resistance than the bare substrate and as-deposited coating. This improvement in the corrosion properties was attributed to the reduction of pits and droplets with annealing temperature.

The development of CrAlN and TiAlN coatings is a major milestone in the advancement of the hard coating due to their high hardness and thermal stability, excellent wear resistance, improved corrosion and oxidation resistance, as compared to the conventional binary TiN and CrN coatings [68,77,98,112–115]. This has been attributed to solid solution strengthening due to the incorporation additional element, such as Al, into the binary system [114,116,117]. Even with the volume of literature on the tribological, thermal and oxidation properties of CrAlN and TiAlN CA-PVD ternary coatings, only very limited and scarce investigation has been conducted on the effect of vacuum annealing on corrosion resistance properties of these coatings.

2.4 Materials and Wear of FSW Tools

Several efforts have been exerted in developing tools with enhanced properties especially for FSW of hard alloys. Table 2-2 summarizes the pros and cons of most commonly used FSW tool materials. However, the short tool life due to wear and the high cost of some tools have affected the wide adoption of FSW for hard alloys [22]. For example, increased

torque means a greater power which is needed especially for higher productivity, however, the load on the tool is thus increased leading to more tool wear and deformation. This consequently means regular tool replacement hence increasing the processing cost. Besides tool steels, which is the commonly used tool material in FSW of magnesium and aluminum alloys as well as aluminum metal matrix composites (Al-MMCs), polycrystalline cubic boron nitride (pcBN), tungsten-based and Si_3N_4 tools have been developed for the FSW of hard alloys [22,118–122]. Tool steels face greater wear when used for welding Al-MMCs than in the welding of soft alloys [22], though with several meters of weld runs typical in commercial applications, the tool also experiences wear with soft alloys [18]. Oil hardened tool steel was utilized in FSW of 4mm thick Al 359 with 20%SiC particulates for up to 1.5 m traverse distance at 500, 750 and 1000 rpm rotation speeds [32]. The authors investigated the tool wear for several rotation speeds at a constant traverse speed of 6 mm/s. They found that the tool wear increased with increasing rotational speed as illustrated in Figure 2-1. Figure 2-2 shows the optical image of the tool wear corresponding to the trend shown in Figure 2-1. The effect of weld traverse distance on the tool wear for various process parameters is shown in Figure 2-3. It is seen that a combination of high rotational speed of 1000rpm and low traverse speeds of 60mm/min and 180mm/min induced the severest wear on the tool within short weld distance.

Prado et al. [123] investigated the tool wear for FSW of 6mm thick aluminum alloy 6061 with 20 vol.% alumina and they compared it with the tool wear during FSW of unreinforced commercial 6061 aluminum alloy. The effect of various rotational speeds at a traverse speed of 1 mm/s was also evaluated.

Table 2-2: Pros and Cons of commonly used FSW tool material.

FSW Tool Material	Tool Steels	pcBN	WC/Co	W-Re
Common Workpiece	Al & Mg alloys, MMCs	Hard alloys: Steels & Ti alloys	Al-MMCs, Steels & Ti alloys	Steels & Ti alloys
Pros	Low thermal conductivity	High hardness; high temp. strength	High temp. Strength & hardness.	high strength than W; tougher and easier to machine than ceramics
Cons	Greater wear with Al-MMCs, low high hardness, chemical wear	Low fracture toughness. High chemical wear; Very high cost due to high-temperature high-pressure (HTHP) process required	Oxidation, chemical wear, low fracture toughness	Re is incredibly expensive High processing cost

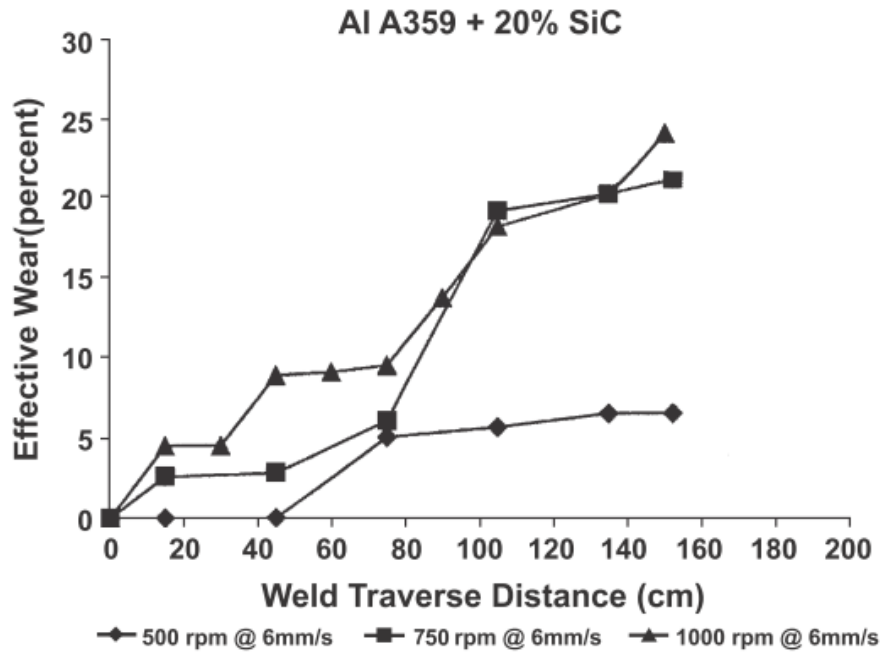


Figure 2-1: Pin tool wear as a percent of initial tool shape projections vs. corresponding MMC FSW weld traverse (or length) at various tool rotation speeds. The traverse speed was constant at 6 mm/s [32].

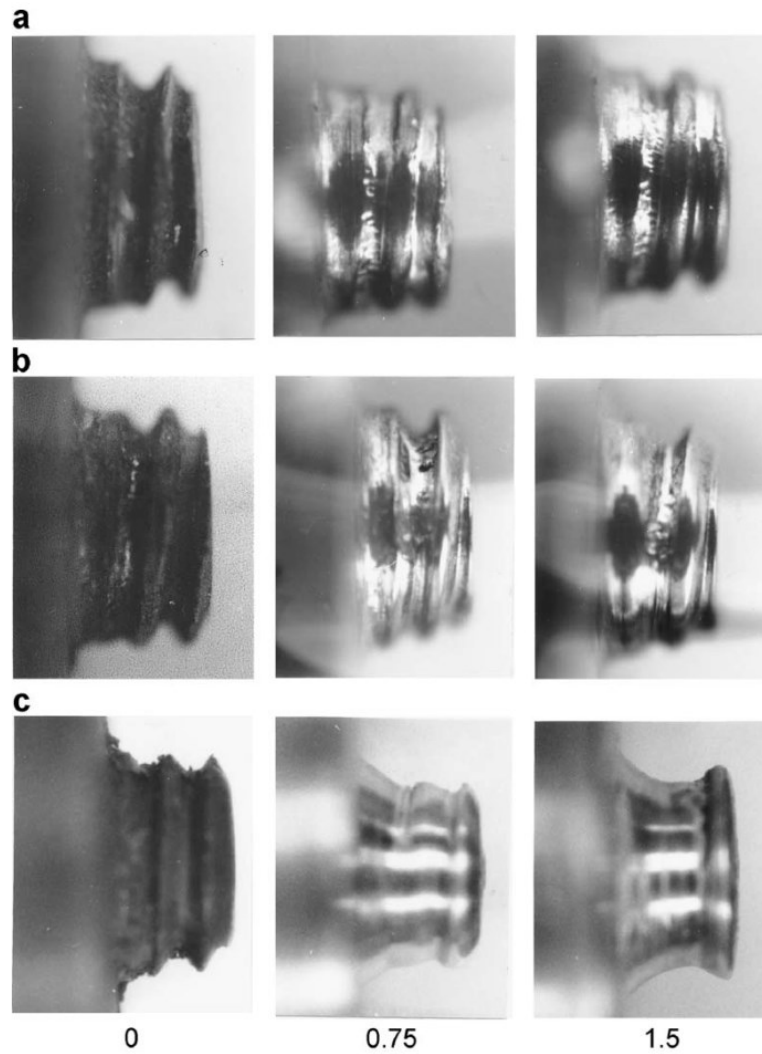


Figure 2-2: Pin tool sequences showing MMC FSW wear features for constant traverse speeds of 6 mm/s and weld traverse distances noted (in meters). (a) R = 500 rpm, (b) R = 750 rpm, and (c) R = 1000 rpm [32].

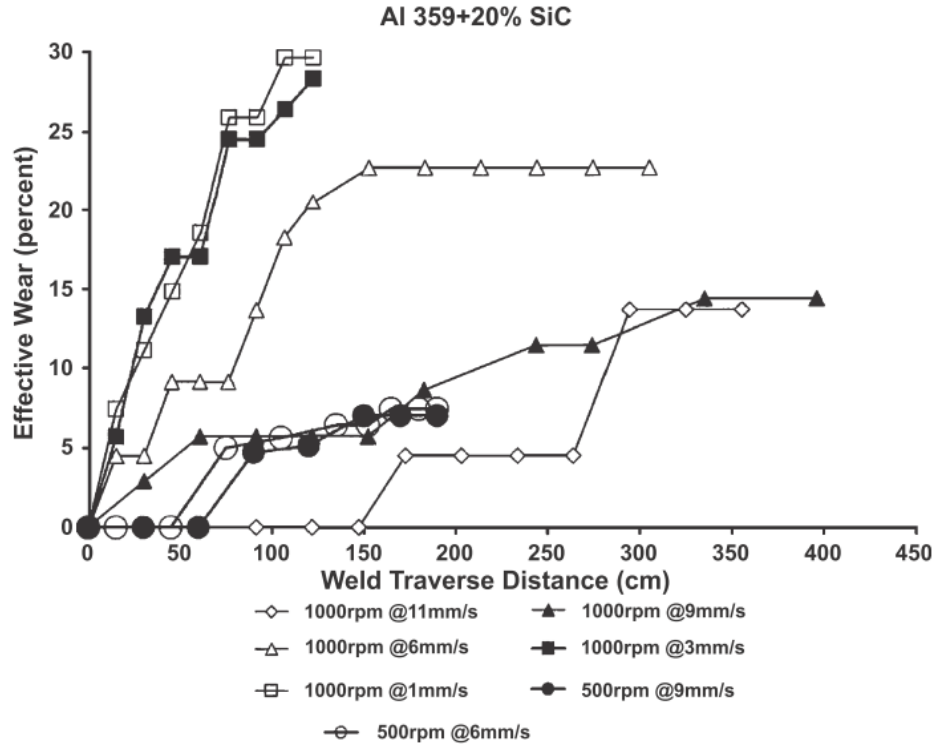


Figure 2-3: Pin tool wear as a percent of initial tool shape projections vs. weld traverse distance for different tool rotation and traverse speeds [32].

The degree of the tool wear after FSW is shown in Figure 2-4 and Figure 2-5 for the respective workpiece. Quantitative measurement of the amount of wear on reinforced alloy workpiece indicated the tool wear increased with increasing rotational speed to the maximum at 1000 rpm and then decline after rotational speed was further increased to 14500 and 2000 rpm. However, no significant tool wear for the FSW of the unreinforced 6061-Al alloy as compared to the reinforced alloy was observed.

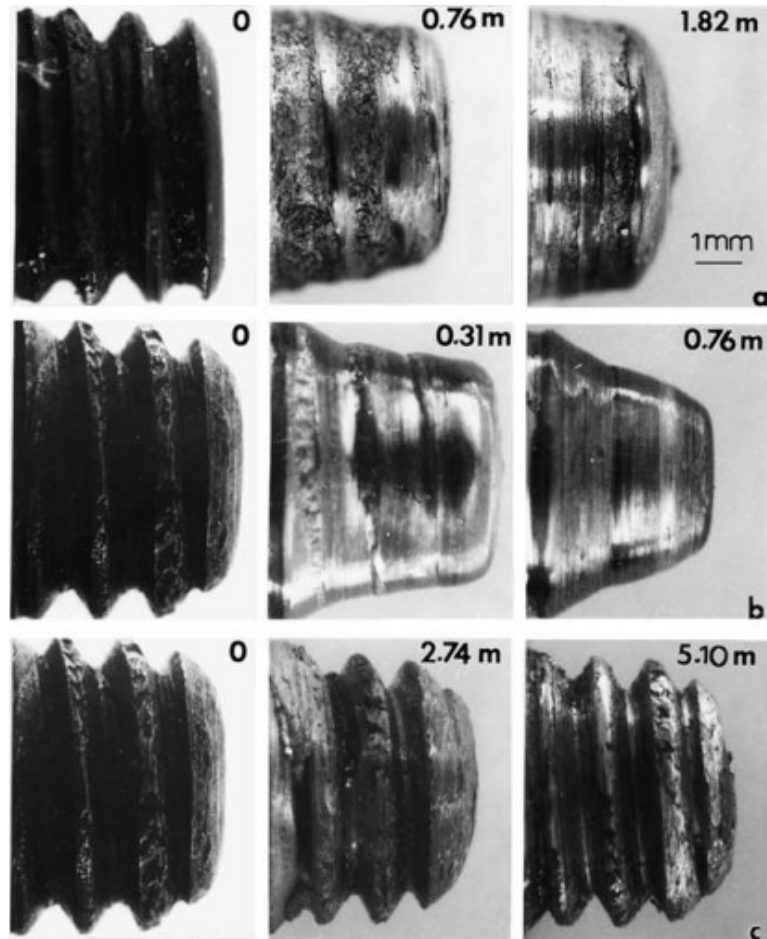


Figure 2-4: Tool (nib) sequences showing FSW wear features. The corresponding locations for linear traverse are indicated in each photograph. MMC FSW at (a) 500 rpm (b) 1000 rpm, (c) 6061 aluminum alloy FSW at 1000 rpm [123].

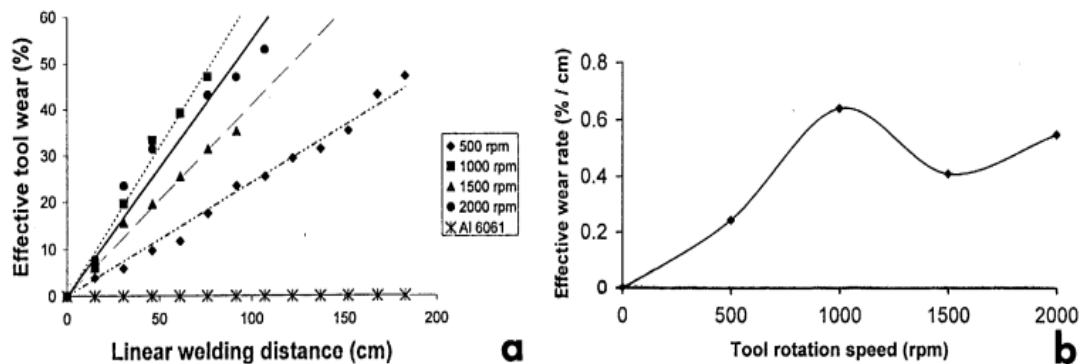


Figure 2-5: (a) Tool pin wear as a percent of the initial pin projection versus corresponding FSW linear traverse in cm. (b) Tool pin wear rate versus rotation speed in rpm [123].

In a similar study the same authors, 5 mm thick 6061-T6 Al with 20% Al_2O_3 reinforcement were friction-stir welded with tool steel material oil hardened and heat treated to 62 Rockwell C hardness [124]. The authors observed the tool wear during the FSW at different traverse speeds at a constant rotation speed of 1000 rpm base on the work of Prado et al. [123] which shows that the highest tool wear rate occurred at 1000 rpm. It was found that the effective tool wear increased with a decrease in the traverse speed as shown in both Figure 2-6 and Figure 2-7. It was also found that the main wear mechanism was erosion by hard alumina particles and that the tool wear was not uniform. This erosion wear is due to material flow from translational or vortex flow perpendicular or parallels to the tool rotation axis. Significant wear of the tool in both studies was recorded with all tool pin featured wearing out completely to attain a self-optimized tool shape. Figure 2-3 and Figure 2-7 show severe wear of FSW tool pin of about 40% during FSW of metal matrix composites (MMC). Also, significant wear of W6Mo5Cr4V2 high-speed steel was observed during the FSW of AA6061 matrix and 55 vol.% SiC particulates aluminum metal matrix (MMC) [125]. Figure 2-8 and Figure 2-9 revealed that the maximum wear occurred on the pin which is depicted in the change in the shape of the pin with welding distance. It was also observed that the radial wear is irregular and vary depending on the location making the pin uneven at various locations of the pin.

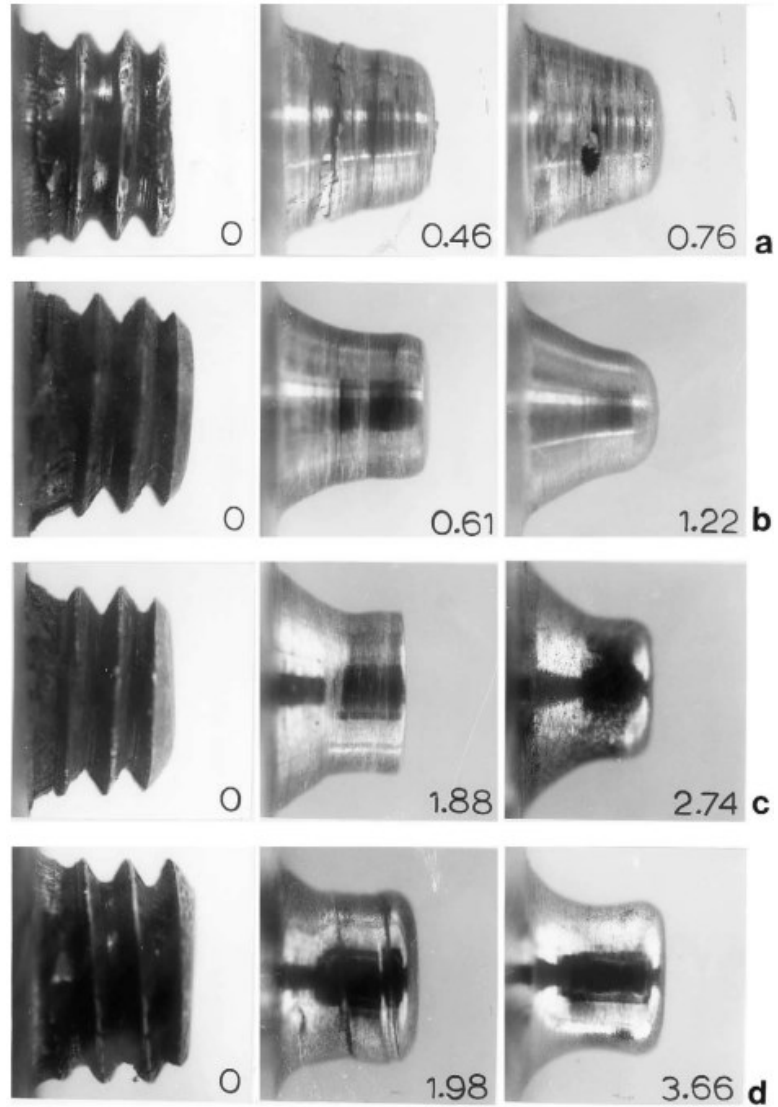


Figure 2-6: Evolution of tool pin wear during the FSW of MMCs at constant tool rotation speed of 1000 rpm for different traverse speed of (a) 1 mm/s (b) 3 mm/s (c) 6 mm/s (d) 9 mm/s (traverse distances in meters is noted on the images) [124].

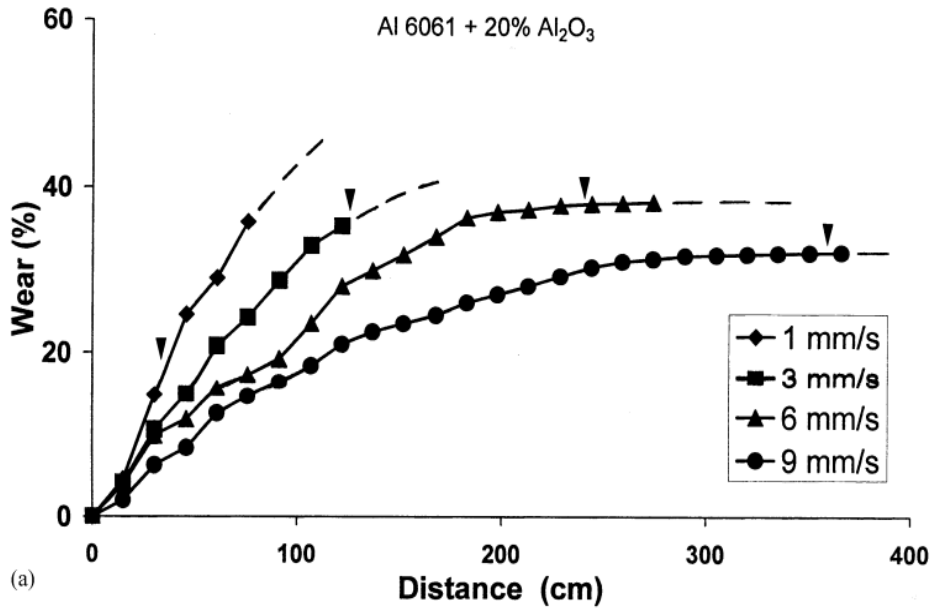


Figure 2-7: Pin tool wear as a percent of initial pin shape projections versus corresponding MMC- FSW linear traverse in cm at various weld speeds noted. Tool rotation constant at 1000 rpm. The arrows on each curve indicate constant weld times of 400 s [124].

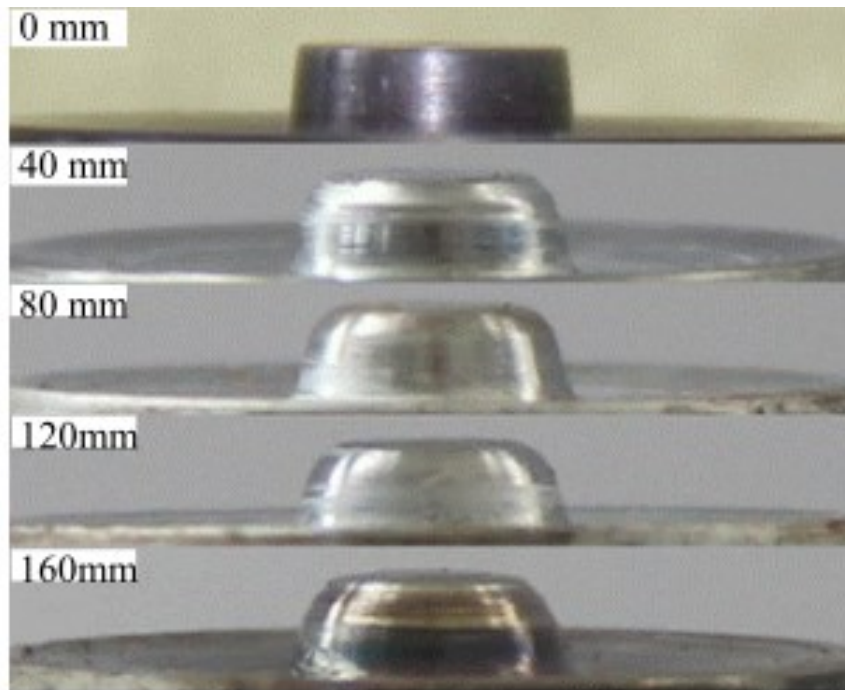


Figure 2-8: Appearance of the welding tool after different welding distances [125].

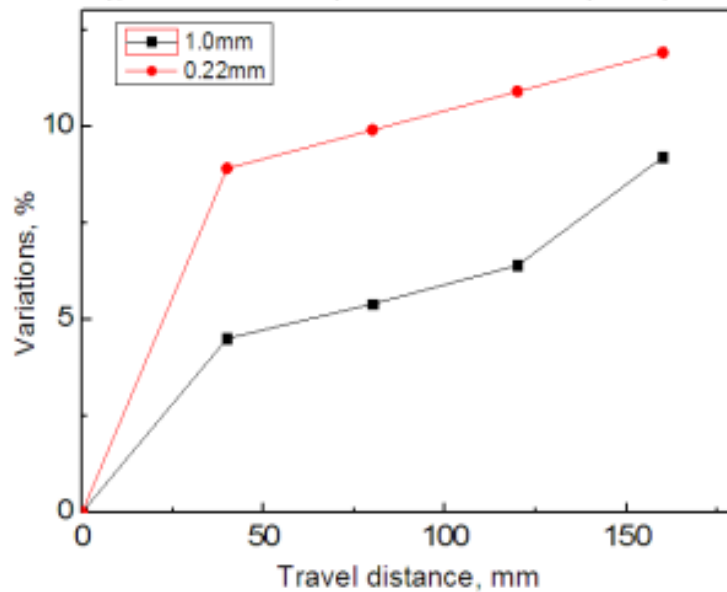


Figure 2-9: Variations in pin diameter at typical locations [125].

The application of pcBN tools is essentially limited because of the high cost of the tool due to the high temperature and pressure required during manufacturing. This is despite their high strength, hardness, and high thermal stability. Also, wear is another challenge with pcBN cutting tools. Diffusion and the chemical reaction have been reported as the main wear mechanism of pcBN cutting tools [126–128]. In addition, the degradation of wear properties due to the presence of binders, since they are usually softer and less stable, and nitrogen pick-up from the worn tool are common problems associated with pcBN tools [126,129]. In relation to FSW, Park et al. [129] investigated FSW of austenitic steel and other steels with pcBN tool. They observed significant nitrogen pick-up between two to five times that of the base material at the advancing side of the austenitic steel. Also, severe tool wear with subsequent reaction of debris formed with the base metal was observed when a pcBN tool was used in FSW of commercially pure titanium (cp-Ti) [130]. The poor

toughness at room temperature of pure tungsten (W) and its susceptibility to wear characteristic as an FSW tool material has led to alloying with carbide and more recently with rhenium (Re). Tungsten-carbide (WC)'s chemical inertness during FSW is yet to be fully understood while the presence of the typical cobalt (Co) binder may also affect the tool thermal stability at high temperature as well as its wear resistance properties. Oxidation at high temperature and chemical reaction with elements of both the workpiece and environmental gases may deteriorate the tool properties [131]. Liu et al. [132] examined the wear characteristics of a 5 mm thick Al-Si alloy reinforced with 30%SiC particulates when it is friction stir welded using a WC-Co tool. It is found that the tool wear was above 20% at extreme wear locations. Images of the worn WC-Co tools are shown in Figure 2-10 while the variations of the shoulder size and pin length as a function of weld distance are respectively shown in Figure 2-11. Extreme wear at specific locations on the pin diameter is evaluated also and shown Figure 2-12. It is obvious that even with hard WC-Co tool, the tool wear at low welding or traverse speed can be quite considerable. Unlike WC, W-Re produces good weld quality with less tool wear due to its improved wear resistance and fracture toughness at ambient and high temperatures. However, the extremely high cost of the rhenium significantly hinders their adoption [22].

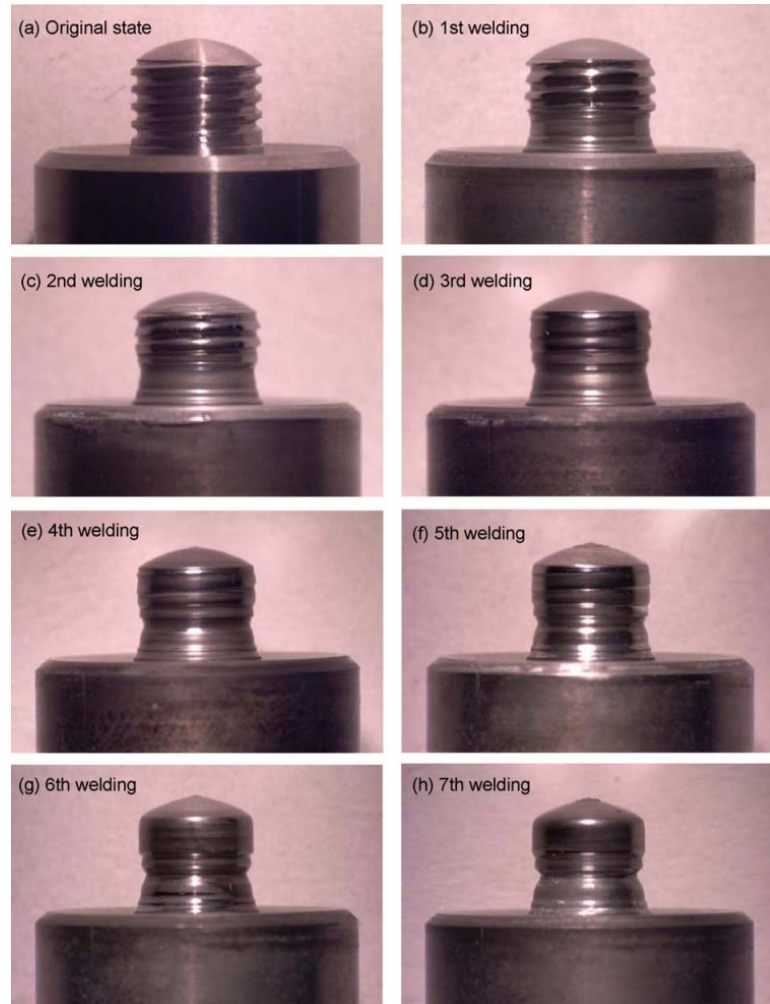


Figure 2-10: Appearance of the threaded tool after each FSW experiment [132].

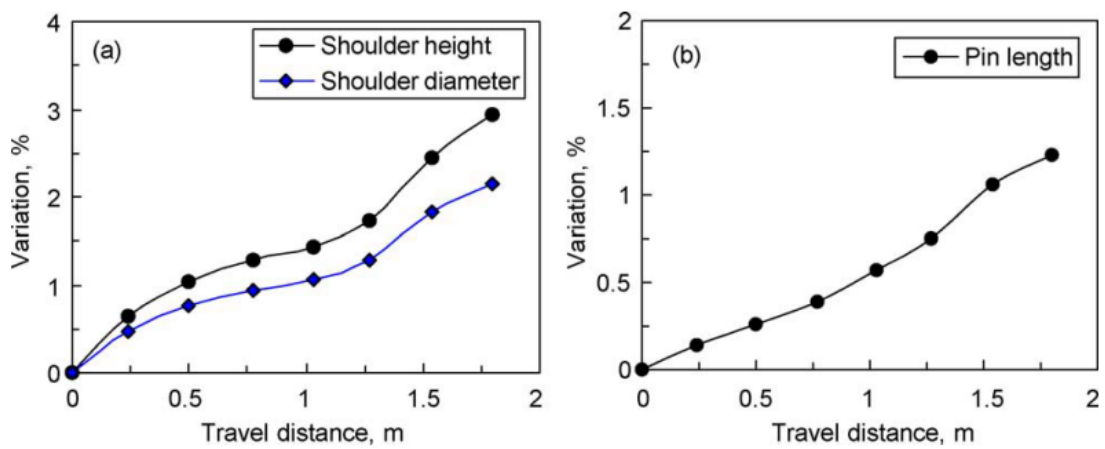


Figure 2-11: Variations in: (a) shoulder size, and (b) pin length [132].

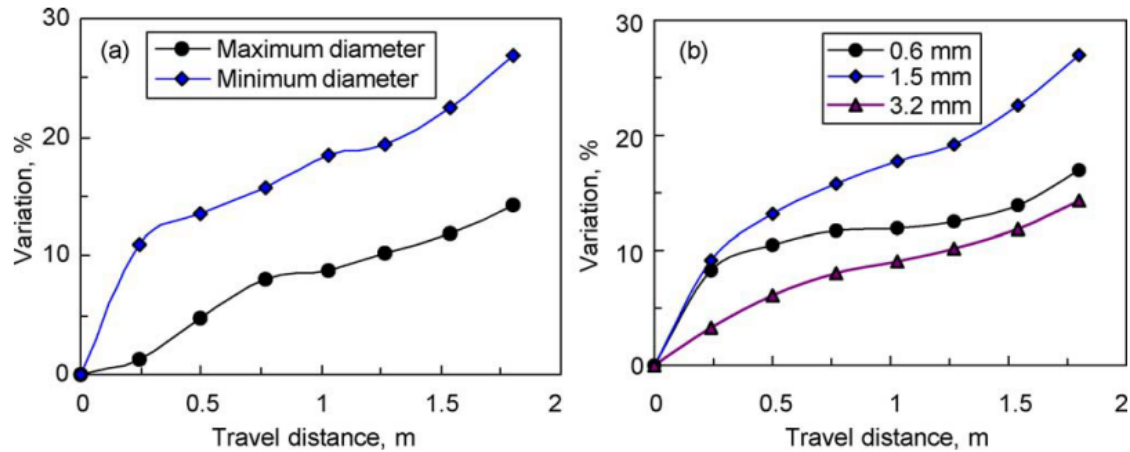


Figure 2-12: Variations in pin diameter at: (a) the extreme-wear locations, and (b) typical locations [132].

Besides, the effect of tool wear on the weld properties and quality, appreciable tool wear increases the cost of FSW process significantly. Therefore, properties such as high strength, improved fracture toughness, enhanced hardness, excellent thermal properties (stability, conductivity, and expansion), chemical inertness with both the workpiece material and the environment and cost-effectiveness become vital considerations for FSW tool material. It is obvious that a single material can hardly satisfy these properties, thus concerted research effort has been geared towards finding an appropriate material and/or design for FSW tool to improve the tool wear resistance and/or reduce the tool cost appreciably [17,21,22,133–138]. This problem of FSW tool wear thus deserves to be looked into from the perspective of hard protective coated FSW tools. A summary of the literature on the FSW tool materials and wear is provided in Table 2-3

Table 2-3: Summary of FSW tool materials and wear condition after FSW process.

Authors, Year, Reference	Matrix Reinforcement, Vol. fraction (%)	Workpiece Thickness	Tool Material	FSW Process Parameters	Tool condition after FSW and Remarks
Prado et al, 2001 [123]	Al alloy 6061 Al ₂ O ₃ , 20%	5mm	O1 tool steel AISI oil hardened	60mm/min 500, 1000, 1500, 2000 rpm	Tool wear of the tool pin reaches maximum at 1000 rpm up to 45% after 70 cm welding distance
Prado et al, 2003 [124]	Al 6061 Al ₂ O ₃ , 20%	5mm	O1 tool steel AISI oil hardened	1000 rpm 60, 180, 360, and 540 mm/min	Effective tool wear decreases with increasing traverse speed. Wear reaches maximum at 1mm/s transverse speed
Fernandez & Murr, 2004 [32]	Al-359 SiC, 20%	4mm	O1 tool steel AISI oil hardened	6mm/s 1000, 750 and 500 rpms	Minimum tool wear occurred with the lowest rotation speed of 500rpm and the effective tool pin wear reached 30% for 1000rpm at 1 and 6 mm/s within 100 cm weld distance
Cavaliere et al., 2004 [27]	6061 + 20% Al ₂ O ₃ and 7005 + 10% Al ₂ O ₃	7mm	O1 tool steel AISI oil hardened	800rpm 56mm/min	No information on tool condition after FSW is available
Liu et al, 2005 [132]	AC4A SiC, 30%	5mm	WC-Co	1500, 2000 rpm 25, 50, 150 mm/min 240, 260, 270 mm weld length	The lower the welding speed, the higher the wear rate, and the maximum wear rate is produced in the initial welding. Wear at tool pin diameter was above 25% after 1.75m weld distance
Marzoli et al, 2006 [26]	AA6061 Al ₂ O ₃ , 20%	7mm	An ultra-hard material	-	The tool was made of an ultra-hard material, able to withstand the strong abrasion of the alumina particles.
Ceschini et al, 2007 [29]	AA6061 Al ₂ O ₃ , 20%	7mm	highly wear resistant steel (an	-	No information on tool condition after FSW is available

			age-hardenable nickel martensite reinforced with 30 vol.% TiC)		
Ceschini et al, 2007 [28]	AA7005 Al ₂ O ₃ , 10%	7mm	high wear resistance material	600rpm 300mm/min	No information on tool condition after FSW is available
Hüseyin Uzun, 2007 [139]	AA2124 SiC, 25 %	6mm	TiAlN-coated HSS-steel tool	800 rpm 120 mm/min	No information on tool condition after FSW is available
Feng et al., 2008 [33]	AA2009 SiC, 15%	8mm	steel tool	600rpm 50mm/min	After a FSW of the composite 400mm in length, it was found that the diameter of the pin was reduced from 8mm to 7.7 mm. This lead to contamination of the weld with the formation of the Cu ₂ FeAl ₁₇ phase. Therefore, it is highly desirable to adopt wear-resistant tool materials to avoid tool wear,
Chen et al., 2009 [140]	AA6063 B ₄ C, 6 and 10.5 %	4.5mm	AISI 4340 steel	600 mm/min 1500 rpm	Tool wear is not uniform and occurs on different surfaces of the tool. About 8.5% and 2.3% reduction in pin length and max. pin diameter respectively
Contorno et al, 2009 [141]	A359 SiC, 20%	3mm	Hardened AISI 1040, Tool was also coated with PVD AlSiCrN or AlSiTiN.	300mm/min 1000 rpm 12, 24 and 36 processing passess	A higher wear resistance and a higher adhesion were found for the AlSiTiN coating. Thus, definitive advantage of the coatings on the hardened tool was not found
Nami et al., 2011 [30]	Al Mg ₂ Si, 15 wt.%	6mm	H13 steel	710–1400 rpm 125 mm/min 1–3 pass(es).	No information on tool condition after FSW is available

Bozkurt et al, 2011 [142]	AA2124 SiC, 25%	3mm	HSS tool	40mm/min 1120 rpm	No tool wear was observed at the welding parameters of 1120 rpm, 40mm/min despite the presence of hard SiC particles
P. Periyasamy et al, 2012 [31]	AA6061 SiC, 10%	6mm	HSS tool	45mm/min 800, 900, 1000, 1100, 1200 rpm	No information on tool condition after FSW is available
I. Dinaharana and N. Murugan, 2012 [24]	AA6061 ZrB ₂ , 5, and 10 wt. %	6mm	high carbon high chromium steel oil hardened	1150 rpm 50 mm/min	No information on tool condition after FSW is available
T. Prater et al, 2013 [143]	Al 359 SiC, 20 and 30 %	5mm	O1 Tool Steel and WC/Co tools	1000 rpm 127mm/min	The wear resistance of WC/Co micrograin and WC/Co submicrograin is clearly superior to that of steel at both 20 and 30% reinforcement levels. Wear experienced by the WC/Co micrograin tool at 30% is nine times less than that observed for the O1 steel tool under the same conditions. In the 30% MMC class, the diamond tool failed during the second weld
D. R. Ni et al., 2013 [144]	AA2009 SiC, 17%	3mm	Cermet tool	1000 rpm 50 mm/min	No information on tool condition after FSW is available
Cioffi et al, 2013 [145]	2124 Al SiC, 25%	15mm	Shoulder: H13 steel Pin: MP159 alloy	300, 550, and 800 rpm 75 mm/min	Tool wear occurs during FSW of this composite. Therefore, the pin used in the welds performed at 300 and 550 rpm was replaced for a new one in the weld conducted at 800 rpm, the most severe wearing conditions.

C. Devanathan and Suresh Babu, 2014 [146]	LM 25 Al alloy SiC, 5%	6mm	TiAlN-coated HSS tool	1200, 1500, 1800 rpm 20, 40, 60 mm/min	No tangible tool wear was observed, only the deposition of aluminum on the tool pin
K. Kalaiselvan et al., 2014 [25]	AA6061 B ₄ C, 12 wt. %	6mm	A tool made of high carbon high chromium steel oil hardened	1000 rpm 80 mm/min	No information on tool condition after FSW is available
Tracie Prater et al, 2015 [16]	Al 359 SiC, 20%	5mm	-	1400 rpm 900mm/min 76, 152, 229 mm weld length	Significant wear was observed and increases with weld length from 33% after 3 ft weld length to 56% after 9ft weld length
Song et al, 2015 [125]	AA6061 SiC, 55%	2mm	W6Mo5Cr4V2 high speed steel	800 rpm 10mm/min	The maximum wear occurs at the pin top while the minimum wear exists in the lower half-part near the shoulder The pin diameter significantly decreases with increasing travel distance. At the welding speed of 10 mm/min, the pin diameter decreased from 11% to 21% after the 160mm weld length.
Yahya B. and Zakaria B., 2017 [147]	AA2124 SiC, 25%	6mm	TiAlN-coated, CrN and uncoated HSS tool	900 rpm 45 and 115 mm/min	AlTiN coated tool has the lowest weight loss ratio. This high wear resistance is due to highest value of hardness of the coated tool with AlTiN

2.5 Coating of FSW Tools

The concept of improving the properties of a surface by coating is long well known, and it has been widely utilized in different industrial applications to enhance productivity, performance and reduce cost. Specifically, hard protective coating plays a significant role in improving the performance and prolonging the life of tools and equipment. Such examples include the compressor blades, cutting tools and boilers [34], as well as in molds and dies [35], and more recently, it is been considered for friction stir welding (FSW) tools [18]. Coating of FSW tools to improve tool properties has been scarcely investigated. Protecting FSW tools with a hard-protective coating layer(s) is a viable option to obtain the specific desired properties during FSW process and may be a suitable alternative to very hard and wear resistance tools which are very costly. Hard coatings have positively impacted in the cutting tool industries with the development of several coatings materials and designs as well as the advancement of the coating technologies. Considering the similarity between the cutting tool and FSW tool, it is expected that hard coatings can significantly abate the problem of tool wear, thus, reduce the high production/operating cost from frequent tool replacement or use of expensive tools [18,21,22] especially in the FSW of MMCs, high strength steels and titanium alloys.

Oshahi et al. [148] in a friction spot welding of high strength steel sheets utilized a bare and coated Si_3N_4 tool for the welding of DP980 steel in a lap arrangement. The coating was a multilayer TiC/TiN coating deposited by chemical vapor deposition (CVD). The tool shoulder and pin diameters were 10 mm and 4 mm respectively with a pin length of 1.5 mm. They observed that Si_3N_4 tool decomposed and contaminated the weld with deposition of silicon and nitrogen, oxygen was also found within the weld zone. This situation was

avoided with TiC/TiN coated tool though additional argon shielding gas was used. However, no information was provided about the coating properties and deposition parameters, rather, the focus was on the properties of the joint. Similarly, Bozkurt et al. [142] developed TiAlN-coated high-speed steel (HSS) tool for FSW of 3 mm thick AA2124/SiC/25p MMC plates. The FSW process parameter used was rotation speed of 1200 rpm and tool traverse speed of 40 mm/min and the tool dimensions are; shoulder diameter = 20 mm, pin diameter = 6 mm and pin length = 2.8 mm. They recorded 19% drop in the tensile strength of the welded section with uniform grain size distribution similar to base metal. However, the properties and the contribution of the TiAlN coating on the tool performance and wear resistance were not evaluated. In another study by Batalha et al. [149] in 2012, they investigated the wear behavior of a PVD AlCrN coating on FSW tool made from WC-6%Co. The tool, 20 mm in shoulder diameter, 5 mm pin diameter tapered at an angle of 30°, was used for FSW of 4mm thick Ti-6Al-4V titanium alloy with 1500 rpm tool rotation speed and 50 mm/min traverse speed. The coating, 5µm thick, was applied to both the pin and the shoulder of the tool. They observed that besides the coating's appreciable adhesion to the workpiece material, Ti, Al, and V were found in the elemental analysis of the tool surface after FSW. Also, the tool pin fractured during the plunging stage as a result of the process parameter and the plunging force being higher than the compressive strength of the tool. The extreme wear of the tool after FSW is shown Figure 2-13. They concluded that the exact contribution of the AlCrN coating could not be evaluated. This is due to the extreme process parameters that were used which led to severe tool wear and pin fracture.

More recently, the influence of AlCrN coating FSW tool on the welding of Al alloy plates was demonstrated [150]. WC tool (MG18, ISO K20-40) was coated with AlCrN coating and compared with an uncoated tool for the FSW of 3mm thick AA5754-H11 Al alloy. They analyzed weld quality, microhardness of weld and the grain size of all tools. A clear conclusion on the influence of the coating on the tool was not established in the paper rather the effect of the shoulder diameter was emphasized. However, it is mentioned that the coating improved the thermal stability and wear resistance of the tool. In another recent work, HSS tool was coated with PVD TiAlN coating of 4 μm thickness for FSW of LM 25 Al alloy reinforced with 5% SiC particles [146]. The tool has a tapered pin with large and small diameters of 6 and 4 mm, respectively with a pin length of 5.7 mm. Three tool rotation speeds of 1200, 1500, 1800 rpm for corresponding traverse speeds of 20, 40 60 mm/min under 6, 7, 8 kN axial loads, respectively, were utilized during the FSW process. They found improved wear resistance of the tool as no tangible wear was observed. However, Al from the workpiece was deposited on the tool pin which is possibly due to plastic deformation. Bozkurt and Boumerzoug [147] recently applied CrN and AlTiN coatings on HSS tool for FSW of 3mm thick AA2124/SiC/25p-T4 MMC. The wear of the coated tools is shown in Figure 2-14 after FSW process was evaluated and compared with the bare tool. It was observed that the high hardness of AlTiN coated tool offered better wear resistance as compared to CrN coated and bare tools.

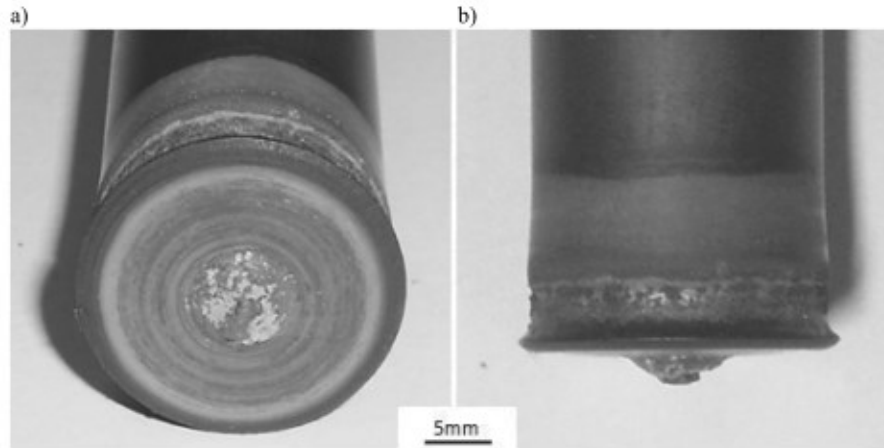


Figure 2-13: (a) Front view of the worn tool after FSW process, (b) side view of the worn tool [149].



Figure 2-14: Micrographic views of (a) ted tool (b) CrN coated tool (c) AlTiN coated tool before and after welding process [147].

CHAPTER 3

OBJECTIVES AND APPROACH

Based on the literature review conducted in the previous chapter, the problem definition for the dissertation is presented in this chapter. This is followed by the objectives and a summary of the approach adopted in achieving the aims of the dissertation.

3.1 Problem Definition

From the literature reviewed, it is observed that ternary and quaternary coatings show better mechanical, wear resistance and oxidation resistance properties both at room and elevated temperature than binary coatings. Also, it is seen that chromium-based nitride coatings exhibited improved oxidation resistance when compared to their titanium-based nitride counterpart. Generally, the coating oxidation resistance, tribological and mechanical properties at the evaluated conditions indicate the prospect in their application for FSW tools. The temperature during FSW process rarely reaches 1000 °C for typical high strength materials such as titanium and steels.

Table 3-1 shows the forging temperature range which is similar to the temperatures encountered during FSW process for commonly friction stir welded materials. Due to the coating formation of dense, hard and stable oxides at elevated temperatures, tool surface properties and wear resistance can be improved. Therefore, CA-PVD coatings comprising of binary and ternary coating system should be investigated as improved coatings for potential FSW tools for high-temperature melting materials.

Table 3-1: Forging temperature range for different alloy groups[151].

Alloy Group	Temp. Range (°C)
Aluminum alloys	440 - 550
Magnesium alloys	250 - 350
Copper alloys	600 - 900
Carbon and low alloy steels	650 - 800
Titanium alloys	700 – 950

Furthermore, findings from the literatures on the role of hard coatings in reducing FSW tool wear shows that very limited research has been conducted. This is despite the enormous and continuous research being conducted in development for advanced coating for wear and tribological applications. Also, no studies have been conducted on coated FSW tool to improve the tool wear resistance during FSW of Al-MMCs where hard particulate pose a serious challenge to the tool. Al-MMCs are increasingly being adopted in many industries due to their high strength-to-weight ratio and FSW is already been used for welding in the aerospace industries. Sequel to the wide difference in tool materials, the significant variation in coating properties due to various influencing coating parameters and different FSW process parameters, it will be difficult to comprehensively understand the behavior of coated FSW tool. Rather, there is a need for a systematic study to explore selected hard coatings with improved wear resistance and suitable mechanical properties for FSW tool for selected welding applications. Also, the coating properties can be tailored relatively more easily to specific FSW tool material. Thus, there is a high prospect in the use of carefully selected hard coating for enhancing FSW tool performance. This is possible through improving tool surface properties, enhancing the tool wear and oxidation resistance at high-temperature with hard PVD coatings. Thereby reduce the tool cost or

frequent tool replacement cost and improve the productivity. Despite these prospects, investigations that have explored these potentials of coated FSW tools are currently very limited. Therefore, a more detailed study is needed to understand suitable coating properties and its compatibility with tool material when used for FSW of low and high strength engineering materials.

3.2 Objectives

The main aim of this dissertation is to characterize TiN, CrN, TiAlN and AlCrN cathodic arc PVD (CA-PVD) coatings and select improved nitride-based coatings for FSW tools for welding of aluminum alloys, aluminum metal matrix composites (Al-MMC) and steels. The coatings are expected to improve the surface properties of the tool, reduce the wear and enhance the oxidation resistance and thermal stability of the tools, thus reducing the overall cost of FSW process.

Specific outlined objectives include:

1. Properties evaluation and characterization of binary (TiN, CrN) and ternary ((TiAl)N, (CrAl)N) cathodic arc PVD (CA-PVD) coatings.
2. Designing and manufacturing of FSW tool. This involves material selection for the tool, tool profile selection/design, and dimensions optimization as well as using appropriate heat treatment process so that the tool attains adequate mechanical strength so as to prevent the premature failure during FSW operations.
3. Deposition of CA-PVD ternary nitride-based MAC coatings on the FSW tool using optimized coating deposition parameters. In this objective, careful sample

preparation procedure and optimum coating parameters will be the major consideration to ensure good coating adhesion to the FSW tool substrate and to achieve improved coating properties.

4. Comparison of bare (uncoated) tool and nitride-based CA-PVD coated tools for FSW for selected materials. Tools will be evaluated comparatively based on weld quality, tool wear resistance and tool life.
5. Evaluate the tool wear resistance performance of the CA-PVD ternary nitride-based coated tools for FSW of commercial Al-MMC and/or steel.

3.3 Approach

To achieve the aforementioned objectives, an initial extensive review of related literatures on the PVD technique and FSW process was conducted. The deposition of CA-PVD coatings and characterization technique to understand their properties were also studied. Thus, TiN, CrN, (AlCr)N and (TiAl)N CA-PVD coatings were deposited and characterized for a proper understanding of the coating properties. Thereafter, they were also evaluated for wear resistance, oxidation resistance in ambient and vacuum conditions and corrosion resistance to compare the performance of the coatings. Based on these initial tests, best-performing coatings were selected for FSW tool. Thereafter, FSW tool design, manufacturing, heat treatment and deposition of coating were carried out. Coated tools were then used for FSW aluminum alloy and Al-MMC and the coatings contribution to wear resistance were then evaluated in comparison to the wear of the uncoated/bare tools.

Microindentation machine (MicroCombi Tester, CSM Instruments, Switzerland) was used to measure the mechanical properties and scratch resistance or adhesion of the coatings to

the tool. Morphological and compositional characterization of coated samples were conducted by scanning electron microscope (SEM) (VEGA3 SBH, TESCAN, Czech Republic) and energy dispersive spectroscopy (EDS) (Oxford, USA) which is attached to the SEM, respectively. X-ray diffractometer (D8 advance XRD, Bruker, USA) with CuK α radiation ($\lambda = 0.154186$ nm) and optical profilometer (ContourGT-K, Bruker, Germany) were used for the structural analysis and for measuring the surface roughness respectively. The FSW process was conducted using a RM-1 friction stir welder (Manufacturing Technology. Inc. USA)

CHAPTER 4

RESEARCH METHODOLOGY

This section provides details of the experimentation conducted throughout the study. Initial characterization and testing of titanium nitride (TiN), chromium nitride (CrN), titanium aluminum nitride or aluminum titanium nitride (TiAlN or AlTiN) and chromium aluminum nitride or aluminum chromium nitride (CrAlN or AlCrN) cathodic arc deposited PVD coatings were conducted. Basic characterization and testing techniques such as microstructural analysis with the help of optical microscope, scanning electron microscope, X-Ray diffraction, microindentation, scratch, corrosion and wear testing were used in evaluating the coating properties. High temperature oxidation tests and vacuum annealing of the coatings were also performed to analyze the oxidation resistance properties and the effect of heat treatment on the coatings respectively. These preliminary tests were the basis for selecting the appropriate coating for FSW tool for the welding test on aluminum alloy and composite.

4.1 Basic Characterization Tests of TiN, CrN, TiAlN and AlCrN Coatings

4.1.1 Sample design and preparation

TiN, CrN, TiAlN and AlCrN or CrAlN coatings were deposited on stainless steel substrate for characterization and initial testing and evaluation. Square samples 25 mm × 25 mm × 3 mm were cut from 304 stainless steel sheets for the substrates. Table 4-1: Chemical composition of 304 stainless steel substrate. Then the substrates were initially ground with

several SiC grit sizes (240 through 600 grit sizes) and finally polished on emery cloth with 0.03 μm alumina paste to a mirror-like surface. The samples were ultrasonicated with acetone to remove residue due to polishing, then dried and cautiously suspended on the planetary for the coating process.

Table 4-1: Chemical composition of 304 stainless steel substrate.

Elements	Cr	Ni	Mn	Si	S	C	P	Fe
Composition wt%	18.76	10.89	1.2	0.6	0.03	0.05	0.045	Balance

4.1.2 Coating deposition procedure

The process of depositing nitride-based coatings using cathodic arc PVD process is an advance deposition technique. Lately, it has emerged to be a famous deposition process in a number of coating industries which is used for a wide range of applications. This is due to the excellent adhesion of its coatings and higher deposition rates [10–12]. This has led to further development of the physical vapor deposition (PVD) process, such as the introduction of the advantageous hybrid technology combined in the Metaplas-Domini modern coating equipment by Metco (Oerlikon Group) [13]. This improvement has subsequently enabled deposition of coatings with excellent interfacial adhesion, increase in layer density, provision of thin, smooth and dense coatings while reducing growth failure and droplets emission significantly. Additionally, these modules are consolidated with the patented arc-enhanced glow discharged (AEGD), an effective plasma cleaning process, thereby improving the properties of the coatings considerably [13].

TiN, CrN, (TiAl)N and (AlCr)N coatings considered in this study were deposited by an industrial sized state-of-the-art cathodic arc physical vapor deposition (CA-PVD) machine shown in Figure 4-1 (Metaplas.Domino Mini, Oerlikon, Germany) incorporated with arc-

enhanced glow discharge (AEGD), an effective plasma cleaning process, and advanced plasma assisted (APA) arc technologies. CA-PVD technique is one of the most promising deposition PVD techniques because of its relatively low deposition temperature, excellent coating adhesion and the high deposition rate [10–12]. With further development, deposition of coatings with enhanced interfacial adhesion, increased layer density with thin, smooth and dense coatings while significantly reducing growth failure and droplets emission are obtainable with CA-PVD machine consolidated with AEGD and APA arc [152].



Figure 4-1: Cathodic arc PVD system.

The coating deposition procedure consisted of five stages: (i) vacuum evacuation to low pressure and testing to ensure chamber is not leaking, gases are flowing accordingly, (ii) arc enhanced glow discharge (AEGD) etching and sample cleaning process, (iii) chamber heating to the deposition temperature and re-evacuation to desired pressure for deposition, (iv) coating deposition process, and (v) cooling stage to avoid oxidation of the coating.

After attaining the desired vacuum of 1×10^{-5} mbar, the substrates were then preheated to 600 °C. During the AEGD etching process, positively ionized argon ions are accelerated at a high voltage via a bias voltage to strike the negatively biased substrate. By bombarding with high energy ions, the substrate surface is cleansed from adsorbed and chemisorbed layers, oils and other impurities, thus enhancing the coating adhesion. The AEGD process is effective in removing surface layer to a depth of 200 – 400 nm. The deposition procedure has been detailed in earlier studies [152,153] and typical parameters used in this study are presented in Table 4-2. The targets made of pure Cr and Ti with 99.99% purity were used for the deposition of CrN and TiN, respectively. While AlTi target with 55 at.% Al and 45 at.% Ti was utilized for the deposition of $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$, and AlCr target with 70 at.% Al, 30 at.% Cr for depositing $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ were used. The evaporator current on Cr and Ti targets was 130 A, and on AlTi and AlCr targets was 150 A, respectively.

The substrate holder shown in Figure 4-2 is a planetary stand capable of triple rotation of substrates. Hexagonal cylindrical dummies where double rotation of the substrate is obtainable were utilized in this study. After insertion into the coating chamber, the substrates were further cleaned by the AEGD etching process which uses Ar^+ ions to bombard the substrate surface to remove both oxides and adsorbed layers. Furthermore, the substrates were pre-heated to about 773 K (500 °C) before the coating process commenced in a high vacuum condition. The coating deposition process was controlled such that a metallic bond-coat consisting of majorly the target element(s) is deposited before gradually introducing the reactive gas. Thus, the binary coatings have pure Ti and Cr bond coat of tens nanometer thickness before the TiN and CrN coatings, respectively,

while the ternary coating bond coat consist of AlTi and AlCr alloy of tens nanometer thickness before the TiAlN and CrAlN coatings, respectively.

Table 4-2: Typical coating deposition parameters.

Process	Parameters	TiN, CrN, TiAlN, CrAlN
AEGD Etching Process	IR Heater (°C)	500 ± 30
	Evaporator Current (A)	80 – 85
	Substrate bias (V)	- 250
	Duration (min)	30
	Argon Pressure (mbar)	1.0 E-2
Coating Deposition Process	Evaporator Arc Current (A)	130 – 150
	Substrate bias (V)	–100 to –80
	IR Heater (°C)	500 ± 30
	Duration (min)	40 – 120
	Nitrogen gas flow rate (ccm)	500
	Charge on Evaporators (Ah)	200 – 1000
	Nitrogen Pressure (mbar)	8.5 – 6.5 E-2

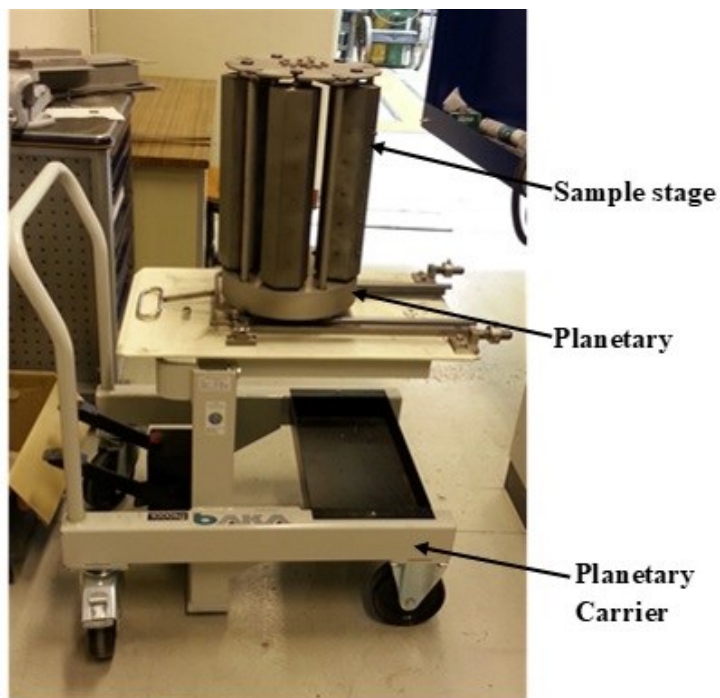


Figure 4-2: Planetary system.

4.1.3 Thickness and roughness measurement

Coating thickness was measured using calotester in which a hard steel ball of 20 mm diameter is continuously rotated against the coating in the presence of diamond slurry. The ball creates a circular crater through the coating thickness due to three-body abrasive wear between the ball, the coating and the slurry. VideoTM software (CSM Instruments, Switzerland) was then used to measure the coating thickness by geometry relationship. The thickness values were obtained from a minimum of three to five measurements at various locations on the coating and the average is reported.

The microscale roughness of the coatings was measured using optical profilometer (ContourGT-K, Bruker, USA) which uses the principle of interferometric to produce a 3D topographical image of the sample by scanning through an area of about 1.66 mm x 2.2 mm (3.5 mm²). Three 1.66 mm x 2.2 mm images were captured from different locations on the 25 mm x 25 mm coated samples with a pixel resolution of 1632 x 786 in order to obtain the arithmetic mean (R_a), root-mean-square (RMS) and the peak-to-valley (PV) distance microroughness values. For nanoscale surface roughness values of the coatings, high performance atomic force microscope (hpAFM, Nanomagnetix Instruments, UK) with 0.01nm AFM resolution using the tapping mode condition of the cantilever was used. Averaged nano-roughness parameters for the R_a , RMS and PV distance were taken from three multiple scan areas of 5 μm x 5 μm (25 μm^2) with 714 x 543-pixel resolution.

4.1.4 Microstructural characterization

Morphological and compositional characterization of coated samples were conducted by scanning electron microscope (SEM) (SEM, JOEL, Japan and VEGA3 SBH, TESCAN, Czech Republic) and energy dispersive spectroscopy (EDS) (Oxford, USA) which is

attached to the SEM, respectively. X-ray diffractometer (D8 advance XRD, Bruker, USA) with CuK α radiation ($\lambda = 0.154186$ nm) and optical profilometer (ContourGT-K, Bruker, Germany) were used for the structural analysis and for measuring the surface roughness respectively. For XRD analysis, evaluated samples were subjected to a $\theta/2\theta$ scan in which the incident X-ray beam was held at a fixed angle while sample stage and the detector rotated. The average grain size of the coating was estimated using Scherrer's equation (Equation 4-1).

$$\text{Average grain size} = \frac{0.9\lambda}{FWHM \cos\theta} \quad 4-1$$

where 0.9 is the shape factor (spherical shape assumed), λ is the wavelength of the X-ray used and θ is the Bragg's angle.

4.1.5 Micromechanical characterization

The mechanical properties of the coatings described by the hardness and elastic modulus was measured using microindentation machine shown in Figure 4-3 (MicroCombi Tester, CSM Instruments, Switzerland). Indentation hardness (***H***) and indentation elastic modulus (***E***) were calculated from load-displacement curve according to Oliver and Pharr model [154]. *H* is a measure of the resistance to permanent deformation or damage and it is determined according to Equation 2 [154] while *E* was calculated from the plane strain modulus *E** using an estimated poisson ratio according to Equation 4-2 to Equation 4-5 [154].

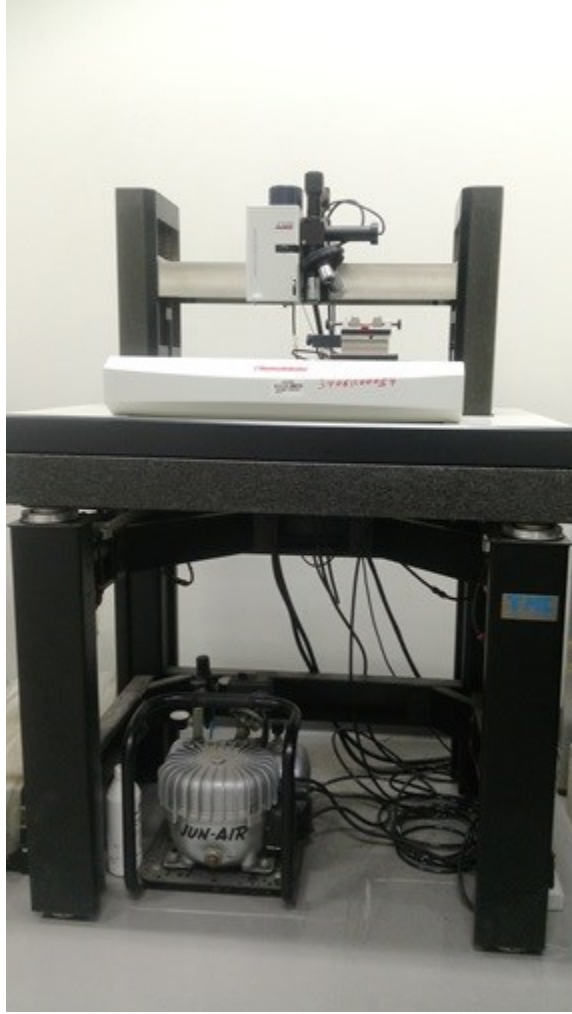


Figure 4-3: MicroCombi Tester for microindentation and scratch testing.

$$H = \frac{F_{max}}{A_p} \quad 4-2$$

$$E_r = \frac{\sqrt{\pi} \cdot S}{2 \cdot \beta \sqrt{A_p}} \quad 4-3$$

$$E^* = \frac{1}{\frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i}} \quad 4-4$$

$$E = E^* \times (1 - \nu_s^2) \quad 4-5$$

Where F_{max} is the maximum test load, A_p is the projected contact area, E_r is the reduced modulus, S is the contact stiffness at F_{max} , β is indenter geometry constant, and ν_i is poison ratio of the indenter (0.07), E_i is the elastic modulus of the indenter (1141 GPa) and ν_s is the poison ratio of the coated specimen (poison's ratio of 0.3 is typical for ceramic coating). Normal load of 20 mN was applied for 10 s dwell time at loading and unloading rates of 20 – 40 mN/min. The applied load was chosen to ensure that the penetration depth is less than 10% of the coating thickness. Mean and standard deviation values from several microindentation measurements are reported.

4.1.6 Scratch characterization

Microindenter shown in Figure 4-3 (MicroCombi Tester CSM Instruments, Switzerland) was utilized for the scratch test. The adhesion of the coatings to the substrate was investigated through the scratch test with a Rockwell C indenter of 100 μ m tip radius. The indenter was pushed with increasingly applied load from 0.03 to 30 N against the coatings at a rate of 0.1 N/s. The scratch speed was 2 mm/min at 6 N/min loading rate over a scanning length of 10 mm. During the test, the normal load, acoustic emission (AE), frictional force ($F\mu$) and the coefficient of friction (COF) were continuously measured and recorded. With the help of optical microscope, AE and COF signals, the cohesive failure (L_{c1}) and adhesive failure (L_{c2}) were estimated. A minimum of three scratch tests were conducted on each coating and the tracks were separated by an adjacent distance of 1mm. To examine the coating resistance to crack propagation, the critical loads were correlated to evaluate how long the coating could survive after the initial cracks (L_{c1}) before the complete delamination of the coating (L_{c2}). Thus, the scratch crack propagation resistance (CPR_S) was defined as in Equation 4-6 as a function of L_{c1} and L_{c2} to comparatively use

the scratch results to indicate coating toughness [155–157] since the K_{IC} method used in determining toughness is not suitable for ductile thin films [49].

$$CPR_S = L_{c1}(L_{c2} - L_{c1}) \quad 4-6$$

4.1.7 Wear and friction experiment

Wear and friction tests were performed using a multipurpose tribometer shown in Figure 4-4 (UMT-3, Bruker, USA) with the ball-on-disc configuration. The counterpart is a 6.3 mm diameter tungsten-carbide (WC) ball with a hardness of HRA 92. The tests were performed in an ambient atmospheric condition at 23 ± 2 °C temperature and 40 ± 5 % relative humidity. The wear test was conducted (wear track radius of 6mm) at a linear speed of 0.11 m/s for a sliding distance of 63m and under a range of applied loads: 15, 20 and 25 N.



Figure 4-4: Multipurpose Tribometer.

The initial contact pressure between the sample and the ball corresponding to these loads were computed according to the Hertzian relationship (Equation 4-7).

$$P = \left(\frac{4WE'^2}{3R^2\pi^3} \right)^{1/3} \quad 4-7$$

Where E' is the composite elastic modulus given by Equation 4-8, W is the applied load, R is radius of ball.

$$\frac{1}{E'} = \frac{(1-\nu_1^2)}{E_1} + \frac{(1-\nu_2^2)}{E_2} \quad 4-8$$

Where E₁ and E₂ are elastic modulus of ball and coating and ν₁ and ν₂ are the Poisson's ratio of the ball and sample respectively. For WC ball, E₁ is 700 GPa and ν₁ is 0.24 [158] and the E₂ and ν₂ of the coating was determined from the microindentation test.

The wear track cross sectional area (A) of the coated sample was obtained using the optical profiler (ContourGT-K, Bruker, USA). Thereafter, the wear volume (V) and specific wear rate (K) of the coatings are then calculated by Equation 4-9 and Equation 4-10, respectively.

$$V = 2\pi rA \quad 4-9$$

$$K = \frac{V}{SF_N} \quad 4-10$$

Where r is the radius of the wear track, S is the sliding distance and F_N is the normal applied load.

4.1.8 Electrochemical tests procedure at room temperature

Corrosion characteristics of the coatings were investigated using the typical three-electrode cell; consisting of a graphite counter electrode, saturated calomel electrode (SCE) as reference electrode and the substrate acting as the working electrode. Gamry Paracell, in

which the reference electrode point of measurement is brought closer to the working electrode by a bridge tube, is utilized with an active substrate area of 0.7855 cm². The corrosion behavior was evaluated in two media; 1M HCl and 3.5% NaCl, prepared with analytical grade reagents and distilled water. All electrochemical measurements were conducted with the Gamry Instrument (Reference 3000TM) high performance potentiostat/galvanostat/ZRA with a computerized system for electrochemical data collection and analysis. Echem Analyst 6.0 software was employed for fitting and analysis of electrochemical data. Corrosion measurements were carried out for coated substrates as well as the blank 304 SS substrate in both media. Substrates were cleaned with distilled and mounted onto the paracell. Before the electrochemical measurements, open circuit potential (E_{corr}) were allowed for 2700 s to enable them attain equilibrium state. The substrates were cathodically and anodically polarized by -500 and 1500 mV against the E_{corr} , respectively, at a scanning rate of 1 mV/s. Tafel plots were obtained from the Potentiodynamic polarization (PDP) tests. Linear polarization resistance (LPR) were conducted at the scan rate of 0.125 mV/s and between -20 and +20 mV against the E_{corr} . Electrochemical impedance spectroscopy (EIS) measurements were carried out with an alternating current at frequencies between 1 MHz and 100 mHz with the acquisition of 10 points per decade, with the signal amplitude of 10 mV at OCP.

4.2 Experimental procedure for annealed coatings

4.2.1 Vacuum annealing of coated samples

Vacuum annealing was conducted using an industrial heavy-duty tube furnace (1500 °C Heavy Duty Furnace, Lindberg/MPH, USA) as shown in Figure 4-5 with three heating zones to ensure uniform heating and temperature distribution within the tube. The furnace

was vacuum pumped by rotary vane pump (Maxima D30A, Fisher Scientific, USA) as shown in Figure 4-5 to a high vacuum environment. Each of the coated sample was thermally treated with a heating rate of 80 °C/min to 700, 800, 900 and 1000 °C annealing temperatures in the high vacuum furnace for a duration of 2 hrs. During the heating cycle, the vacuum was maintained at a pressure of about 70 ± 2 mTorr (~ 90 μ bar). The samples were then furnace cooled to room temperature then prepared for further characterization.



Figure 4-5: Furnace and pumping system for vacuum annealing.

4.2.2 Corrosion test procedure for annealed Coatings

Corrosion characteristics of the bare substrate, as-deposited and annealed coatings were investigated using Gamry ParaCell, a typical three-electrode cell suitable for flat samples. The cell consists of saturated calomel electrode (SCE) as reference electrode, the sample as the working electrode and graphite as the counter electrode. The cell uses a bridge tube to advance the reference electrode closer to the working electrode and has an electrolyte capacity of about 400 mL with an active sample area of 1.766 cm². The corrosion behavior

was evaluated in 1M HCl solution, prepared with analytical grade reagents and distilled water. The corrosion tests were conducted using USB high performance potentiostat/galvanostat/ZRA (Gamry Instruments Reference 3000TM) connected to a computerized system. Echem Analyst 6.0 software was employed for fitting and analysis of electrochemical data. Samples were cleaned with distilled water before mounting onto the ParaCell and then they were allowed for 1hr to enable the open circuit potential (OCP) attain equilibrium state. EIS measurements were carried out with an alternating current at frequencies between 1 MHz and 100 mHz at an AC voltage of 10 mV. For the PDP test, the samples were cathodically and anodically polarized by –500 and 1500 mV respectively with respect to the reference electrode potential at a scanning rate of 0.5mV/s. The corrosion potential (E_{corr}) and current density (I_{corr}) were found from the interception of the extrapolation of the anodic and cathodic Tafel curves

To quantitatively evaluate the corrosion protection performance, the protective efficiency (E) of as-deposited and annealed coatings with reference to bare 304 SS sample was evaluated using the Equation 4-11 and Equation 4-12 according to the obtained parameters from EIS and PDP, respectively.

$$E_{eis} = \left(1 - \frac{R_{ct}}{R_{ct}^o}\right) \times 100 \quad 4-11$$

$$E_{pdp} = \left(1 - \frac{I_{corr}^o}{I_{corr}}\right) \times 100 \quad 4-12$$

Where R_{ct} and R_{ct}^o are the charge transfer resistance values, I_{corr} and I_{corr}^o are the corrosion current density values, for the coatings and the bare 304 SS sample, respectively.

4.3 Oxidation Test Procedure (Thermogravimetric Analysis)

The thermogravimetric analysis (TGA) measurement was conducted in Cahn Thermax 700 TGA system shown in Figure 4-6 under a nitrogen (99.999% purity) purge gas at approximately 100 ml/min flow rate. TiN, CrN and AlCrN coated samples were heated at a rate of about 20 °C/min and isothermally held in ambient air at 800, 900 and 1000 °C for 5 hrs. AlTiN coated samples were tested at 900 and 1000 °C using same heating rate and isothermal duration. The weight gain was continuously measured and recorded by a built-in microbalance. The reported weight gain was for the isothermal duration, the oxidation during the ramping stage was negligible. After completion of the isothermal period the thermax furnace automatically switched off. Samples are allowed to cool to room temperature before further characterization.



Figure 4-6: Cahn Thermax 700 TGA system.

4.4 Mechanical and Tribological Characterization of AlCrN Coated Flat Spark Plasma Sintered W-25%Re-HfC Composite

4.4.1 Tool material development

The tool material was developed from a semi-alloyed tungsten-rhenium alloy (W-25wt.% Re) and hafnium carbide (HfC) powders via mechanical alloying (MA) technique to obtain nanostructured particle sized powders with uniform distribution of the reinforcement. During the mechanical alloying process, 10 vol.% of HfC powder were dispersed as reinforcement in the nanocrystalline W-25% Re alloy. Spark plasma sintering (SPS) was utilized for the consolidation of the composite powder material. Details of the synthesis, consolidation and characterization of the W-25%Re-10 vol.% HfC FSW composite tool material are presented in an earlier published work [159]. The main MA parameters used for the tool material in the study are milling rotational speed of 150 rpm for 15 h milling time with a ball-to-powder ratio of 5:1. The SPS consolidation parameters are 50 MPa compaction pressure at a temperature of 1800°C for a duration of 10 min. The mechanical, structural and morphological properties of the developed composite material have been presented elsewhere [159].

4.4.2 Characterization of AlCrN coated W-25%Re-HfC sample

The cathodic arc aluminum chromium nitride (AlCrN) PVD coating was deposited on the disc-like sintered W-25%Re-10vol.% HfC composite substrate with a diameter of 25 mm and 3 mm thickness. It was ground, polished and cleaned with acetone prior to deposition. The substrate roughness, before the coating was deposited, expressed in the arithmetic mean (R_a) and root-mean-square (RMS) values was $0.25 \pm 0.04 \mu\text{m}$ and $0.35 \pm 0.07 \mu\text{m}$, respectively.

4.4.3 Tribological properties

The wear test was conducted on a multipurpose tribometer (UMT-3, Bruker, Germany) with a ball-on-disc configuration. Hardened steel counterpart of 6.3 mm diameter and HRC 62 hardness was used for the test. The Young modulus and Poisson's ratio of 207 GPa and 0.28 respectively are typical for hardened steel ball, thus these values were used in calculating the Hertzian contact pressure. The tests were performed in an ambient atmospheric condition at 23 ± 2 °C temperature and $40 \pm 5\%$ relative humidity. The experimental parameters for the wear test are shown in Table 4-3. The wear behavior of the AlCrN coated and uncoated W-25%Re-HfC composite tool material was comparatively evaluated. The specific wear rate was obtained by measuring the net weight using a high resolution analytical weight balance in Figure 4-7 (AUW220D, Shimadzu Analytical Balance, Japan). The resolution and repeatability of the weight balance are 0.01mg and ≤ 0.1 mg respectively. The specific wear rate is expressed as mass loss per unit sliding distance per applied load (mg/kNm) accordingly.

Table 4-3: Wear test parameters for coated and uncoated W-25%Re HfC.

Load (N)	Rotational speed (rpm)	Track diameter (mm)	Sliding distance (m)	Sliding speed (m/s)
30	800	12	500	0.50



Figure 4-7: Analytical weight balance.

4.5 AlCrN Coated FSW Tool for Welding 6061-T6 Aluminum Alloy

4.5.1 Materials and FSW tool design

Alloy steel 4140 grade was used for the FSW tool material due to its reasonable combination of toughness and strength. It is a chromium and molybdenum strengthened low-alloy steel with good wear resistance and fatigue strength. The nominal composition is shown in Table 4-4. Various tool geometries from simple to complex exist for FSW tool [22]. However, the ease of deposition of the coating on the tool becomes a major

consideration. PVD is a line-of-sight deposition process which makes it practically difficult to deposit PVD coatings on tools with complex geometry or features. Hence, a plain conical pin on a featureless shoulder is considered in this study. The dimension commonly recommended for the tool design is a shoulder to pin ratio of 3:1 and pin length of 0.85 - 0.95 of the thickness of the workpiece. Thus, the tool was manufactured with the following dimension; shoulder diameter of 18mm, pin diameter is 6mm at the root and 4mm at the tip. The shoulder was concaved 2° towards the center to reduce dissipation of frictional heat. The workpiece is a 6mm thick 6061-T6 aluminum alloy, thus the pin length was 5.6 mm. The FSW tool was then hardened by water quenching and tempering heat treatment process to 55-56 HRC hardness. However, the FSW tool to be coated was not tempered, it is expected that it will be tempered during the deposition process. After coating the hardness was approximately 40 HRC. For characterization and tribological analysis, coated and uncoated 4140 samples were also prepared in a similar manner.

Table 4-4: Chemical composition of 4140 Alloy Steel.

C	Mn	P	S	Si	Cr	Mo	Ni	Cu	V	Fe
0.361	0.894	0.0141	0.0287	0.243	1.07	0.162	0.0829	0.23	0.013	Bal.

4.5.2 Deposition and characterization of AlCrN coated FSW tool

The cathodic arc aluminum chromium nitride (AlCrN) PVD coating was deposited with the parameters shown in Table 4-5 on the alloy steel 4140 tool substrate. It was ground, polished and cleaned with acetone prior to deposition. The substrate roughness, before the coating was deposited, expressed in the arithmetic mean (R_a) and root-mean-square (RMS) values was $0.25 \pm 0.04 \mu\text{m}$ and $0.35 \pm 0.07 \mu\text{m}$, respectively.

Table 4-5: Deposition parameters for AlCrN coated FSW tool.

Coating Parameters	AlCrN Coating
AEGD Etching duration	30min
Nitrogen gas flow rate	500 sccm (99.996% Purity)
Planetary rotating speed	2 rpm
Cathode amperage hour (Ah)	600Ah
Coating temperature	450 ⁰ C $\pm$ 20 ⁰ C
Coating pressure	6.50E-2 mbar
Coating bias voltage range	Between -80 and -100V
Deposition Time	120min

4.5.3 Wear and friction test for AlCrN coated 4140 alloy steel

Wear and friction tests were performed using a multipurpose tribometer (UMT-3, Bruker, USA) with the ball-on-disc configuration. The counterpart is a 6.3 mm diameter tungsten-carbide (WC) ball with a hardness of HRA 92. The tests were performed in an ambient atmospheric condition at 23 ± 2 °C temperature and $40 \pm 5\%$ relative humidity. The experimental parameters for the wear test were as follows: Normal load of 20N were used for a sliding distance of 700m at 0.2m/s linear speed, and the wear track diameter is 16mm. The wear resistance of the coated and hardened FSW tools was compared. The wear resistance was also quantified based on weight loss, by measuring the net weight using a high resolution analytical weight balance shown in Figure 4-7 (AUW220D, Shimadzu Analytical Balance, Japan). The weight balance has a minimum display of 0.01 mg and repeatability of ≤ 0.1 mg. The wear rate is then expressed as mass loss per unit sliding distance per applied load (mg/kNm).

4.5.4 Evaluation of AlCrN coated FSW tool

FSW test was conducted on a 6061-T6 aluminum alloy of $180 \times 90 \times 6$ mm dimension, using a RM-1 friction stir welder shown in Figure 4-8 (Manufacturing Technology. Inc.

USA). Full penetration bead on plate weld was performed with AlCrN coated 4140 and uncoated 4140 alloy steel tools on the workpiece. The bead on plate weld is similar to the butt weld except that in a butt weld the plates need to be perfectly aligned and maintained throughout the welding process. Thus, more rigorous pre-weld preparation procedure is required. Moreover, bead on plate will eliminate the complication that may arise from the gap effect between butted plates. Typical FSW process parameter of 1000 rpm, plunging speed of 25 mm/min, traverse speed of 200 mm/min and a tilt angle of 2° was utilized for a weld distance of 150 mm/pass. Three passes and three plunges were performed using each tool. The mechanical, macrostructural and microstructural properties of the weld produced by coated and uncoated tools were characterized by analyzing the weld using microindentation, optical microscope, pixera, scanning electron microscope, and energy dispersive spectroscopy. The tool wear is quantified by measuring the variation in pin length at the end of the three passes and plunges using Equation 4-13.

$$\textbf{Variation (\%)} = \frac{PL^o - PL^i}{PL^o} \times \textbf{100} \quad \textbf{4-13}$$

Where PL^o and PL^i are the pin length before and after FSW of the workpiece, respectively.

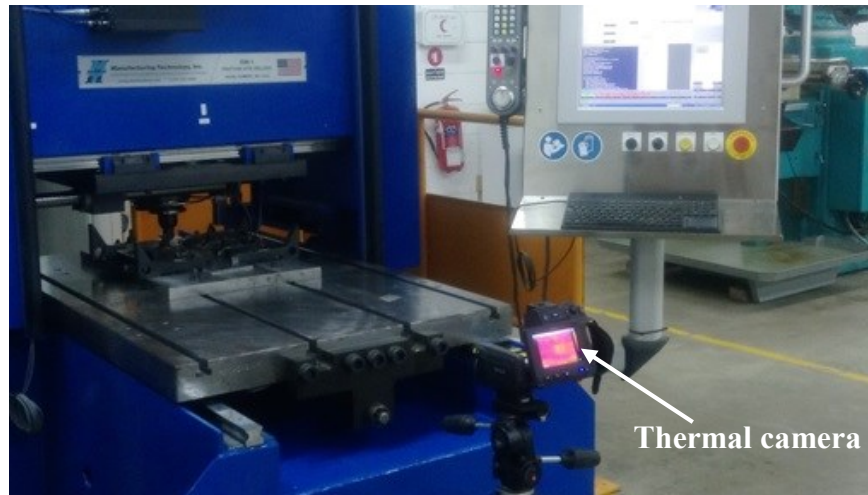


Figure 4-8: RM-1 Friction Stir Welder and FLIR Thermal Camera.

4.6 FSW Coated Tools for Aluminum MMC

4.6.1 Material and tool design

The Al-MMC workpiece used in this study is an aerospace grade aluminum alloy 2124 (main elements are Al-Cu-Mg) reinforced with 17vol% SiC (AA 2124-17% SiC) supplied by Aerospace Metal Composite Limited designated as 2124/SiC/17p. The reinforcement has an average particle size of 3 μm and manufactured via mechanical powder metallurgy process using high energy mixing process and thereafter hot isostatic pressed (HIP) to formed panels of 400 x 400 x 8 mm. The HIP panels were then solution heat treated and cut into strips of 200 x 50 x 8 mm and then face milled to properly align the strips for the FSW process.

The FSW tool was designed from chromium and molybdenum hot work tool steel H13 grade due to its hot-hardness property, better hardenability and its excellent combination of high toughness and resistance to thermal fatigue. The tool is designed as a featureless conical shape tool due to the line-of-sight PVD deposition process. This makes it

practically difficult to deposit coatings on tools with complex geometry or hidden features. The tool has a shoulder diameter of 18 mm and pin root diameter of 8mm tapered to 4 mm. The H13 FSW tool was then hardened in oil from 1050 °C in argon atmosphere and immediately tempered at 550 °C for about 1hr in a single stage tempering process. The hardness of the hardened H13 tool was 52 – 56 HRC. Similarly, H13 tool steel square samples with dimension 30 x 30 x 8 mm were also prepared and coated under same conditions for mechanical and scratch test.

4.6.2 Deposition and characterization of FSW coated tools for Al-MMC

Prior to coating deposition, the surface preparation of the heat treated H13 FSW tools was carried out by grinding up 600 grit size and cleaned in acetone. Aluminum chromium nitride (AlCrN) and titanium aluminum nitride (TiAlN) cathodic arc PVD coatings were deposited using an industrial size cathodic arc PVD machine (Metaplas.Domino Mini, Oerlikan, Germany). The machine is equipped with two evaporators carrying the targets, with elemental composition is Al – 29.5 at.% Cr and Al – 45 at.% Ti for depositing AlCrN and TiAlN coatings respectively. The substrate roughness, before the coating was deposited, expressed in the arithmetic mean (R_a) and root-mean-square (RMS) values was 0.25 ± 0.04 and 0.35 ± 0.07 μm , respectively. The deposition procedure has been detailed in earlier studies [152,160] and specific parameters used in this study are presented in Table 4-6.

Table 4-6: Deposition parameters for FSW coated tools for Al-MMC.

Coating Parameters	AlCrN and TiAlN
AEGD etching duration	30 min
Nitrogen gas flow rate	500 sccm (99.996 % Purity)
Planetary rotating speed	2 rpm
Cathode amperage hour	800 Ah
Coating temperature	450 ± 20 °C
Coating pressure	8.5×10^{-2} – 6.5×10^{-2} mbar
Coating bias voltage range	Between –80 and –100 V
Deposition rate and duration	~ 5 $\mu\text{m/hr}$ 80 min
Coating thickness	6 – 8 μm

4.6.3 Evaluation of FSW coated tools for Al-MMC

Pairs of edged milled AA 2124–17% SiC each of $400 \times 50 \times 8$ mm dimension were firmly held on 10 mm thick steel backing plate and butt welded using FSW. The FSW process was conducted using the RM-1 friction stir welder (Manufacturing Technology. Inc. USA) shown in Figure 4-8. AlCrN coated H13 (AlCrN-H13), TiAlN coated H13 (TiAlN-H13) and hardened uncoated H13 (or bare H13) tools were used in performing 380 mm long single pass butt weld on the AA 2124-17% SiC MMC workpiece. FSW process parameter of 1000 rpm, plunging speed of 25 mm/min, traverse speed of 60 mm/min and a tilt angle of 1° was utilized. The combination of a high rotation speed of 1000 rpm and a low traverse speed of 60 mm/min is used to induce the severest welding condition on the tool. These parameters have been reported to impose the maximum tool wear during FSW of Al-MMCs [123,124,161]. During the FSW process, the spindle torque, axial and traverse forces were also measured. In addition, the temperature of the tools was measured continuously for the entire welding distance using an advanced infrared thermal imaging camera (FLIR-T660, FLIR, PORTLAND) shown in Figure 4-8. The camera was focused at the point of contact between the tool and the workpiece. The mechanical and

microstructural properties of the weld produced by coated and uncoated tools were characterized by analyzing the weld using microindentation, optical microscope, scanning electron microscope, and energy dispersive spectroscopy. The tool wear was quantified by weight loss method. This was accomplished by measuring the net weight before and after FSW process, using the analytical weight balance (AUW220D, Shimadzu Analytical Balance, Japan) shown in Figure 4-7. The wear rate is expressed as mass loss per unit weld distance (g/m).

CHAPTER 5

CORROSION AND WEAR TEST FOR THE COATINGS AT ROOM TEMPERATURE

The corrosion resistance behavior of the coatings (TiN, CrN, CrAlN and TiAlN) in acidic and salt solutions are presented in the first section of this chapter. While the tribological behavior involving the ball-on-disc wear and scratch tests of the coatings are discussed in the second section of the chapter.

5.1 Corrosion Resistance Behavior of Coatings in 1M HCl and 3.5% NaCl Solutions

5.1.1 Coating characterization

The surface roughness of the coatings was measured as-deposited using starrett R200 stylus profilometer. Table 5-1 shows the average result of the amplitude parameters R_a for each coating. RMS is the average spacing between profiles peaks at the mean line. However, both parameters are measured within the sampling length. The R_a values obtained suggest that the deposition process is similar for all coatings. However, CrAlN coatings possess the deepest valley as well as the highest numbers of peaks. This can possibly be attributed to the relatively higher numbers of macroparticles as a result of the high content of low melting temperature aluminum element. In contrast, TiAlN shows better surface roughness parameters owing to its lower peak height and lower number of peaks. Figure 5-1 shows the calotest optical micrograph where both diameters – internal and external, made by the ball crater can be seen, from which the thickness of the coating is calculated. The

thicknesses of coatings obtained from the calotest were uniform and approximately 1.80 μm . Average thickness of three calotest measurement of each of the coatings is shown in Table 5-1. Cross section SEM image of TiAlN coating is shown in Figure 5-2 indicating that the newly developed coatings were dense, uniform and continuous.

Table 5-1: Surface Roughness Amplitude Parameters for the Coatings.

Coatings	$R_a(\mu\text{m})$	RMS (μm)	Thickness (μm)
TiN	0.073 ± 0.008	0.423 ± 0.12	1.85 ± 0.04
CrN	0.068 ± 0.009	0.425 ± 0.10	1.82 ± 0.02
CrAlN	0.080 ± 0.016	0.289 ± 0.06	1.83 ± 0.03
TiAlN	0.060 ± 0.012	0.672 ± 0.30	1.80 ± 0.02

Table 5-2: Elemental Composition of the Coatings.

Composition (at.%)	TiN	CrN	CrAlN	TiAlN
N	48.6	47.4	49.2	47.8
Al			33.3	26.1
Ti	51.4			26.1
Cr		52.6	17.5	

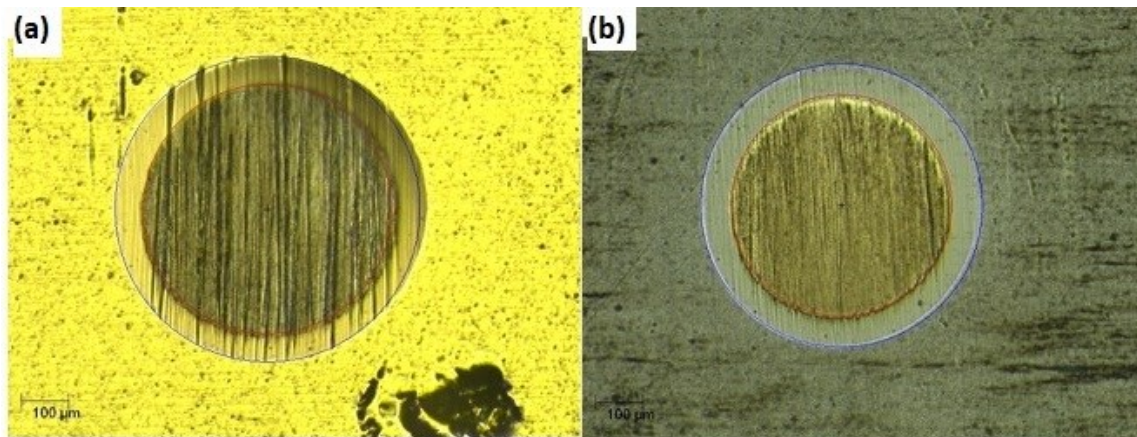


Figure 5-1: Typical Calotest Micrograph showing coating thickness of (a) TiN and (b) CrAlN.

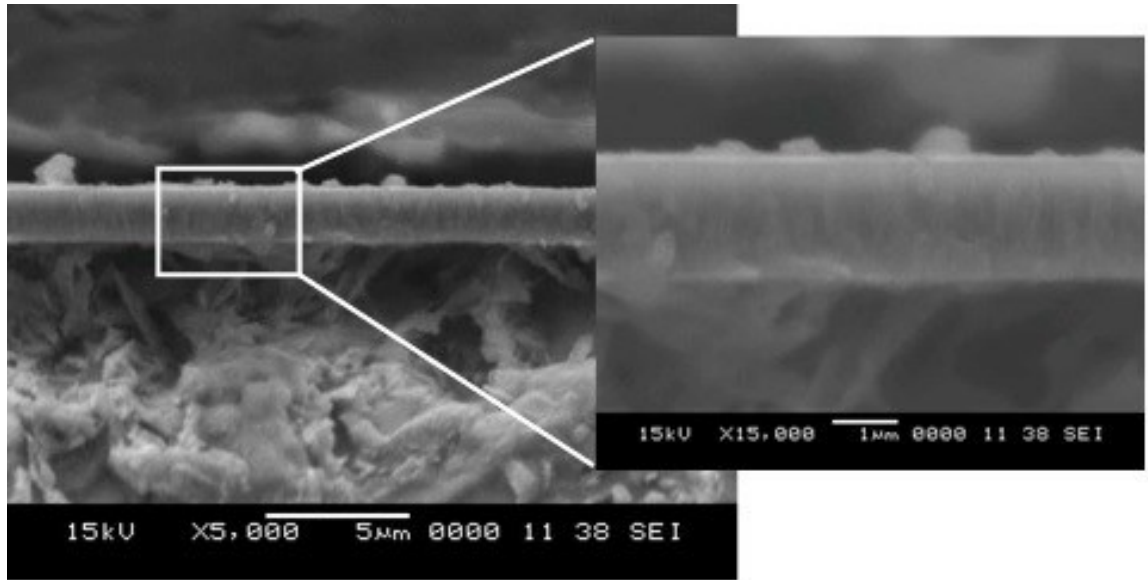


Figure 5-2: Typical cross section SEM images showing the thickness and microstructure of TiAlN coating.

Table 5-2 illustrates the chemical composition of each of the coatings. The stoichiometric phases of the binary nitride coatings are CrN and TiN, respectively. The ternary nitride coatings have non-stoichiometric ratios as $\text{Cr}_{0.33}\text{Al}_{0.67}\text{N}$ and $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ for CrAlN and TiAlN coating systems, respectively. The atomic ratio of the elements in the target material used for the deposition of the ternary coatings for Al/Cr system was 2:1 and 1:1 for Ti/Al system. The X-ray diffraction pattern for the coatings is shown in Figure 5-3. The substrate peaks are denoted as SS in the figure (Figure 5-3a) and appears at the corresponding angles in the coated substrates as in Figure 5-3(b – e). For TiAlN coating, the (111) and (222) orientations were observed, however, its preferred crystallographic plane (111) peak showed reduced intensity. This is due to the high content of Al which causes the coating to become partly amorphous or at least reduces the crystallinity. Similar situation was observed for the CrAlN coating XRD peak. Ding et al. [68] have shown how the increase in Al/Cr and Al/Ti atomic ratio resulted in the gradual and sudden decrease in CrAlN and

TiAlN diffraction peaks, respectively. TiN and CrN XRD diffraction patterns reveal that the coatings are single phase with B1 NaCl cubic structure.

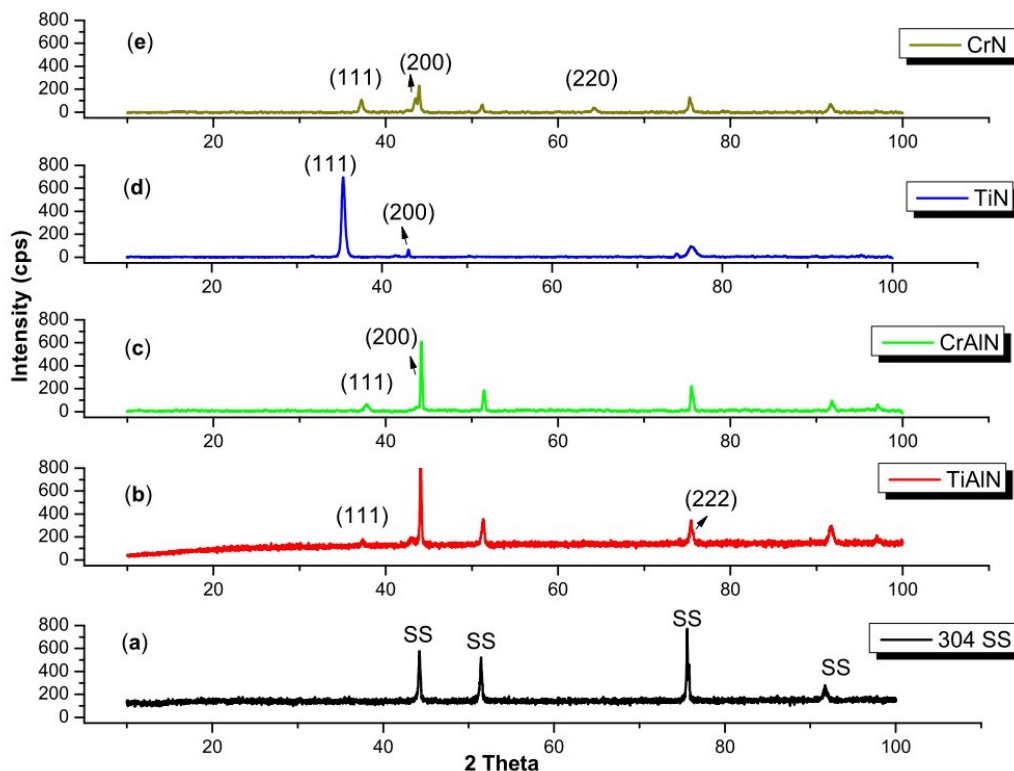


Figure 5-3: X-Ray Diffraction patterns for coated samples and substrate.

5.1.2 Electrochemical measurements

5.1.2.1 Open circuit potential (E_{corr}) measurement

Figure 5-4 and Figure 5-5 show the variation of E_{corr} with time for the coatings and the blank substrate in 1M HCl and in 3.5% NaCl, respectively. The E_{corr} of all coated substrates attained equilibrium state after 2700s with a significant shift in the E_{corr} towards the negative direction compared to the blank substrate. This is due to relative chemical inertness and physical barrier of these coatings. The open circuit potential of CrN and TiAlN coatings were noblest in HCl solution, while CrN and TiN approached much noble

E_{corr} values in NaCl solution. However, open circuit potential of the coatings shifted more to the positive values in the chloride solution than in the acidic solution. It can be remarked that the displacement of the E_{corr} of the coated substrates to more noble values indicate a noticeable improvement of the substrate resistance to corrosion susceptibility.

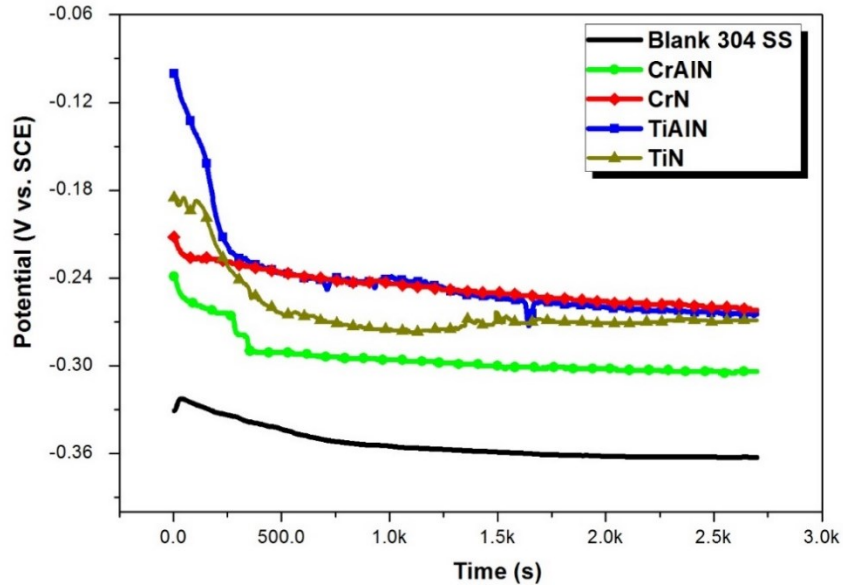


Figure 5-4: Open Circuit Potential in 1M HCl Solution.

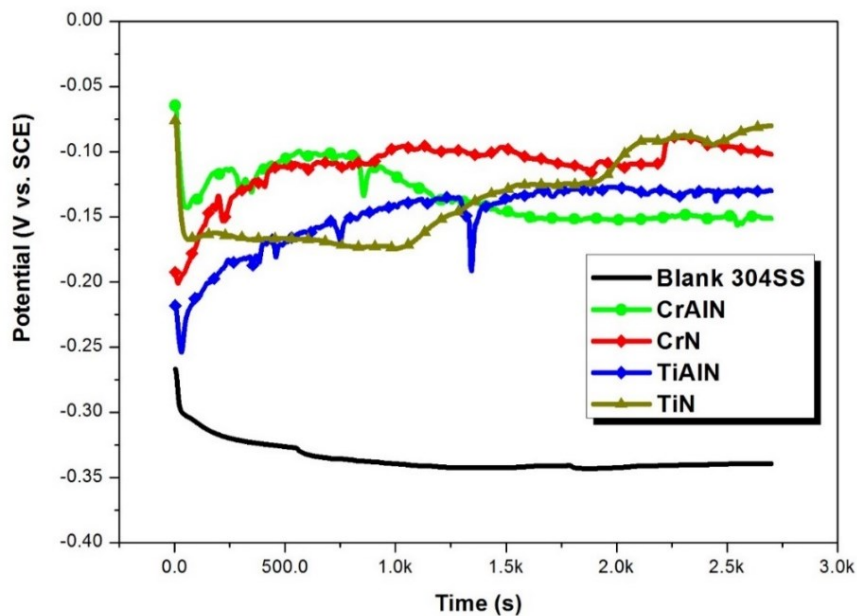
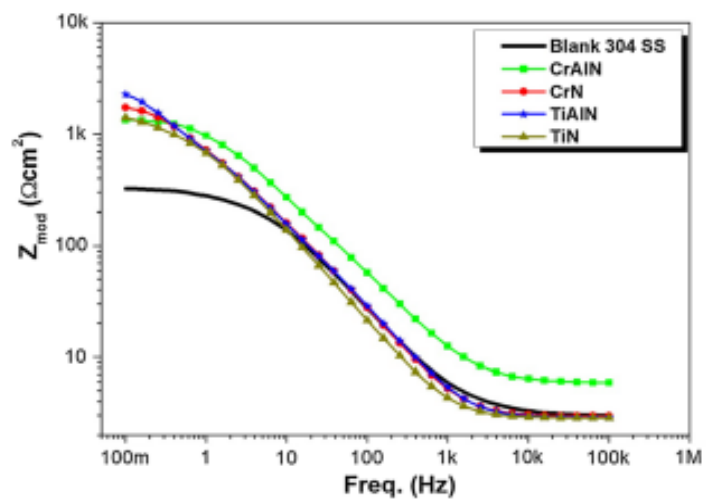


Figure 5-5: Open Circuit Potential in 3.5% NaCl Solution.

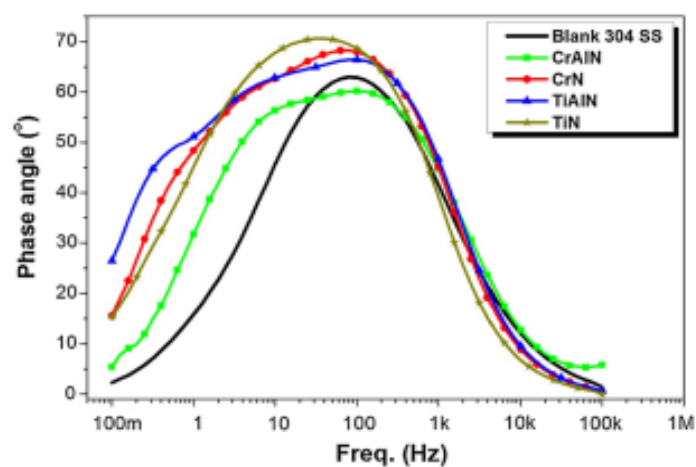
5.1.2.2 Electrochemical impedance spectroscopy (EIS) measurement

The EIS measurements were conducted in 1M HCl and in 3.5% NaCl solutions in order to investigate the influence of the coatings on the kinetics and characteristics of the electrochemical process. Figure 5-6 and Figure 5-7 show the fitted experimental data of the modulus, phase angle and Nyquist plots in these media, respectively.

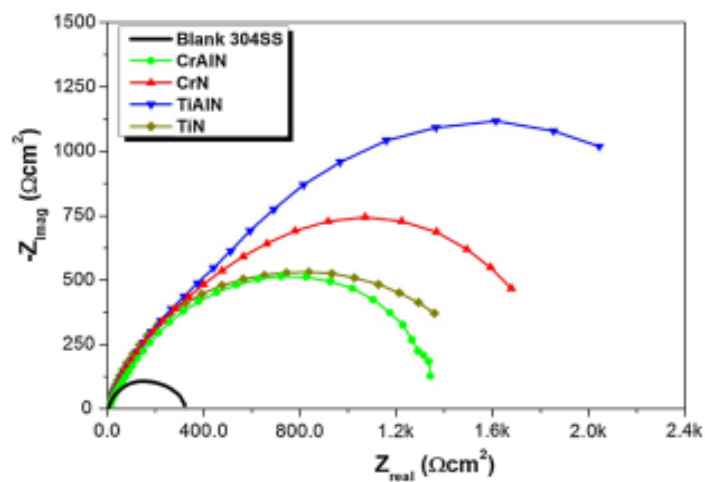
The blank substrate in both solutions displayed one time constant, which is attributed to the capacitive behavior of the double layer (C_{dl}) parallel to the charge transfer resistance (R_{ct}) which provides resistance to corrosion. The bode diagrams in both solutions show a two-time constant at low frequencies. This phenomenon, as indicated by the two maxima points observed from the phase angle plot of the bode diagram, is noticeable at the low frequency region of the diagram especially in the NaCl solution. Also, the maxima from the phase angle plot were all lower than 90° . In HCl solution, the Nyquist plots for the coatings show similar semicircular shape to that of the substrate but enlarged with high resistance (Figure 5-6). The shape of the Nyquist plot in NaCl solution is typically an incomplete semicircle with the coatings exhibiting enlarged diameter compared to the blank substrate (Figure 5-7). This is associated with the charge transfer controlled reaction [162]. Surface roughness, frequency dispersion of time constants as a result of local inhomogeneity in the dielectric material, relaxation and porosity in mass transport effects are other reasons put forward to describe these behavior as noted in some studies [163,164]. Constant phase elements (CPE) are thereby necessary in the equivalent circuit to cater for deviations from ideal dielectric material behavior as a result of surface inhomogeneities etc. This will ensure accurate simulation of EIS data and enable the determination of the element parameters using the least square analysis.



(a)



(b)



(c)

Figure 5-6: (a) Plots of Modulus, (b) Phase angle and (c) Nyquist, in 1M HCl Solution.

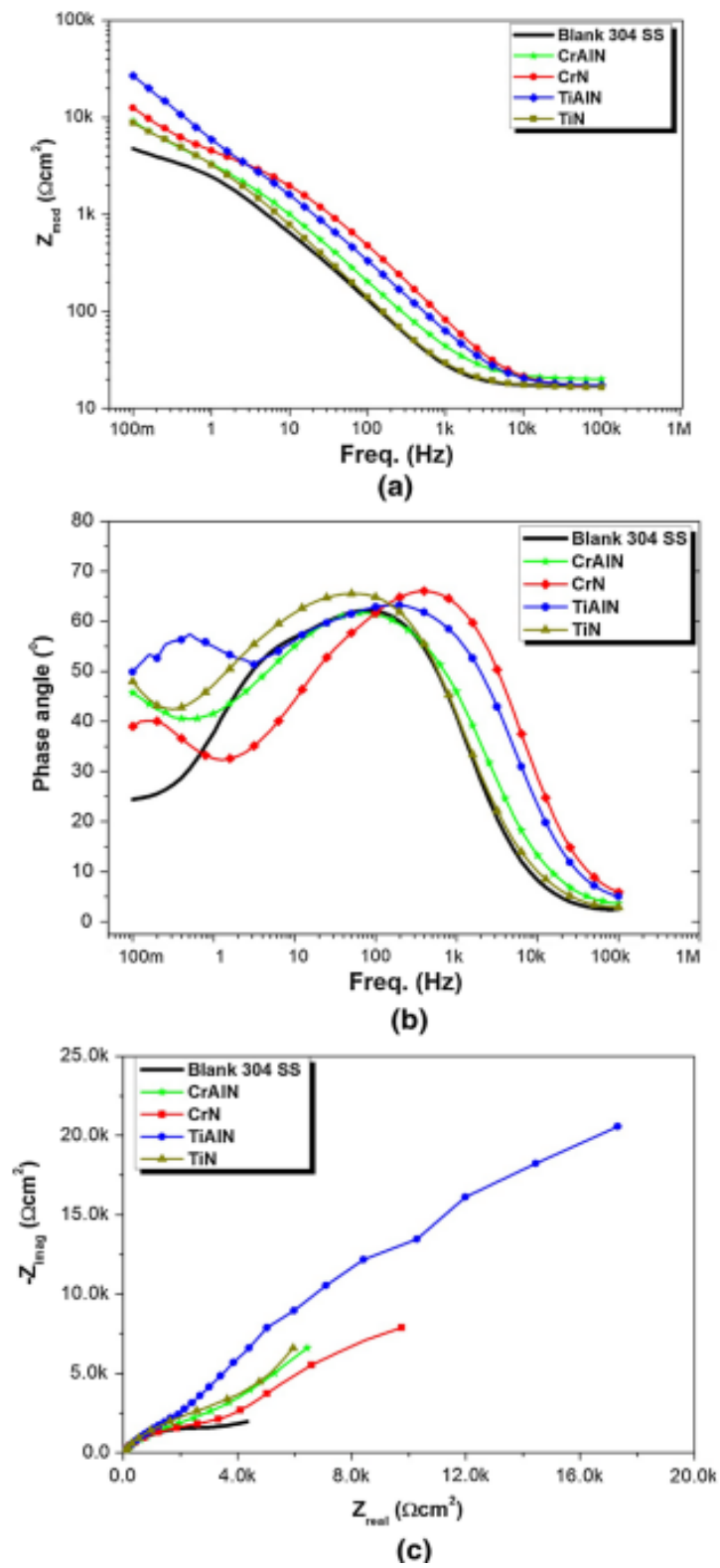


Figure 5-7: Bode plots of (a) Modulus, (b) Phase angle and (c) Nyquist, in 3.5M NaCl Solution.

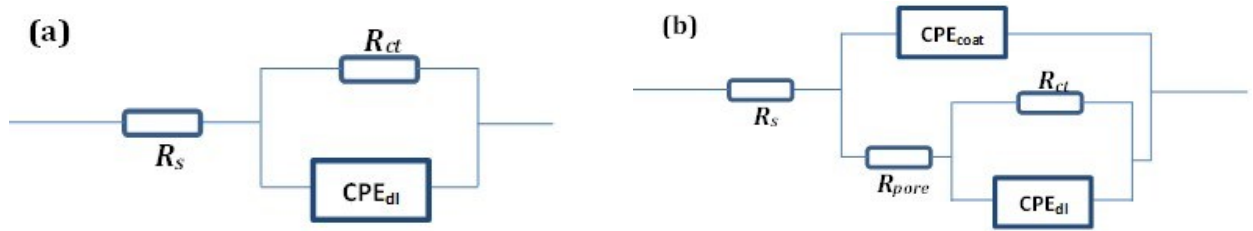


Figure 5-8: Equivalent circuits to fit the EIS data in both media for (a) substrate and (b) coatings.

The equivalent circuit used to simulate the electrochemical response of the substrate is shown in Figure 5-8(a). It consists of a constant phase element (CPE_{dl}) accounting for the double layer capacitance in parallel with the charge transfer resistance (R_{ct}), both in series with an electrolyte (solution) resistance (R_s) between the working and the reference electrodes. Figure 5-8(b) depicts the equivalent circuit used to simulate the electrochemical response of all coatings; in addition to the equivalent circuit of the substrate, it has a constant phase element (CPE_{coat}) and a charge transfer resistance of the coating against porosity (R_{pore}), both serially connected to the electrolyte resistance (R_s). The CPE was employed to replace the capacitance parameters (C_{dl} and C_{coat}) in circuit due to the deviation of C_{dl} and C_{coat} from its ideal capacitive behavior. The CPE is well-defined by the following relation $Z = Y_0^{-1} (j\omega)^{-n}$, where Z is the impedance of the CPE, j is the imaginary number ($j^2 = -1$), ω is the angular frequency (radians per second (rad s^{-1})), Y_0 and n are the frequency independent parameters. n value ranges from 0 to 1 depending on the surface roughness. For the perfect surface, the value of n is 1 and the impedance of CPE is that of pure capacitor [165].

Table 5-3 and Table 5-4 represent the optimum EIS parameters for TiN, CrN, CrAlN and TiAlN coatings in 1M HCl and 3.5% NaCl solutions, respectively. In HCl solution, it is observed from the obtained parameters that CrAlN exhibited the highest resistance to electrolyte penetration through pinholes or pores present in the coating and TiAlN showed the highest charge transfer resistance. Also, in NaCl solution, TiAlN and CrN coatings presented higher resistance to both pores and charge transfer while TiN coating exhibited the least pore resistance in both media. However, when compared to the blank substrate, all coatings presented significant improvement in charge transfer resistance as elucidated by the EIS parameters. By comparing the heterogeneous factor (n_{dl}), it is clearly indicated that CrAlN displayed highest n_{dl} and TiN exhibited the lowest n_{dl} values in HCl solution. On the other hand, TiAlN exhibited highest n_{dl} and CrN exhibited lowest n_{dl} value in NaCl solution. Further, the n_{dl} values of CrAlN and TiAlN coatings were close to 1 (ideal capacitor) indicating that both compact and defect-free layers are highly insulating and resistant. Whereas, the lower n_{dl} values of TiN and CrN suggest the presence of defects [166]. The developed coatings in this study however possess improved resistance to defects and pores compared to reported results by William Grips et al. [69] for magnetron sputtered nitride coatings in similar 3.5% NaCl solution. This is generally associated to the deposition process because magnetron sputtered coatings are usually less dense and less adherent to the substrate when compared to cathodic arc PVD coatings.

Table 5-3: Simulated EIS Parameters for Blank and Coated Substrates in 1M HCl Solution.

Substrates	R_s ($\Omega \text{ cm}^2$)	CPE_{coat} ($\mu\text{F}/\text{cm}^2$)	n_{coat}	R_{pore} ($\Omega \text{ cm}^2$)	R_{ct} ($\text{k}\Omega \text{ cm}^2$)	CPE_{dl} ($\mu\text{F}/\text{cm}^2$)	n_{dl}
Blank	3.01	-	-	-	0.32	215.0	0.799
CrN	2.96	132	0.871	718.70	1.74	201.0	0.702
TiN	2.84	134	0.901	676.30	1.41	196.0	0.545
CrAlN	5.89	147	0.752	971.60	1.35	67.50	0.999
TiAlN	2.88	365	0.507	703.30	2.28	66.60	0.940

Table 5-4: Simulated EIS Parameters for Blank and Coated Substrates in 3.5% NaCl Solution.

Substrates	R_s ($\Omega \text{ cm}^2$)	CPE_{coat} ($\mu\text{F}/\text{cm}^2$)	n_{coat}	R_{pore} ($\text{k}\Omega \text{ cm}^2$)	R_{ct} ($\text{k}\Omega \text{ cm}^2$)	CPE_{dl} ($\mu\text{F}/\text{cm}^2$)	n_{dl}
Blank	16.91	-	-	-	4.76	67.80	0.752
CrN	17.05	9.45	0.829	4.54	12.55	120.00	0.516
TiN	16.56	41.90	0.805	3.28	8.88	151.00	0.597
CrAlN	20.06	34.00	0.775	3.33	9.23	144.00	0.564
TiAlN	17.32	18.40	0.788	5.92	26.89	30.50	0.727

5.1.2.3 Potentiodynamic polarization (PDP) and linear polarization resistance (LPR) measurements

Figure 5-9 and Figure 5-10 show the PDP curves for the blank and coated substrates in 1M HCl and in 3.5% NaCl. In both media, the substrates anodic and cathodic polarization curves indicated a well-defined Tafel, clear active, passive and trans-passive regions of corrosion. The polarization curves of coated SS substrates were considerably different from that of the blank SS substrate. A primary observation of these polarization curves illustrates the nobler shift in the E_{corr} and significant reduction in the i_{corr} of the coated samples which reveals improved corrosion protection performance relative to the blank substrate. Table 5-5 and Table 5-6 show values of the corrosion potential (E_{corr}), corrosion current density (I_{corr}), corrosion rate (CR), anodic (β_a) and cathodic (β_c) tafel slopes extrapolated from the curves for each sample in the respective media. In addition, the corrosion protective efficiency of the coatings (P_i) can be estimated using Equation 5-1 [167], by comparing the corrosion current density of the coated (I_{corr}^c) and substrate (I_{corr}^s) in each medium.

$$P_i (\%) = \frac{I_{corr}^s - I_{corr}^c}{I_{corr}^s} \times 100\% \quad 5-1$$

The linear polarization resistance (LPR) plots for the steel substrate and the coatings in 1M HCl and 3.5% NaCl are shown in Figure 5-11 and Figure 5-12, respectively. The polarization resistance R_p was obtained from the slope of the LPR plots measured at the E_{corr} . The Stern Geary equation relates the corrosion current density I_{corr} with the R_p through Equation 5-2 [74,167].

$$I_{corr} = \frac{1}{2.303} \frac{\beta_a \beta_c}{R_p (\beta_a + \beta_c)} = \frac{Z}{R_p} \quad 5-2$$

Where β_a and β_c is the anodic and cathodic Tafel slopes, respectively, obtained from the PDP curves, R_p is the slope of the LPR plots and Z is a function of the Tafel slopes based on PDP curve.

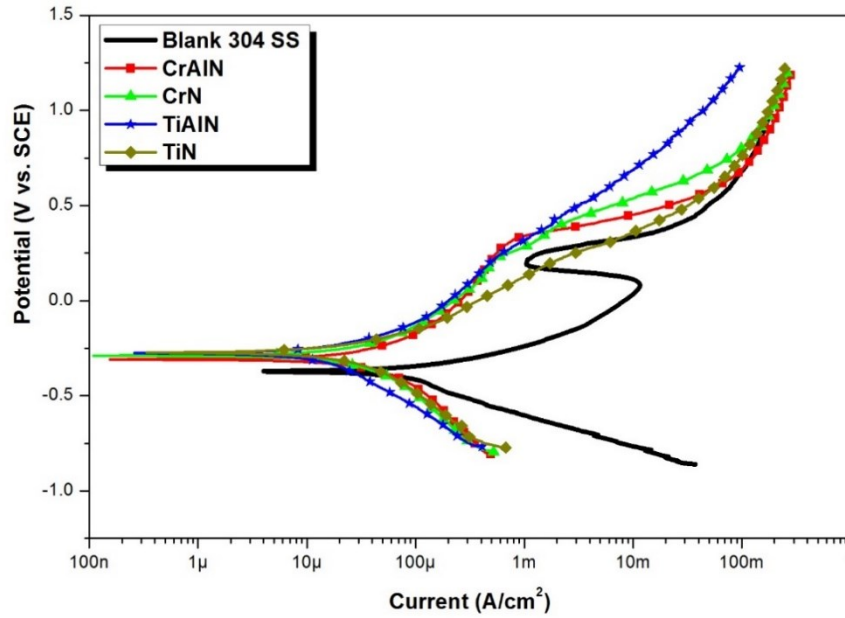


Figure 5-9: Potentiodynamic polarization curves in 1M HCl Solution.

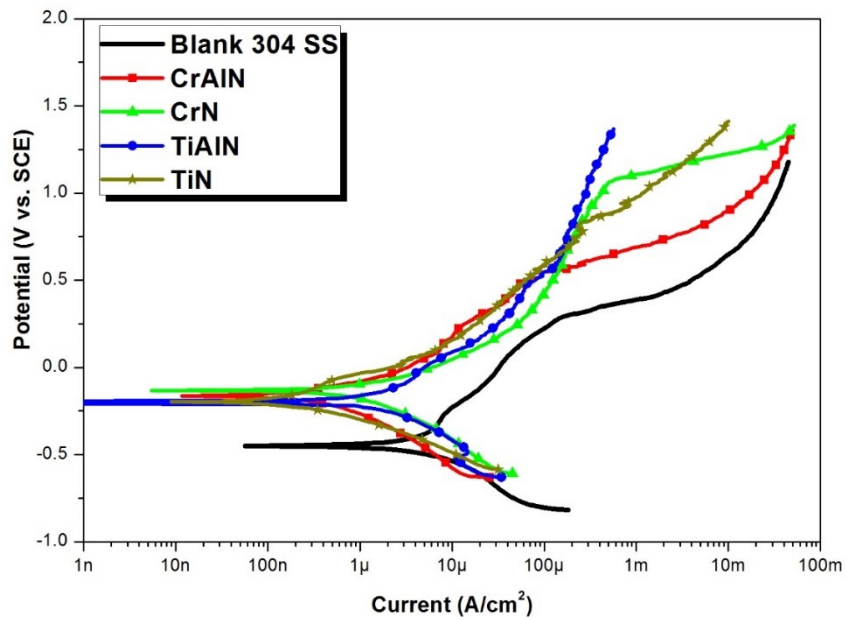


Figure 5-10: Potentiodynamic polarization curves in 3.5% NaCl Solution.

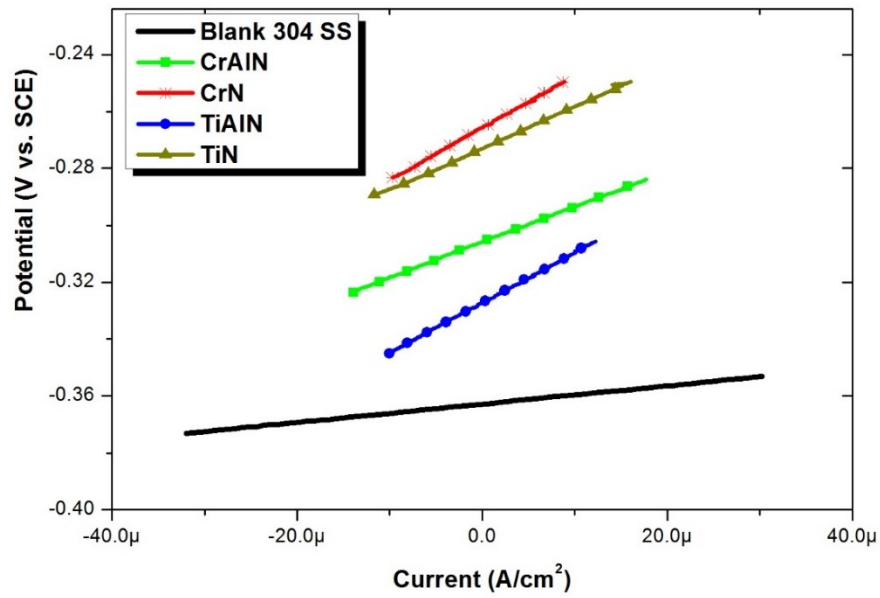


Figure 5-11: Linear Polarization Resistance curves in 1M HCl solution.

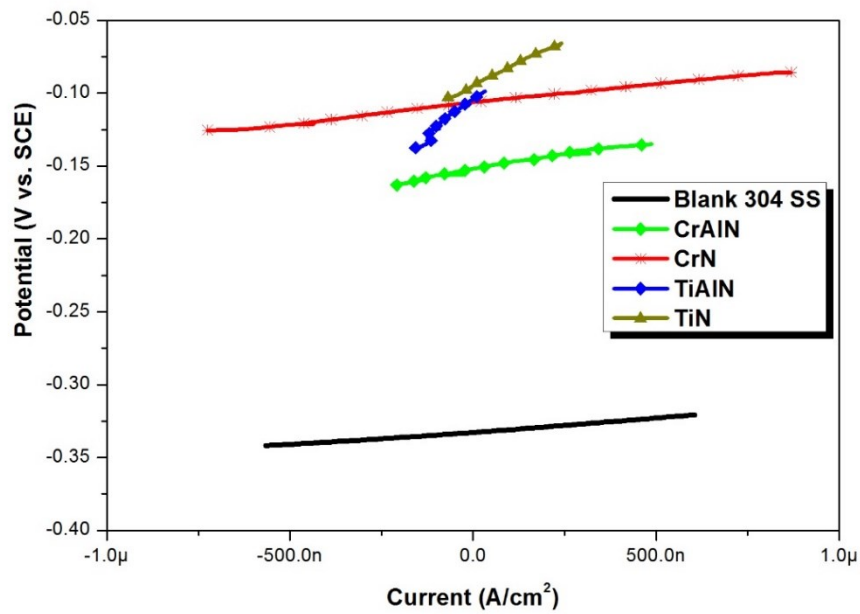


Figure 5-12: Linear Polarization Resistance curves in 3.5% NaCl solution.

Electrochemical test is capable of detecting pores connectivity and permeability in coatings resulting from microstructural defects and cracks within the coating. The porosity F can be

calculated quantitatively using the electrochemical methods according to Equation 5-3 [168,169].

$$F (\%) = \left[\frac{R_{pm}}{R_p} \times 10^{(-|\Delta E_{corr}/\beta_a|)} \right] \times 100\% \quad 5-3$$

Where, ΔE_{corr} is the corrosion potential difference between the substrate and coating obtained from the OCP curves, R_p is the polarization resistance of the coating-substrate system, β_a the anodic Tafel constant of substrate and R_{pm} is the polarization resistance of the substrate. The corrosion rates, protective efficiency and the porosity obtained from the PDP and LPR tests are presented in Table 5-5 and Table 5-6 for 1M HCl and 3.5% NaCl solutions, respectively. Similar electrochemical findings have also been reported by Ibrahim et al. [170] for CrN, TiN and Ti(Al)N coatings in 0.5 NaCl solution. It can be observed from the results that the corrosion density is well reduced for the coated samples in comparison to the blank substrate in both media. Also observed is that the acidic medium is more severe than the chloride medium for the substrates as indicated by the corrosion rates. The protective efficiency of TiAlN coating (79% and 99.5% in HCl and NaCl solution, respectively) and porosity (0.017% and 0.042% in HCl and NaCl solution respectively) were excellent when compared to that of TiN. Though TiN also shows significant improvement in its protective efficiency against corrosion to about 94% and 97% in HCl and NaCl solution, respectively, with relatively less degree of porosities. The incorporation of aluminum to form TiAlN coating is thought to be responsible for enhanced properties as also reported by Cegil et al. [74]. The same phenomenon occurs in the case of CrAlN coatings when compared to CrN coating. Generally, it was observed that the ternary coatings (TiAlN and CrAlN) exhibited lower corrosion rates compared to the

binary coatings (TiN and CrN). It is reported that large and straight diffusion path for electrolyte is a common feature of columnar microstructure associated with PVD binary hard coatings [68].

Table 5-5: PDP and LPR Data in 1M HCl Solution.

Substrates	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	CR (mpy)	R_p ($\text{k}\Omega/\text{cm}^2$)	P_i (%)	F (%)
Blank	-373	91.90	119.8	250.3	53.46	0.316	-	-
TiN	-272	33.10	227.6	408.7	19.27	1.755	63.98	0.026
CrN	-289	48.80	377.5	529.9	28.41	1.830	46.90	0.034
TiAlN	-275	19.40	203.4	406.1	11.28	2.773	78.89	0.017
CrAlN	-308	32.90	248.6	273.2	19.17	1.243	64.20	0.073

Table 5-6: PDP and LPR Data in 3.5% NaCl Solution.

Substrates	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	CR (mpy)	R_p ($\text{k}\Omega/\text{cm}^2$)	P_i (%)	F (%)
Blank	-449	8.93	584.6	268.2	5.193	19.13	-	-
TiN	-196	0.29	378.5	174.7	0.169	140.70	96.74	0.050
CrN	-133	1.24	189.8	309.6	0.719	22.88	86.11	0.241
TiAlN	-201	0.04	71.4	68.6	0.024	170.50	99.53	0.042
CrAlN	-161	0.40	173	256.0	0.231	46.42	95.55	0.133

The inclusion of aluminum atoms in the ternary coatings is known to refine the usual columnar microstructure resulting in fine microstructure. This dense microstructure obstructs the diffusion of electrolyte by disrupting the connectivity of the pores. Furthermore, the presence of aluminum led to the formation of a dense and passive oxide layer which results in the observed low current density and porosity; hence, the observed improved corrosion resistance behavior of CrAlN and TiAlN coatings as shown in Table 5-5 and Table 5-6. Different observation has been reported to compare between TiAlN and CrAlN coatings considering their corrosion resistance behavior in acidic and chloride solutions. Some studies [68,74,171] have shown that CrAlN coatings exhibited better corrosion resistance while TiAlN coatings have also received similar commendation over CrAlN coatings [113,167]. In both cases, the corrosion resistance behavior has always been attributed to the formation of passive thin oxide layers with the claim that Cr forms denser oxide layer than Ti and vice versa. The presence of surface defects, pores, pinholes, impurities and inclusions can influence the tenacity and performance of the oxide layer formed. In this study, it is observed that TiAlN exhibited better protective efficiency and lower porosity compared to CrAlN due to its lower corrosion rate and higher polarization resistance, respectively. This may be attributed to dense, less porous and more tenaciously adhered coating to the substrate than CrAlN coating as suggested by the electrochemical analysis.

5.1.3 SEM Analysis of Corroded Surface

SEM surface morphology of corroded area for the blank and coated samples in HCl and NaCl media were analyzed to evaluate the extent of damage. Figure 5-13 and Figure 5-14 show the SEM images of blank and coated substrates in HCl and NaCl solutions

respectively. It is observed that in both media the coated samples indicated less damage compared to the blank after the PDP test. In HCl solution, formation of deep and wide craters was prevalent on the substrate (Figure 5-13a) while the coated samples show relatively shallow and less number of pits. Also observed on the surface of some coated substrates is the formation what can be described as corrosion products. These products can either positively or negatively influence the corrosion resistance of the coating. If dense and less porous, it will thereby result in a barrier that hinders increase diffusion and reduces the charge transfer as possibly occurred for TiAlN and CrAlN coatings. However, if it is porous and loose, then the diffusion of electrolyte charges to the underlying substrate will be increased. The severity of HCl solution on the substrates can also be observed from the SEM images. CrN exhibited the highest damage in both media while TiN and CrAlN show a lesser percentage of the affected area or damaged surface. This behavior coupled with their estimated porosity values and protective efficiencies from Table 5-5 and Table 5-6 shows that TiN follows CrAlN coatings closely in its corrosion resistance behavior after TiAlN coating. TiAlN coatings, as also substantiated from the SEM images, have the highest protective efficiency.

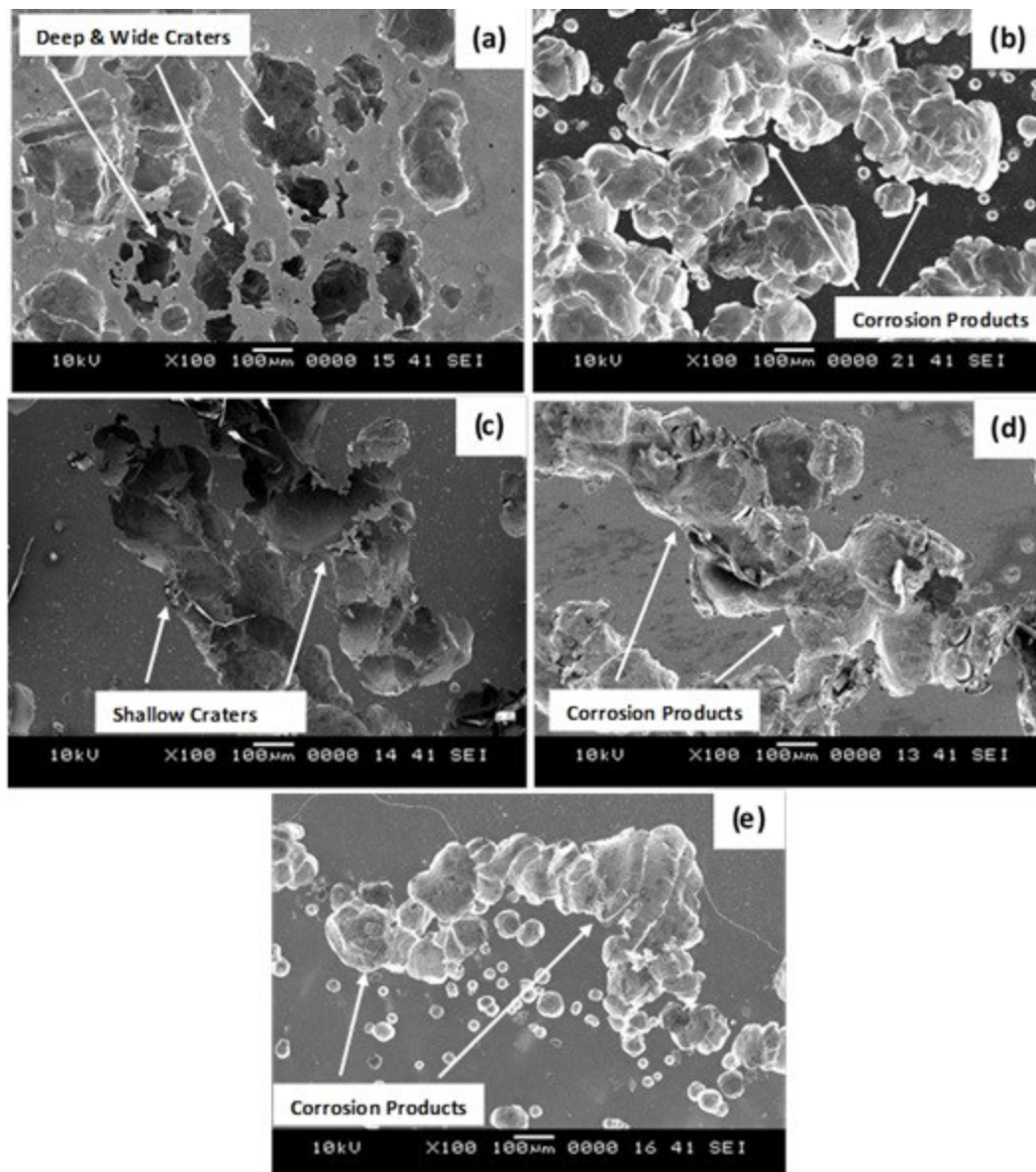


Figure 5-13: SEM Images of Corroded area of (a) 304 SS Substrates (b) CrN (c) TiN (d) CrAlN and (e) TiAlN coatings in 1M HCl Solution.

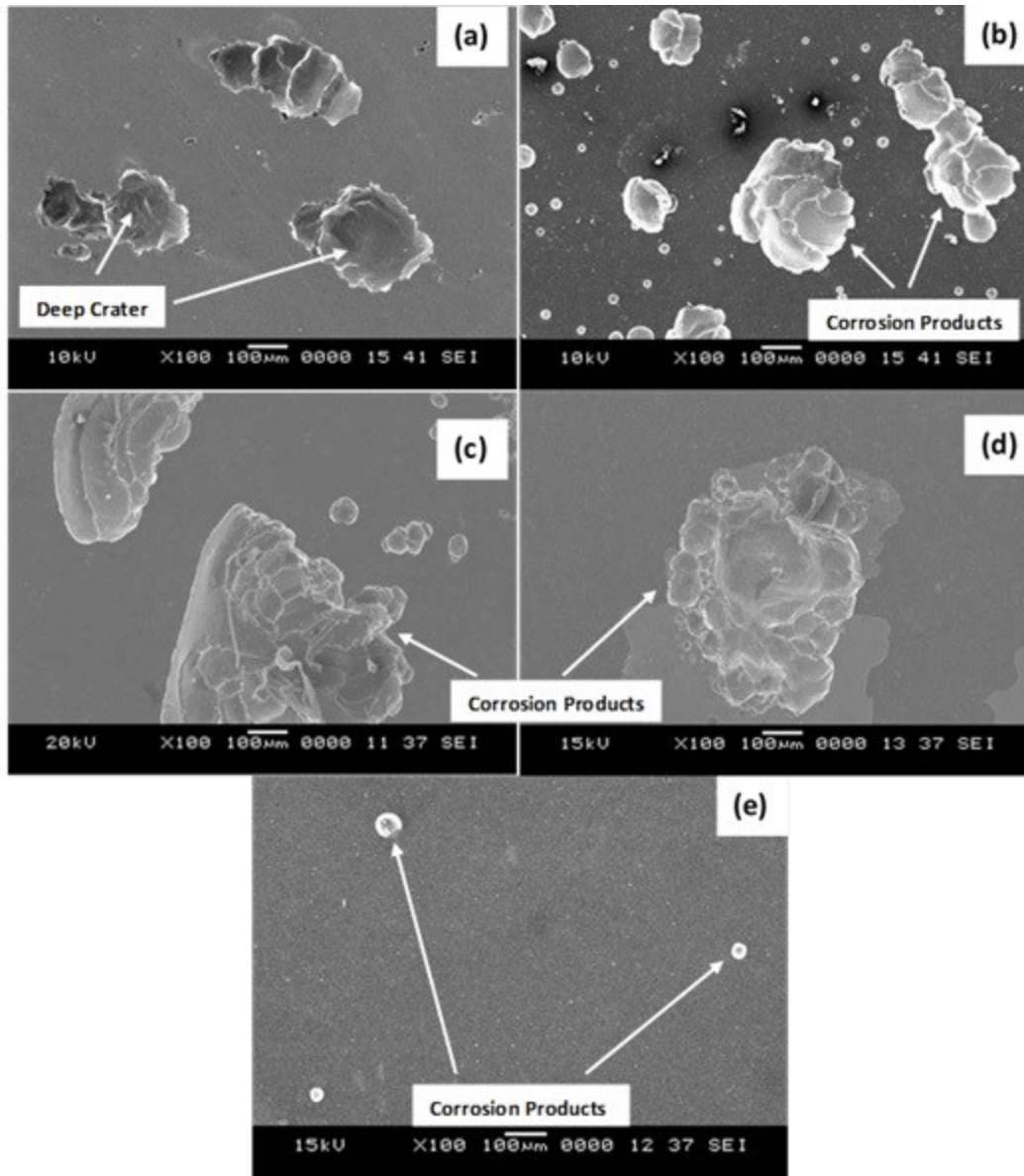


Figure 5-14: SEM Images of Corroded area of (a) 304 SS Substrates (b) CrN (c) TiN (d) CrAlN and (e) TiAlN coatings in 3.5% NaCl Solution.

5.2 Scratch and Wear Behavior of TiN, CrN, AlTiN and AlCrN Coatings

5.2.1 Surface characterization

Surface morphologies of the coatings are shown in Figure 5-15 with the characteristic microparticles and micropits associated with PVD coatings. The origin of these defects is inherent in the deposition process where molten metal droplets solidify en route from the target to the substrate often due to the low melting point elements via stationary and quasi-stationary processes or explosive emission [172,173]. Boxman et al. [172] described the theory of defects on CA-PVD coatings and its generation, transport, effect on coating and control of microparticles. Generally, these defects are between 1 – 40 μm in diameter [174]. However, the majority of the surface defects in this study are less than 1 μm in diameter which indicate considerable reduction in the size of these defects. This is sequel to the characteristic high plasma density of modern cathodic arc PVD process and hence effective and efficient deposition of dense coating is attained with reduced micro particles. They are generally undesirable as they affect the surface roughness and morphology of the coating and can result in high friction and wear, localized coating failure and pitting corrosion [152,174,175]. Table 5-7 shows the chemical composition and thickness of coatings deposited on the steel substrate in the current study. The binary coatings are stoichiometric while the ternary nitride coatings are non-stoichiometric and have non-stoichiometric ratios of $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ and $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$, respectively. The coating thickness is usually influenced by the deposition rate. The thickness of binary coatings is slightly higher due to the higher deposition duration as compared to that of the ternary coating.

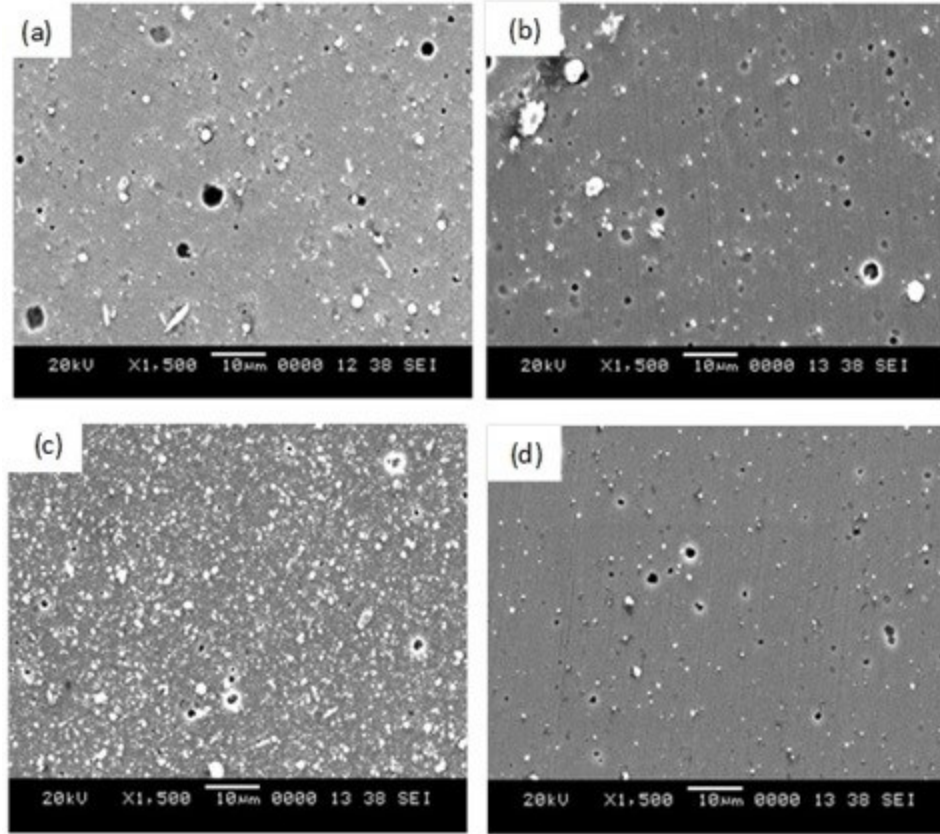


Figure 5-15: SEM micrographs showing macroparticles (a) CrN, (b) TiN, (c) $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ and (d) $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$ thin monolayer coatings.

Table 5-7: Chemical and mechanical properties of coated samples.

Coatings	Composition (at%)				Thickness (μm)	H (GPa)	E (GPa)	H/E	H^3/E^2 (GPa)
	Ti	Cr	Al	N					
TiN	51.4	-	-	48.6	2.14 ± 0.2	22.5 ± 8	205 ± 47	0.11	0.27
CrN	-	52.6	-	47.4	2.06 ± 0.1	27.7 ± 7	211 ± 19	0.13	0.48
$\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$	26.1	-	26.1	47.8	1.50 ± 0.1	33.5 ± 5	249 ± 59	0.14	0.61
$\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$	-	17.5	33.3	49.2	1.82 ± 0.1	32.3 ± 7	249 ± 71	0.13	0.54

The charge on the cathodes of the binary and ternary coatings are similar (200 Ah) but the deposition duration differs because of the difference in the arc current (see Table 4-2). The observed difference in the variation of the thickness at similar deposition duration can be attributed to factors such as the density of the evaporated material, chemistry of the

compound formed after reaction of the reactive nitrogen gas and the ease of transporting and depositing on the substrate. The thickness of the coatings is between 1.5 – 2.0 μm which is well within acceptable range to compare tribological performance among the coatings.

The roughness values as measured from AFM are shown in Table 5-8. AFM morphological images showing the surface texture of the coatings are shown in Figure 5-16. The most widely used parameter to describe the surface texture of PVD coatings is the amplitude roughness parameter (RA). For these coatings the RA, which are the peaks above the mean center line results from the macroparticles, ranges between 12 and 60 nm. The low surface roughness is due to lower coating thickness subsequent upon less deposition time of approximately 45min. The lower the deposition time, the lower the number of macroparticles that will be deposited and thus, reduction in the growth defects. Ali et al. [176] showed that as the deposition time reduces from 120 to 30 min the RA values decreased from 0.62 to 0.21 μm for cathodic arc TiN coatings. The RMS values show a wide deviation between shapes and distributions of peaks and valleys, consequently, coatings with high RMS will exhibit high PV as observed for TiN and $\text{Al}_{0.67}\text{Cr}_{0.33}\text{N}$ coatings. Among all, $\text{Al}_{0.67}\text{Cr}_{0.33}\text{N}$ coating demonstrated the highest roughness while CrN coating exhibited the finest texture. The higher roughness of the ternary coatings is attributed to the presence of low-melting point Al which is one of the main causes for the characteristic surface defects of cathodic arc PVD coatings. The surface roughness influences the friction and wear behavior of the coatings, rougher surfaces increases the contact pressures due to low real contact area, hence results in higher friction coefficient and increased wear of the counterpart surface as reported by Harlin et al.[177]. This is

because high asperities will contribute to the ploughing component of the friction and abrade a soft counterface more severely.

Table 5-8: Surface roughness of coated samples.

Coating	RA (nm)	Roughness RMS (nm)	PV (nm)
TiN	24.7 ± 1.0	43.2 ± 1.2	401 ± 17
CrN	12.4 ± 0.4	18.9 ± 0.1	224 ± 27
Al _{0.50} Ti _{0.50} N	30.4 ± 4.4	43.9 ± 5.5	329 ± 41
Al _{0.68} Cr _{0.32} N	59.0 ± 8.0	86.6 ± 16.2	711 ± 93

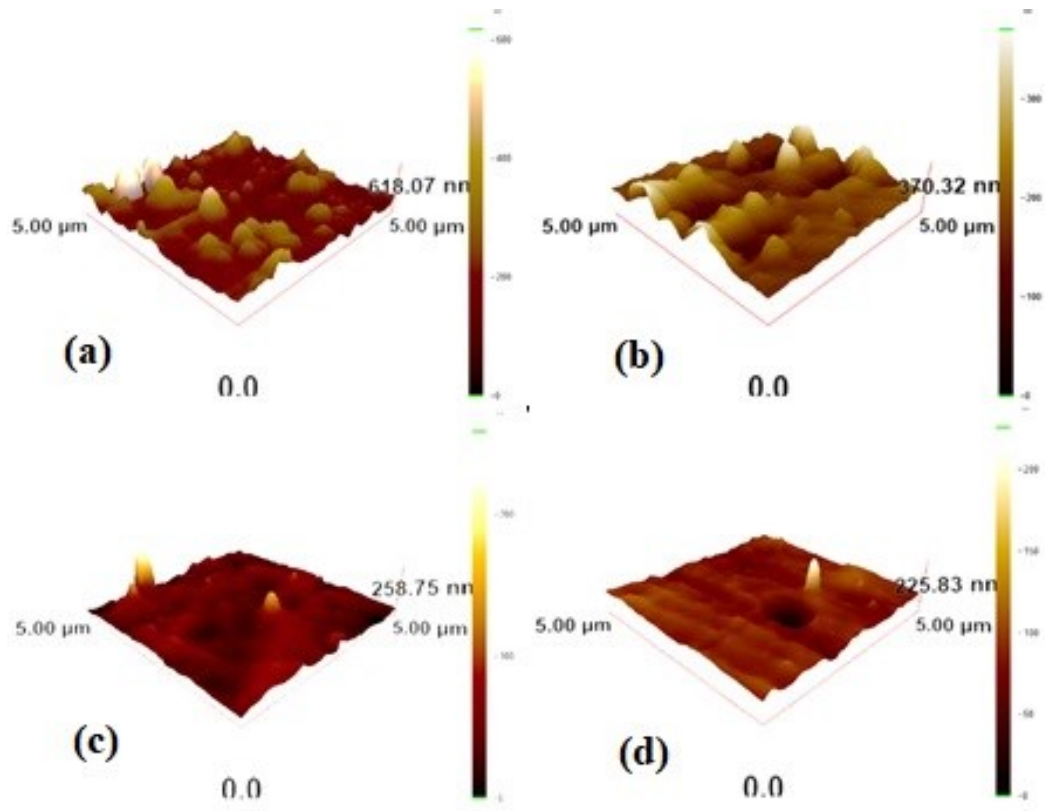


Figure 5-16: AFM 3D images of the surface nanoroughness of (a) AlCrN (b) AlTiN (c) CrN and (d) TiN, coatings.

5.2.2 Micromechanical characterization

Table 5-7 also shows the obtained micromechanical properties of the coatings. The average hardness of TiN and CrN are 22.5 GPa and 27.7 GPa, respectively, while that of Al_{0.50}Ti_{0.50}N and Al_{0.68}Cr_{0.32}N are 33.5 GPa and 32.3 GPa, respectively. The elastic modulus of TiN, CrN, Al_{0.50}Ti_{0.50}N and Al_{0.68}Cr_{0.32}N are 205 GPa, 211 GPa, 249 GPa and 249 GPa, respectively. The microhardness and elastic modulus of the substrate as measured under 5N maximum load is 3.0 ± 0.072 GPa and 167 ± 6.5 GPa, respectively. Compared to the substrate properties, the coatings have tremendously improved the surface mechanical properties. These figures revealed that ternary coatings possessed higher mechanical properties than the binary coatings. This is associated with increase in the lattice distortion due to the incorporation of Al to form the ternary coatings. The relationship between H and E as described through elastic strain to failure (H/E) and plasticity index or resistance to plastic deformation (H^3/E^2) are significant parameters that indicate the wear resistance properties of PVD coatings [178]. The coatings H/E and H^3/E^2 values are given in Table 5-8. It has been reported that the higher the ratios H/E and H^3/E^2 , the higher is the elastic strain to failure and resistance to plastic deformation respectively [179]. The coatings in this study possessed higher strain to failure and plasticity index factors than similar coatings reported in some published work [178–182]. It is seen that CrN exhibited higher elastic strain and toughness sequel to its higher plastic resistance as compared to TiN coating. Similarly, Al_{0.50}Ti_{0.50}N possessed higher H/E and H^3/E^2 than Al_{0.68}Cr_{0.32}N coating indicating its improved strain and plastic resistance properties. Although, CrN and Al_{0.68}Cr_{0.32}N have similar elastic strain to failure factor, the plasticity index of Al_{0.68}Cr_{0.32}N is 13 % higher. This improved properties of the ternary coatings is

due to their high hardness and low modulus (~ 250 GPa) as compared to the elastic modulus (450 - 570 GPa) reported for the same coatings by Mo and Zhu [64]. Hardness and elastic modulus of PVD coatings are controlled by chemical composition and deposition parameters. It has been shown that composition and deposition parameters can be tailored accordingly to desired mechanical properties [52,179]. High H value with a corresponding low E are more desirable and results in higher elastic strain and better plasticity index and are believed to enhance the coating wear resistance [179,182]. Furthermore, it has been shown that these ratios can be directly related to the wear resistance of hard PVD coatings [178].

5.2.3 Scratch behavior

Scratch test was used to evaluate the coating adhesion by determining the critical loads and scratch crack propagation resistance (CPR_S). The cohesive strength, L_{c1} , was determined by the AE signal and it corresponds to the first acoustic emission signal which indicates the initiation of a crack within the coating. The COF curve in conjunction with the optical images were utilized in determining the adhesive strength, L_{c2} . Figure 5-17 and Figure 5-18 show the AE and COF as a function of applied normal load, respectively. The AE signals are suitable for detecting cohesive micro cracks at very small loads especially where the failure mode is predominantly brittle. The initiation of crack within the coatings was captured with the AE signal as indicated in Figure 5-17. CrN and TiN exhibited higher cohesive strengths of 6.26 and 5.14 N, respectively, compared to that of $Al_{0.68}Cr_{0.32}N$ and $Al_{0.50}Ti_{0.50}N$ with 3.24 and 2.95 N, respectively.

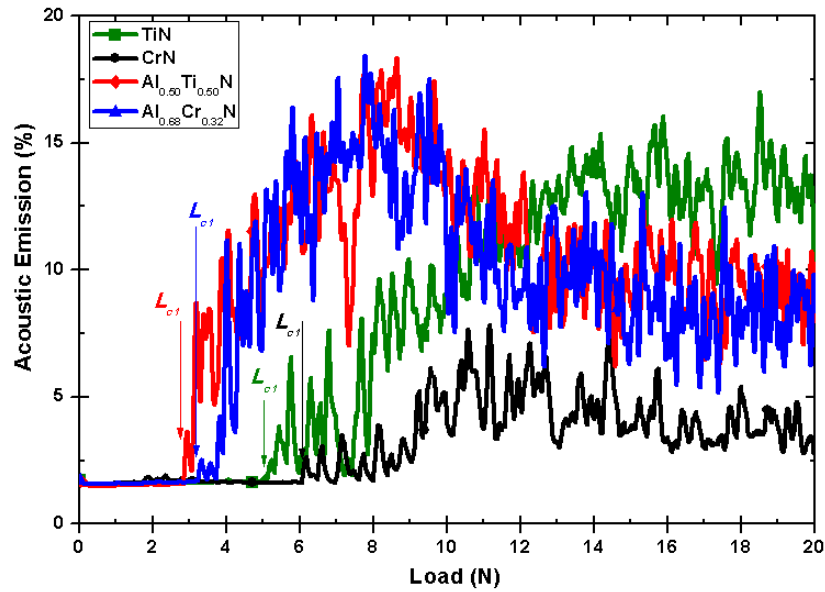


Figure 5-17: Acoustic emission (AE) signal as a function of applied load.

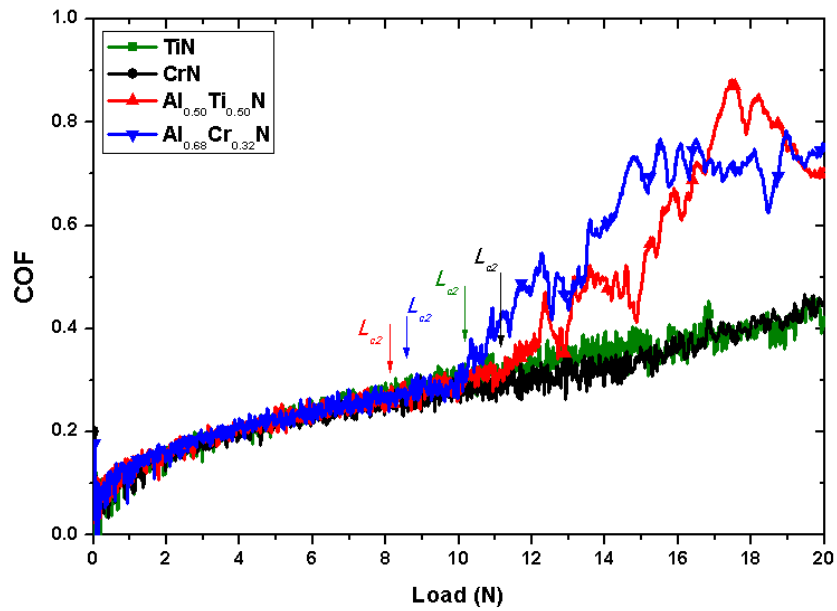


Figure 5-18: Scratch test coefficient of friction (COF) as a function of applied load.

The improved adhesion may be attributed to the presence of pure Cr and Ti bond coat of tens of nanometers deposited before the actual nitride deposition. In $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ and $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$ coatings, the bond coats are AlCr and AlTi alloy, respectively. Additionally, the higher compressive stresses in the binary coatings as compared to the ternary coatings can delay failure and thus improve adhesive strength [183,184]. Adhesive strength of the ternary coatings was obtained from the evolution of the COF as indicated in Figure 5-18. After adhesive failure, a sudden and a steep increase in the COF of the ternary coating can be observed. Close observation of the optical images of the scratch shows that the ternary coatings failed just before the abrupt increase in the *COF*. However, the *COF* of the binary coating increased linearly with applied load. The adhesive strength of the binary coatings was determined by microscopic observation of the scratch because no change of the *AE* or *COF* curves was observed at failure. This can be because the energy released accompanying the coating failure is not sufficient to be detected by *AE* detector and the failure does not involve coating delamination in which case the indenter will be in direct contact with the substrate and thus results in sudden rise in the COF. Figure 5-19 shows the comparison of the critical loads and the CPR_S . The adhesive strength (Lc_2) of CrN, TiN, $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ and $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$ coatings was found to be 11.35, 10.84, 8.75 and 8.07 N, respectively, while the CPR_S was found to be 31.86, 29.30, 17.85 and 15.10 N^2 , respectively. It should be noted that the adhesive strength is relatively small because of the high maximum stress imposed on the coating by the sharp indenter (indenter radius is 100 μm). Xie and Hawthorne [181] have shown that the critical loads of thin coatings depend on the indenter radius for similar indenter geometry and decreased with decreasing indenter radius. For example, they obtained critical loads of 2, 43 and 153 N with indenters of radius

50, 200 and 500 μm , respectively, for TiN coating. Similar effect by the indenter radius and indenter type on the critical loads has also been reported [185–187].

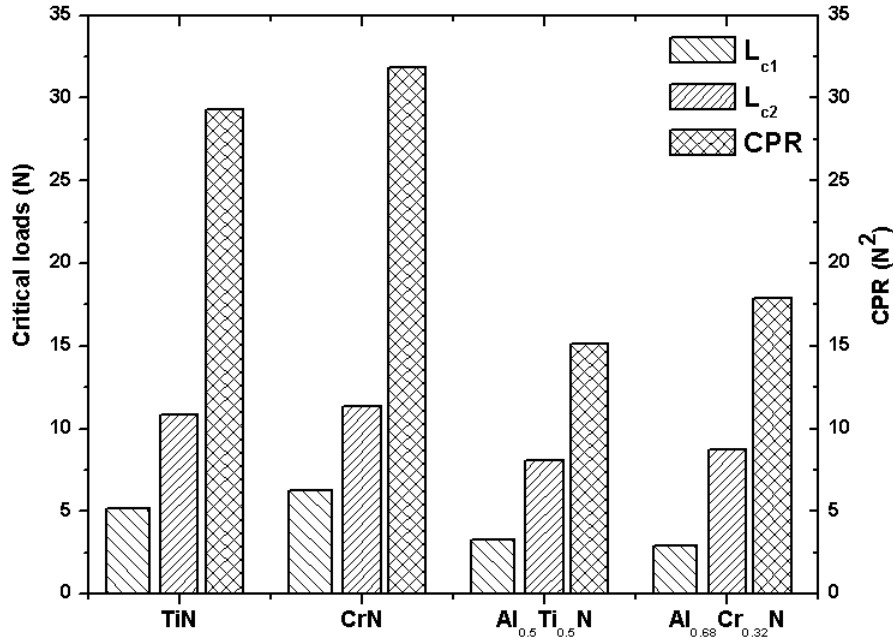


Figure 5-19: Critical loads (L_{c1} and L_{c2}) and the CPR of the coatings.

The binary coating exhibited improved adhesion to the substrate coupled with higher cohesive strength compared to the ternary coatings. The improved adhesion can be attributed to the strong bonding of the pure Cr and Ti bond coat to the substrate. Furthermore, the binary coating modulus of elasticity is similar to that of the steel substrate (~ 200 GPa) [181], hence reducing the mechanical mismatch which can increase the failure tendency. They also exhibited better scratch resistance than the ternary coatings as indicated by the CPR_S values. Considering the coating and substrate hardness, the coatings scratch failure mechanism can be expected to fall on the hatched region in scratch map in Figure 5-20, as illustrated by Bull [188]. According to Bull, a hard coating on soft substrate

is essential for the preferred ductile fashion failure, and as the hardness of the coating increases the failure mode transforms to buckling and through thickness cracking.

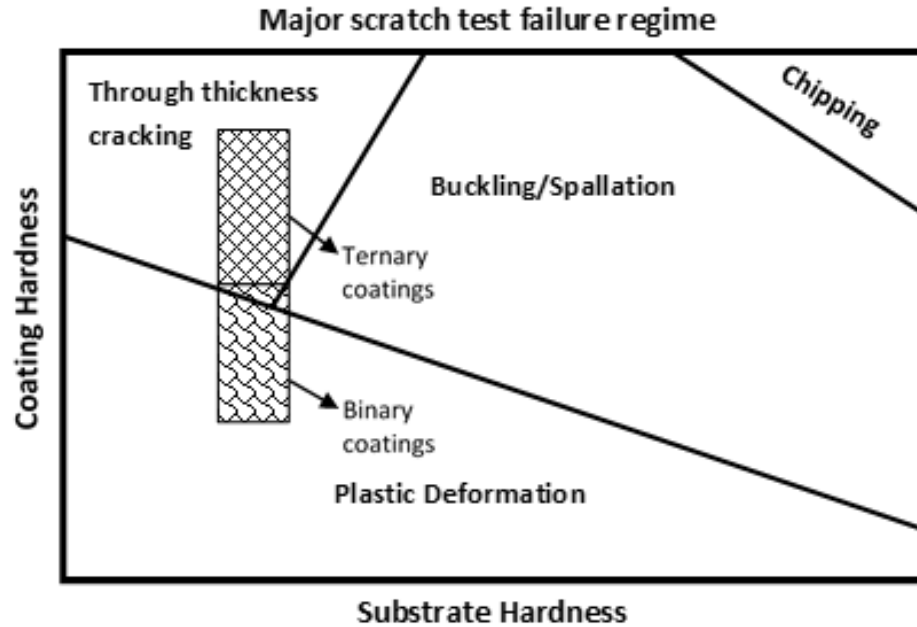


Figure 5-20: Scratch Map showing the main failure modes as function of substrate and coating hardness, (redrawn from S. J. Bull [188]).

Figure 5-21 shows the optical microscopic image of the complete scratch track of the coated samples and it can be observed that the ternary coating suffered severe damage within the range of load used as compared to binary coatings. High magnification observation (Figure 5-22) of the scratch shows that the mechanism of the coatings failure differs for the binary and ternary coatings. It is seen that the binary coatings show predominantly tensile cracking failure, which is a form of adhesive failure where the coating plastically deforms into the track causing severe tensile stresses in the coating. Hertzian cracks were also observed which were pushed into the track by the indenter causing further cracking of the coating. This failure mechanism was described by Bull [189].

Figure 5-22 shows optical images of the track for the binary coatings which reveals the occurrence of tensile cracks mainly within the track with significantly large groove formation. Increase cracking occurs at higher scratch loads and the coating is plastically further deformed into the track without delamination. This explains why the scratch *COF* curve (Figure 5-18) remains almost uniform throughout the track unlike in the ternary coatings where coating failure causes the *COF* to increase sharply.

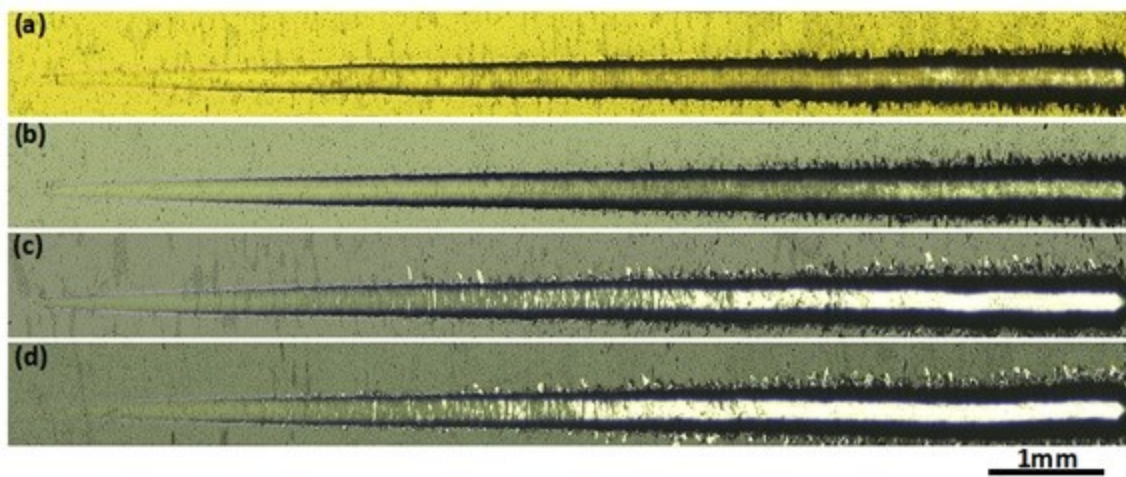


Figure 5-21: Scratch track of (a) TiN (b) CrN (c) Al_{0.50}Ti_{0.50}N (d) Al_{0.67}Cr_{0.33}N coatings.

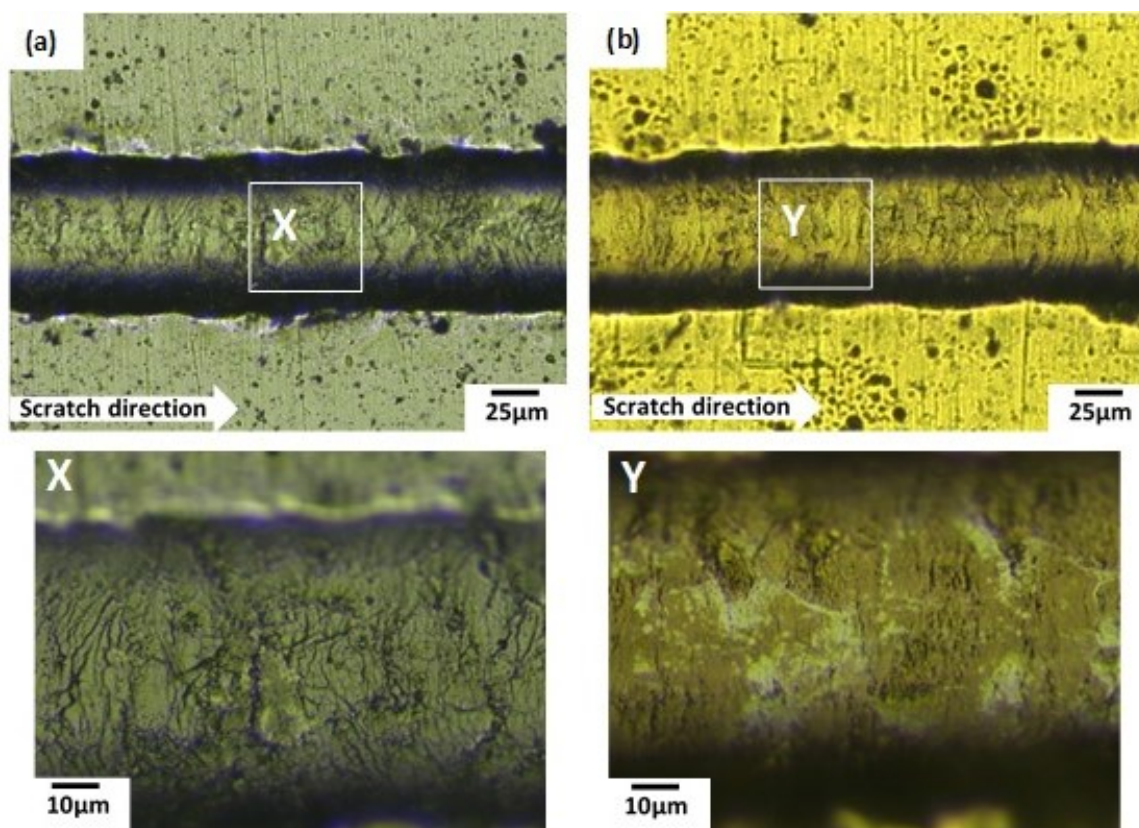


Figure 5-22: Optical images of the scratch track of the binary coatings (a) CrN and (b) TiN at load corresponding to the upper critical load (L_{c2}) (inserts X and Y showing the cracks in CrN and TiN coating respectively).

The optical images of the track for the ternary coatings are shown in Figure 5-23. It is observed that both coatings exhibited similar failure mode consisting of through thickness cracking with spallation damage within the track and chipping of the coating on both sides of the track, leading to a gross spallation of the coatings as can be observed in Figure 5-21. This failure mode is associated with the differential elastic recovery between the coating and the substrate, as well as the need for elastic energy stored by large compressive stresses ahead of the moving indenter to be released [188–190]. The high hardness and low toughness of the ternary coatings as compared to the binary coating is responsible for the

failure mode observed. The scratch behaviors of both the binary and ternary coatings follow the hatched area in the failure-mode map shown in Figure 5-20.

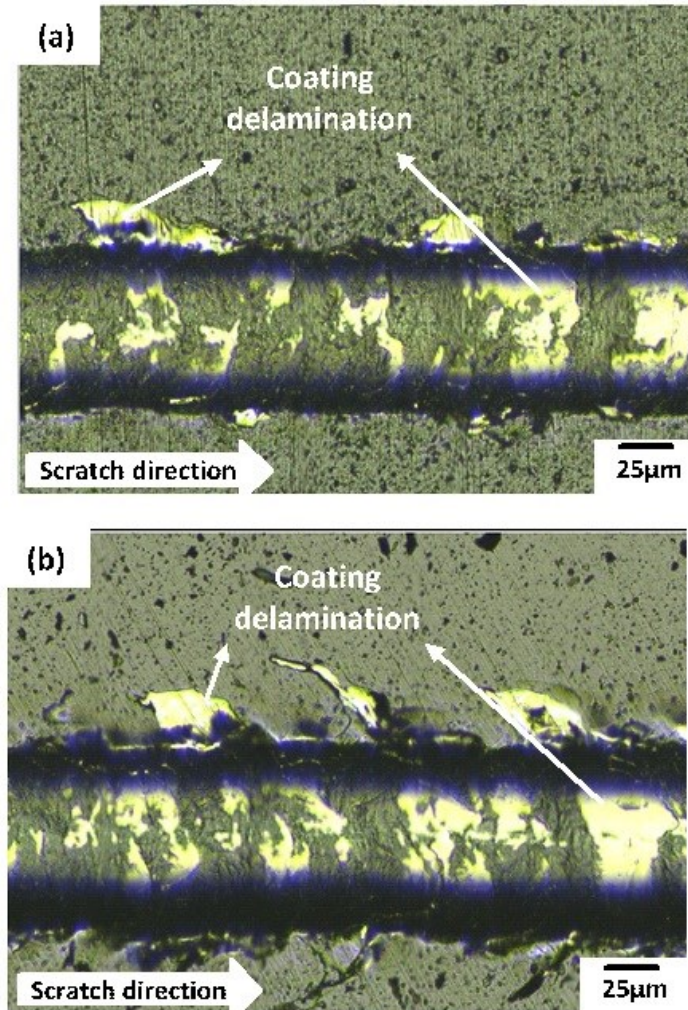


Figure 5-23: Optical images of the scratch track of the ternary coatings (a) $\text{Al}_{0.67}\text{Cr}_{0.33}\text{N}$ and (b) $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$ at load corresponding to the upper critical load (L_{c2}).

5.2.4 Wear characterization

Table 5-9 shows the Hertzian initial contact pressures during the wear experiments at different normal loads. The variation in the initial contact pressure is due to the difference in the elastic modulus and hardness of the coatings. The *COF* curve as a function of sliding

distance for the wear test is shown in Figure 5-24. CrN exhibited the lowest *COF* as expected due to its low surface roughness with a stable curve while Al_{0.50}Ti_{0.50}N has the highest *COF* with considerable fluctuation. Besides the coating chemical composition, the surface roughness is an important parameter that usually influence the *COF* of the coating. It is reported that rougher coatings increases the contact pressure and often results in higher *COF* [191]. The average steady state *COF* of CrN, TiN, Al_{0.68}Cr_{0.32}N and Al_{0.50}Ti_{0.50}N coatings were between 0.3-0.4, 0.4-0.5, 0.45-0.55 and 0.60-0.75, respectively. The binary coatings exhibited low *COF* compared to their ternary counterpart and this can be attributed to their low surface roughness when compared to the ternary coatings. The presence of Cr can also be the reason for the reduction in the *COF* in CrN and Al_{0.68}Cr_{0.32}N coatings as compared to TiN and Al_{0.50}Ti_{0.50}N, respectively, due to the formation of chromium oxide layer which could act as solid lubricant as result of its low shear strength, especially at elevated temperature during sliding.

Table 5-9: Initial contact pressure during wear test.

Load (N)	Initial Contact Pressure (MPa)		
	15	20	25
TiN	786	865	932
CrN	798	878	946
Al_{0.50}Ti_{0.50}N	866	953	1027
Al_{0.68}Cr_{0.32}N	866	953	1027

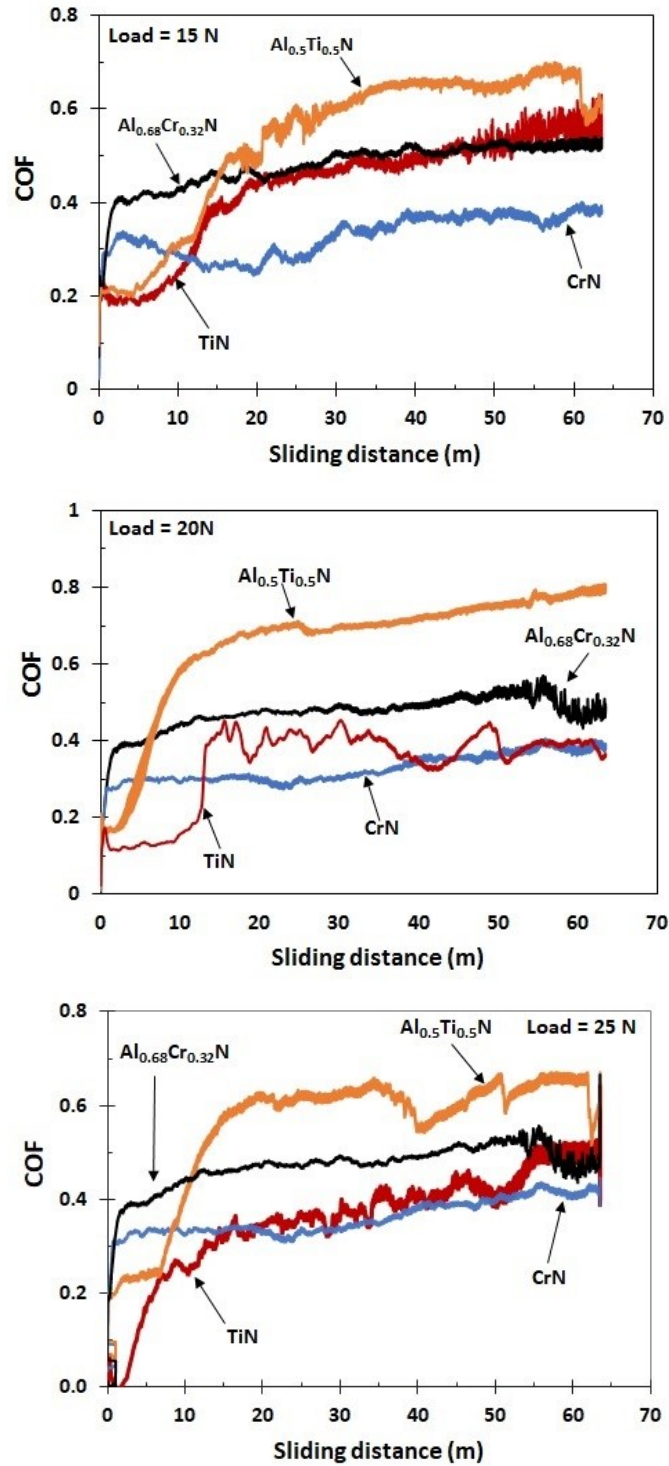


Figure 5-24: COF graph as function of linear distance at different normal loads.

Figure 5-25 shows the typical wear track profile of the coatings after the wear test was performed for 1670 cycles. The profile of the coatings reveals that the wear depth of the binary coating is deeper and rougher as compared to that of the ternary coatings. $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ coating exhibited the smoothest wear track profile among the coatings. EDS analysis on the wear tracks as shown in Figure 5-26 for the binary coatings showed that none of the coatings failed under the tested conditions. Figure 5-27 shows the wear volume and corresponding wear rate as a function of normal load and the corresponding SEM images of the wear track for the binary coatings are shown in Figure 5-28. The wear volumes of the coatings showed that TiN coating has the highest wear volume at all tested normal loads and that the ternary coatings exhibited reduced wear volumes and an improved wear resistance.

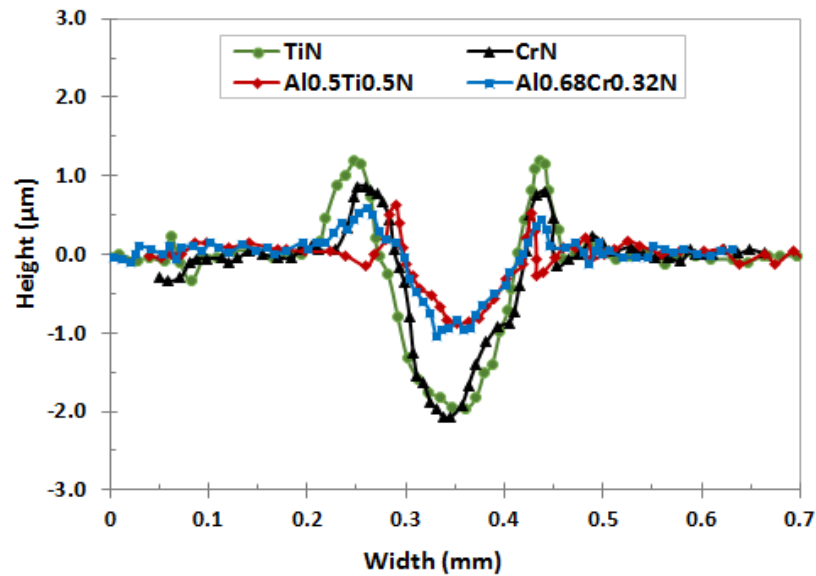


Figure 5-25: Wear track profile of the coatings (wear test parameters: 25 N normal load and 0.105 m/s linear velocity).

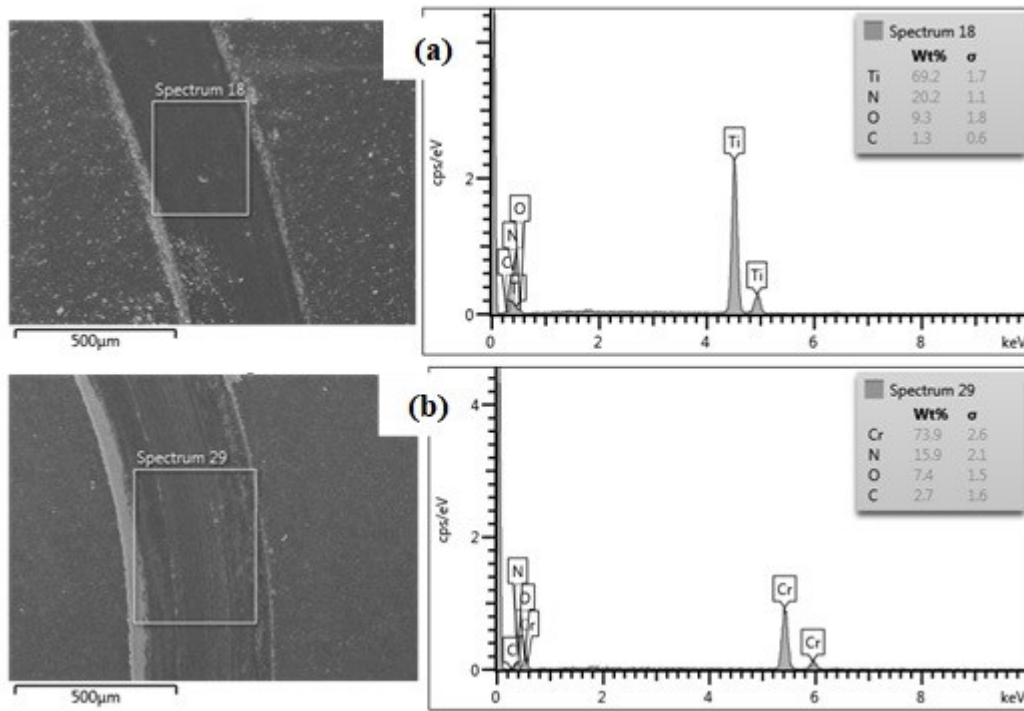


Figure 5-26: EDS analysis of the wear track for (a) TiN (b) CrN (wear test parameters: 25N normal load and 0.105 m/s linear velocity).

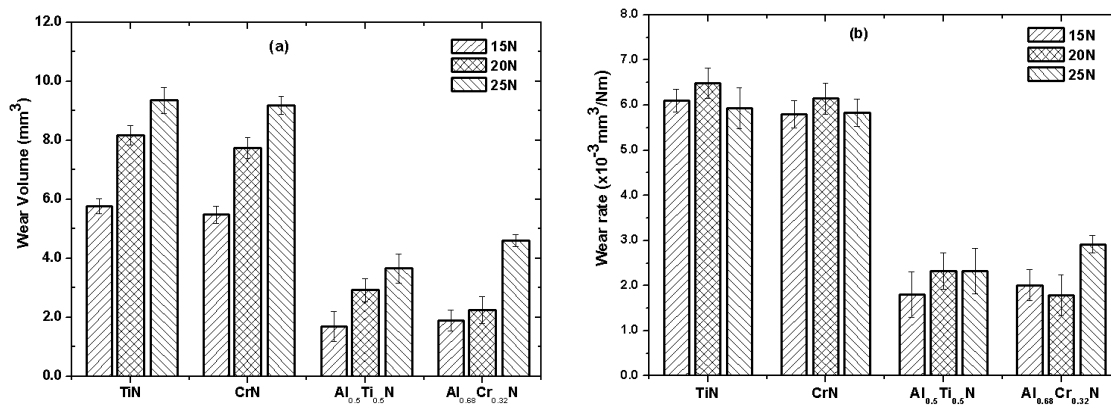


Figure 5-27: (a) wear volume and (b) wear rate of the coatings for the respective normal loads.

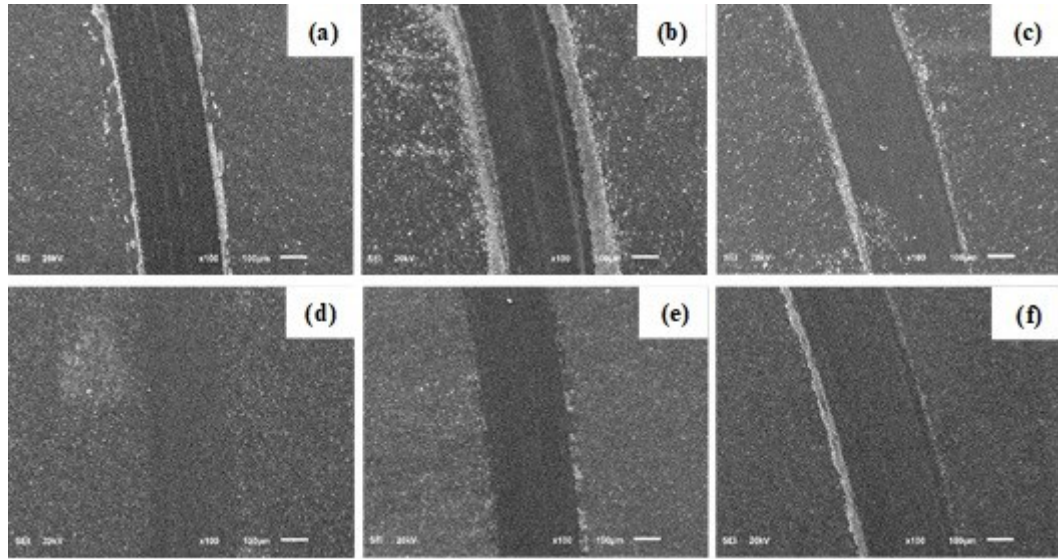


Figure 5-28: SEM images of the wear tracks for (a) – (c) TiN and (d) – (f) CrN at different normal loads; (a) & (d) 15 N, (b) & (e) 20 N, (c) & (f) 25 N at linear speed of 0.105 m/s.

The wear volume for the binary coatings increased by about 40 % when the normal load was increased from 15 to 20 N and further increase in the normal load to 25 N results in more than 60 % increase in the wear volume. Increase in the wear volume was observed for $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ to about 20% and 140% after increasing the load from 15 to 20 N and 25 N, respectively. The wear volume of $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$ increased by about 70% and 110 % after increasing the load to 20 and 25 N, respectively. It can be observed that coatings with deeper wear depth at initial normal load of 15 N exhibited lower percentage increment in wear volume after the load was increased to 20 and 25 N, while those with shallow wear depth at 15 N demonstrated higher percentage increment with increase in normal load to 20 and 25, respectively. This behavior indicates that as the wear depth and thus the volume increased the effect of normal load decreased. The higher mechanical properties of the ternary coatings confer them with the improved wear resistance and in addition they

possessed higher H/E and H^3/E^2 ratios. It is observed that as the normal load increased the wear track became larger resulting in an increase in the wear volume for all coatings. This is expected due to the dependence of the contact pressure on the normal load; increasing the load means higher contact pressure.

The specific wear rate of the coatings as estimated according to Equation 4-10 is shown in Figure 5-27(b). The wear rate of the binary coatings is almost similar under the different applied normal load. The wear rate appears to be constant at an average of $6 \times 10^{-3} \text{ mm}^3/\text{Nm}$ under these loading conditions. This suggests that the wear mechanism for the binary coatings does not change with increasing normal load at least not significantly to have influenced the wear rate and that the wear rate was steady within the tested conditions. However, in the case of the ternary coatings, the wear rate for $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ at normal loads of 15 and 20 N is approximately $2.0 \times 10^{-3} \text{ mm}^3/\text{Nm}$ but increased to $3.0 \times 10^{-3} \text{ mm}^3/\text{Nm}$ at 25 N normal load. While for the $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$ coating, the specific wear rate increased from 1.8×10^{-3} to $2.32 \times 10^{-3} \text{ mm}^3/\text{Nm}$ when the normal load was increased from 15 to 20 N. However, further increase to 25 N the wear rate remained constant at $2.32 \times 10^{-3} \text{ mm}^3/\text{Nm}$. It is interesting to note that the change in the specific wear rate at specific normal load is influenced by the change in wear mechanism since the wear severity solely depends on the acting wear mechanism.

It can be observed from Figure 5-27 that the ternary coatings demonstrated better wear resistance than the binary coatings with an average of 68, 67 and 55 % improvement in the wear resistance at 15, 20 and 25 N normal loads respectively. Though the binary coatings have lower COF , but their wear rates were higher. This can be attributed to the wear mechanism acting during the test which was evaluated by closely examining the SEM

micrographs of the wear track for the different coatings as shown in Figure 5-29. Accumulated debris is obvious at the wear track edge and fractured debris within the wear track for TiN and CrN coatings. This is an evidence of abrasive wear mechanism which contributed to the high wear rate of these coatings. Additionally, the debris may be active as a third body abrasive agent during sliding before they were expelled to the edges of the wear track. At the same time, new debris are subsequently formed due to the continuing abrasive wear and this sequence occurs repeatedly throughout the duration of the wear test. In addition, the EDS on the wear track of binary coatings indicated that oxidation also contributed to the wear mechanism. TiN coating have the least oxidation resistance among the coatings [75].

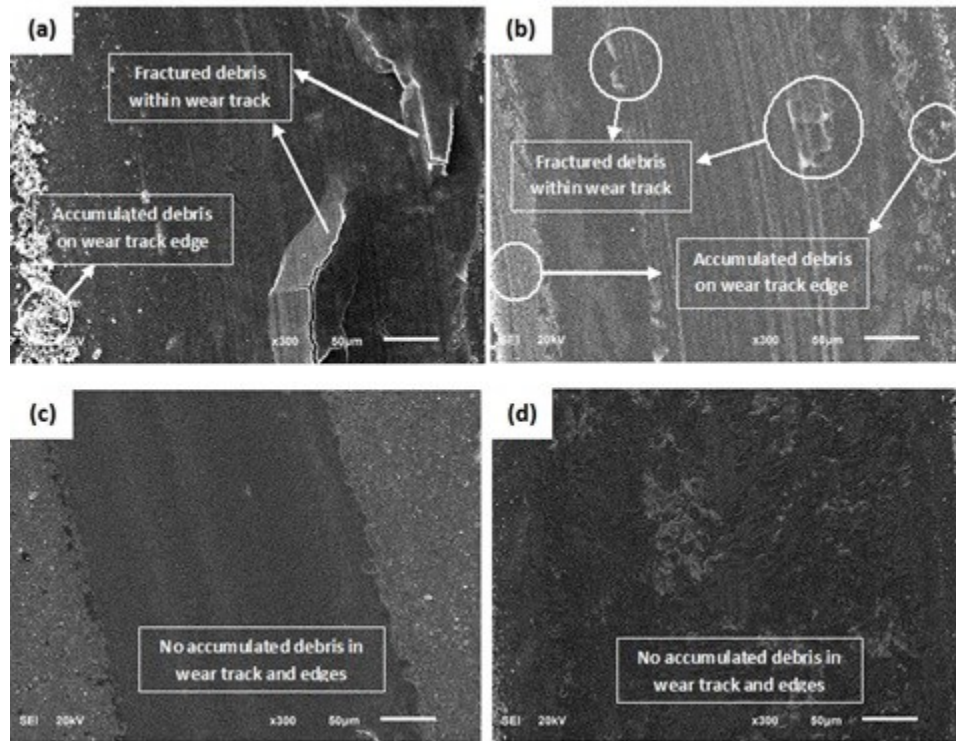


Figure 5-29: SEM images of typical wear track showing the wear mechanism of (a) TiN (b) CrN (c) Al_{0.68}Cr_{0.32}N and (d) Al_{0.50}Ti_{0.50}N.

During the wear test, an increase in localized temperature leads to oxidation of the coating and formation of TiO_2 . As for CrN, the oxidation products are chromium oxides which are relatively more stable than TiO_2 [76]. Figure 5-30 (a – f) show the images of the ball counter face used for the binary coatings while Figure 5-30 (g – l) show the counter face ball after the wear test on ternary coatings at different loads. The black spots on the counter face is the tribo-oxide layer which is well adhering to the ball even after cleaning with acetone. Large accumulation of tribo-oxide debris can be seen on the counter face with TiN coating while the counter face balls for CrN coating showed relatively low tribo-oxide layer due to its better oxidation resistance. These counter face images agree with the EDS analysis where higher oxygen concentration was detected on TiN wear tracks. Comparatively, the micrograph of the wear track for ternary coatings is devoid of accumulated debris and the wear tracks are considerably smoother. The absence of both debris on the edges and fractured debris within the track suggest that the wear mechanism is mainly by plastic deformation without or with little brittle failure of the coatings. EDS analysis of the wear track also revealed the presence of considerable percentage of oxygen within the wear track. This indicates the oxidation of the coating and the possible formation of TiO_2 , Al_2O_3 and Cr_2O_3 oxides. It is important to know that tribo-oxide layer formed could be either of detriment or benefit to the wear behavior. However, Al_2O_3 and Cr_2O_3 oxides are known for better wear resistance as a result of their thermal stability and strong adhesion, making the ternary coatings more wear resistant. In comparison between $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ and $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$ coatings, considering that their mechanical properties are similar, it is observed that $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$ coating exhibited slight improvement in wear resistance over $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$

coating. Unlike in $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$ where substantial tribo-oxide layers were observed, the counter face ball on $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ showed scanty tribo-oxides which might be associated with its high thermal stability and oxidation resistance. The huge tribo-oxide layers can play a role in the marginal improvement in the wear resistance of $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$ coating. Thus, it is seen that the relatively low wear resistance of $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ coating is associated to the numerous surface defects and consequently the high surface roughness coupled with its relatively low plastic deformation resistance (H^3/E^2). The high Al content in $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ coating may also led to the formation of hexagonal AlN phase which increased the wear rate via adhesion as observed by Lin et al.[180]. In a similar work, Sanchez et al. [192] showed that with Al content between $0.63 < x < 0.69$, $\text{Cr}_{1-x}\text{Al}_x\text{N}$ exhibited poor wear resistance and suggested that it was due to the higher surface roughness and thus increased the adhesive component of the wear.

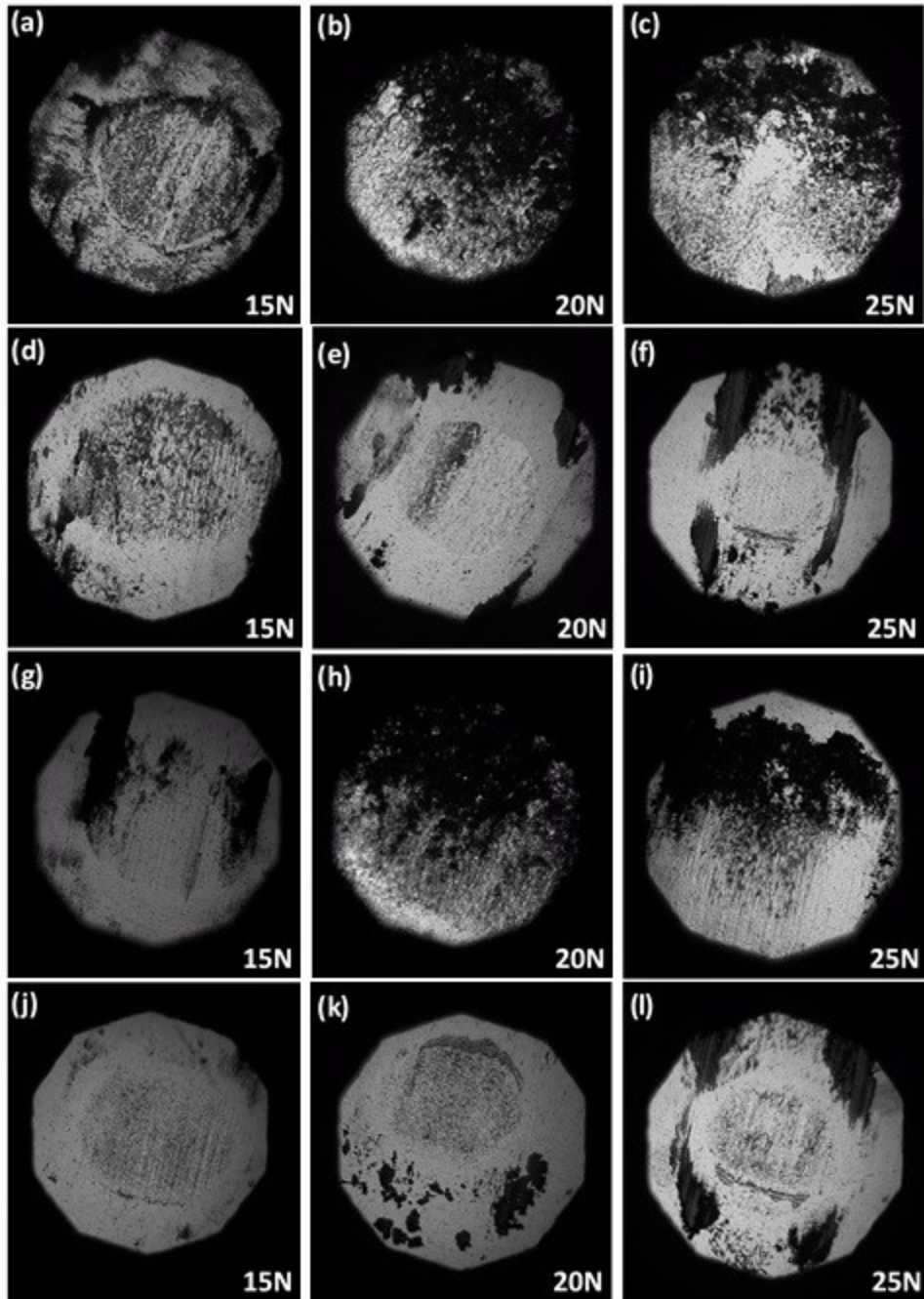


Figure 5-30: Images of the ball counterface after wear test using different normal loads on TiN (a – c), CrN (d – f), $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$ (g – i) and $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ (j – l) coatings.

CHAPTER 6

HIGH TEMPERATURE EVALUATION OF THE COATINGS

This chapter contains two sections. The first section describes the oxidation resistance behavior through an in-situ isothermal heating cycle at different temperatures of TiN, CrN, AlCrN and AlTiN coatings. The second section presents the results of the investigation of the effect of vacuum annealing on the mechanical and corrosion resistance behavior of CrAlN and TiAlN coatings.

6.1 Oxidation Behavior of TiN, CrN, AlCrN, and AlTiN

In-situ isothermal oxidation resistance behavior of TiN, CrN, AlCrN and AlTiN coatings was investigated at different temperatures; 700, 800, 900 and 1000 °C. This test was conducted on fully-coated samples (i.e. all the surfaces are coated) to be able to characterize the interface so as to understand the extent of protection at these temperatures.

6.1.1 Characterization of the as-deposited coatings

6.1.1.1 Coating thickness

Samples with approximate size of $25 \times 15 \times 3$ mm were cut from 304 stainless steel. To conduct oxidation test on all-surface-coated steel samples, it is necessary to ensure the entire surface and edge of the substrate were coated. This is critical to prevent a section of the sample to be preferentially oxidized, thus giving delusive information about the kinetics, weight gain and microstructural development. Thus, the samples were carefully

designed to tactically get rid of one of the sample dimensions. Consequently, the thickness of the samples was chamfered to eliminate the thickness dimension resulting in a three-dimensional sample with zero thickness at the edges as shown in Figure 6-1.

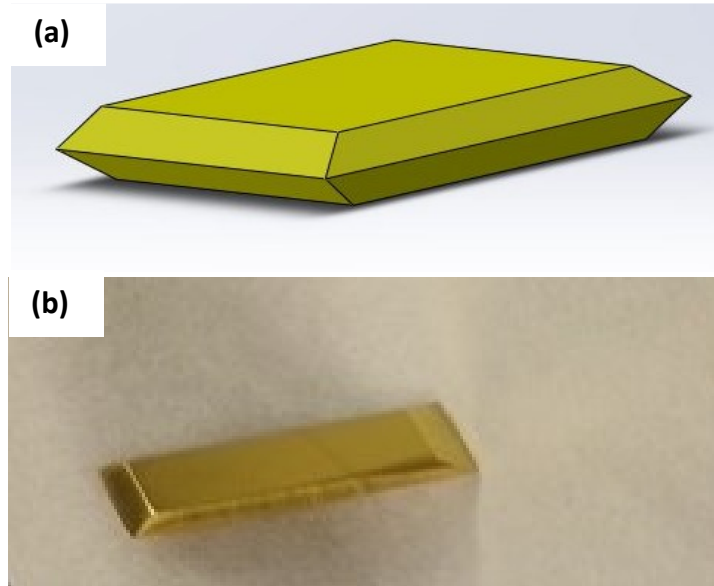


Figure 6-1: (a) Schematics of the designed substrate to ensure entire surfaces are coated with double rotation of the disc on the planetary (b) All-surface TiN Coated Steel Sample.

6.1.1.2 Microhardness measurement

The microhardness test of the as-deposited coatings was conducted using the CSM microcombi tester with a load of 20mN; this is chosen to avoid the substrate influence in the measurement. Table 6-1 also shows the average of ten hardness measurements for each of the coatings and the corresponding maximum penetration depth. The maximum penetration depth for the coatings were well below 180nm, confirming that the penetration depth is below 10% of the coating thickness. The hardness of AlCrN and TiAlN coatings were 24GPa and 19GPa, while that of CrN and TiN coatings were 12GPa and 16GPa respectively. All the coatings significantly improved the substrate hardness (~ 3 GPa) to

over 300%. The elastic modulus of the coatings is also shown in Table 6-1 to be between 180GPa and 350GPa with TiAlN having the highest modulus. It can be seen that the hardness of the ternary coatings is higher than the binary coatings. The incorporation of Al in the lattice improved the hardness over the binary coatings due to solid solution strengthening [114].

Table 6-1: Mechanical properties and maximum penetration depth of the as-deposited coatings.

Coating	Thickness (μm)	Mechanical Properties		Max. depth (nm)
		Hardness (GPa)	Modulus (GPa)	
CrN	1.82 ± 0.02	12.12 ± 0.90	187 ± 18	160
TiN	1.85 ± 0.04	15.60 ± 0.92	242 ± 10	130
AlCrN	1.83 ± 0.03	23.70 ± 0.64	313 ± 66	106
TiAlN	1.45 ± 0.02	18.89 ± 0.75	342 ± 36	119

6.1.1.3 Composition and surface morphology

The EDS analysis indicated the coatings have same composition as illustrated in Table 5-2. The as-deposited coatings are rich in nitrogen which constitutes over 45at% of the coatings. The binary coating has a stoichiometry composition of CrN and TiN while the ternary coatings are $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ and $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$. SEM images of the coatings surface morphology are shown in Figure 6-2. Macroparticles or droplets which are typical features of surface morphology of cathodic arc coatings can be observed on the surface of the coatings. Among the causes of macroparticles is the resident time of dense plasma on the cathode material before it is accelerated to the substrate. In addition, low melting point elements such as Al have high particle erosion rate and thus produces more and larger macroparticles. Macroparticles were reduced with the help of the magnetic field steered arc feature inbuilt

in the PVD machine used in this study. However, comparatively, AlCrN coating still has the highest macroparticles due to the high Al content.

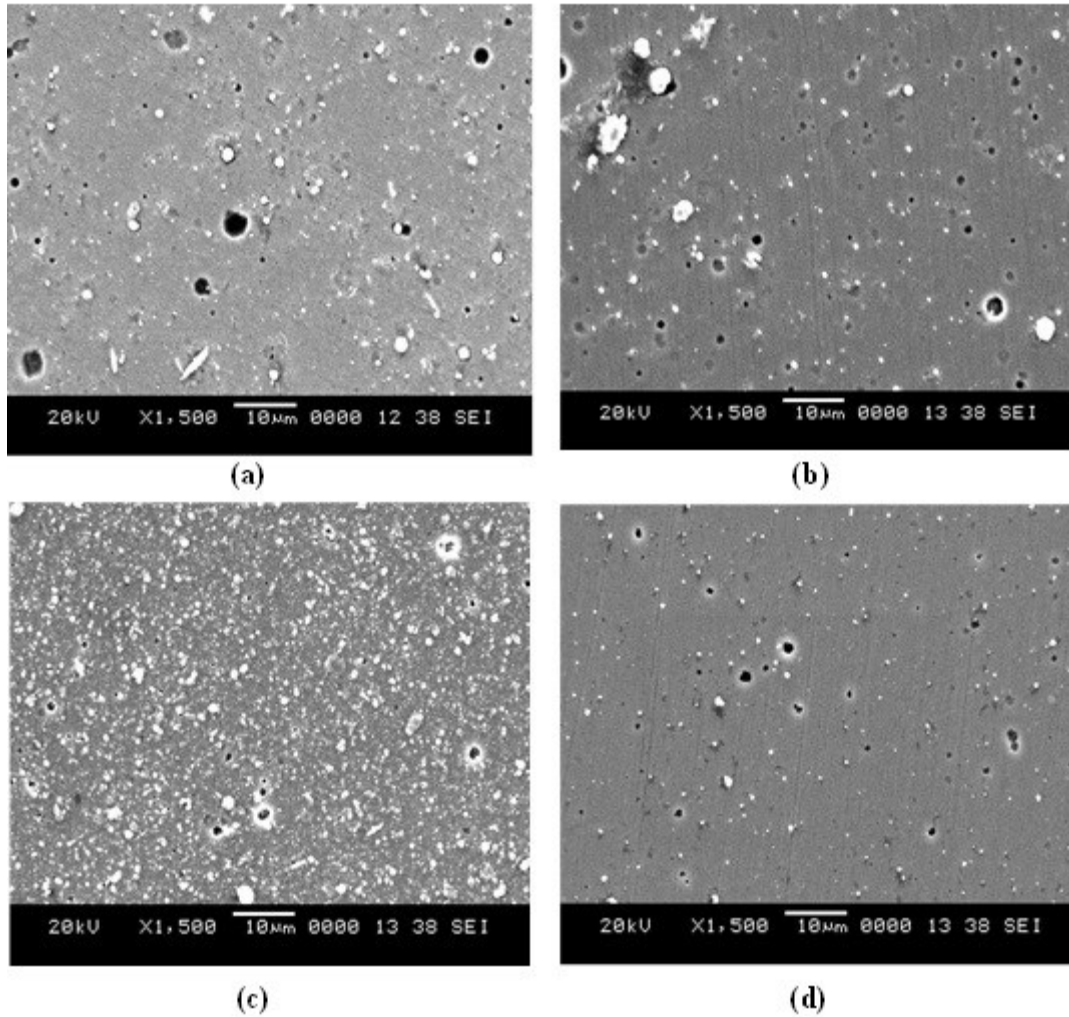


Figure 6-2: SEM micrographs showing macroparticles (a) CrN, (b) TiN, (c) AlCrN and (d) TiAlN thin coatings.

Also, low melting point elements such as Al have high particle erosion rate and thus produces more and larger macroparticles. Usually, these particles are between 1 – 40 μm in diameter [174]. The majority of the macroparticles on the coated samples are less than 1 μm in diameter. Thus, these particles were relatively reduced with the help of the

magnetic field steered arc feature inbuilt in the PVD machine used in this study. However, comparatively, AlCrN coating exhibited the highest macroparticles due to the high Al content. Macroparticles are disadvantageous because they influence the surface roughness and morphology of the coating thereby causing drawbacks such as localized coating failure and pitting corrosion [174,175].

6.1.2 Characterization of the coatings after oxidation

6.1.2.1 Surface Characterization

SEM images of the surface morphology of TiN coating after oxidation at different temperatures are shown in Figure 6-3. For all temperatures at which TiN coatings were tested, significant delamination and damage of the coating and oxides formed was observed. A closer observation of the SEM images revealed that at 900°C and 1000°C oxidation temperatures, the coating has been completely oxidized and extremely damaged with numerous detached scales found on the substrate. Thus, the steel substrate was entirely exposed to an extent that substrate grains were visible at higher magnification as shown in Figure 6-3(c) – (d). Severe oxidation of the coating led to significant compressive stresses within the formed oxides and consequently resulting in the breakdown and delamination of the oxides. At temperature of 1000°C, the steel substrate was found to have oxidized with noticeable damage as can be observed from Figure 6-3(e) – (f). EDS analysis of the oxidized TiN coating shown in Figure 6-4 confirms the presence of Titanium (Ti) and oxygen (O) as the main elements of the delaminated scales and the constituents of stainless steel were detected for the exposed region. The oxygen content in the coating after isothermal oxidation at 800°C, 900°C and 1000°C for 5hrs reached 54.70, 57.58 and 57.80 at.%, respectively. Also, nitrogen (N) was not detected at any of the temperatures

confirming its complete release to the gas phase and subsequent replacement by oxygen according to Equation 6-1.



The XRD patterns for the TiN coatings as deposited and oxidized are shown in Figure 6-5. The as-deposited coating XRD pattern confirms the TiN and stainless steel (ss) substrate peaks. However, on exposure to high temperature, rutile TiO₂ peaks were seen buttressing the composition analysis. With increased temperature, TiO₂ and Fe₂O₃ peaks intensity increased while the TiN peak diminished.

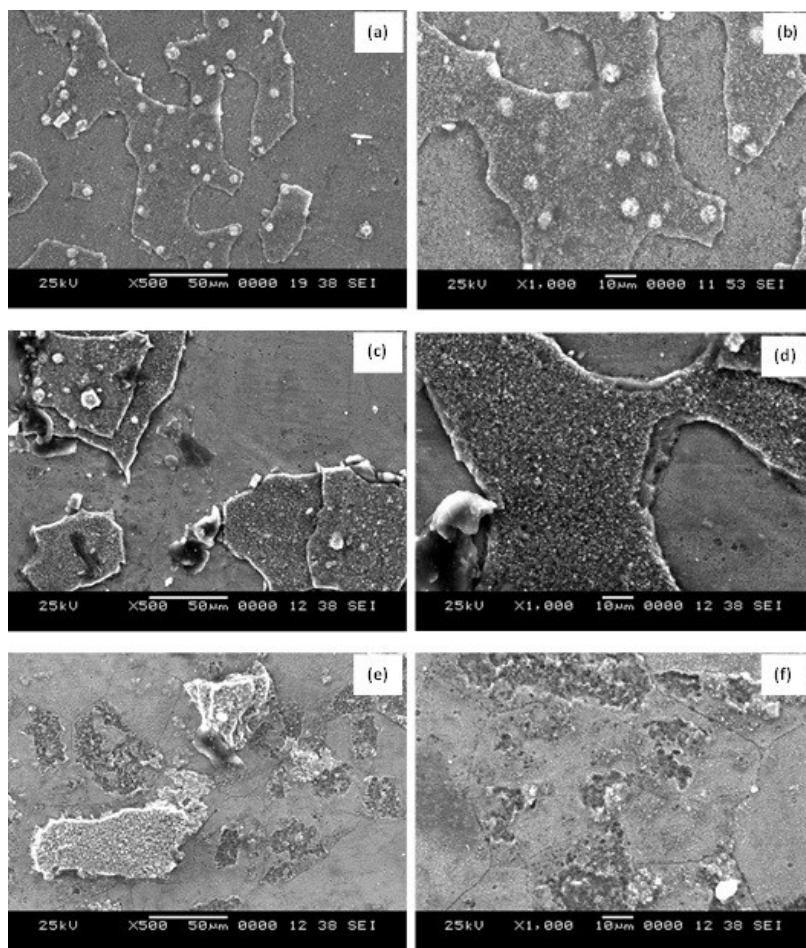


Figure 6-3: SEM Surface morphology of TiN Coatings after oxidation for 5 hrs at (a) & (b) 800 °C, (c) & (d) 900 °C, (e) & (f) 1000 °C.

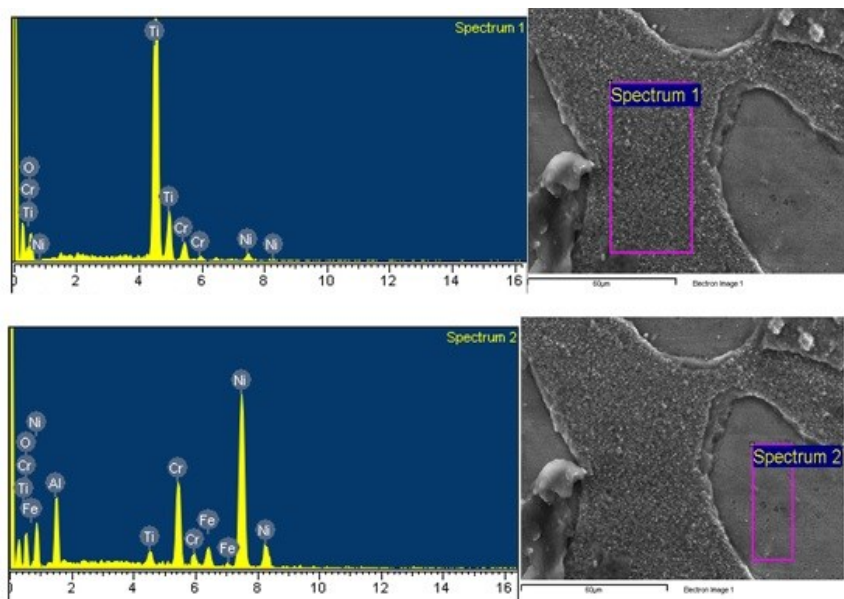


Figure 6-4: EDS analysis of the TiN Coating after oxidation at 900 °C for 5 hrs.

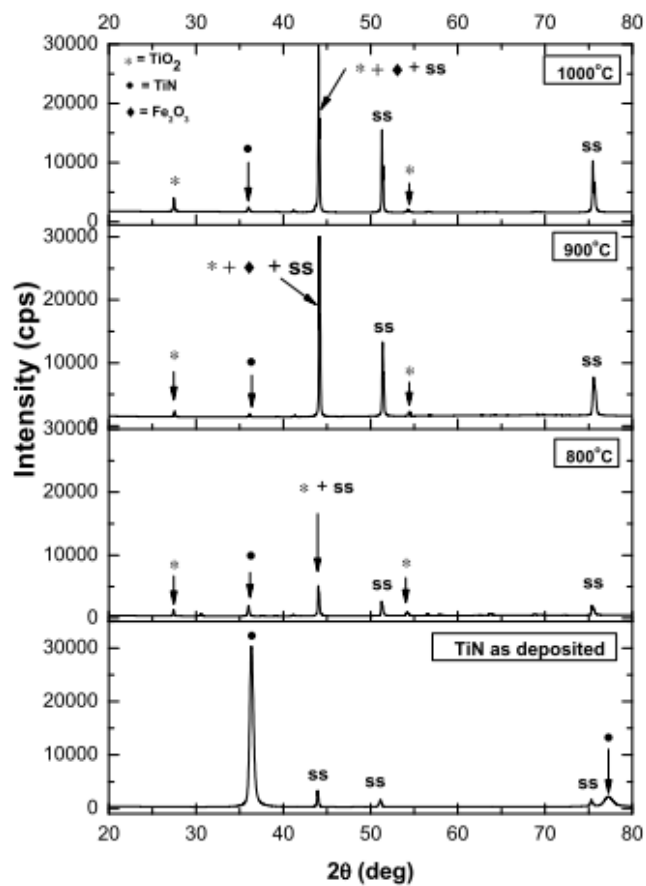


Figure 6-5: XRD patterns of TiN coating as deposited and after oxidation at different temperatures.

Oxidation test for TiAlN coating was conducted only at 900°C and 1000°C temperatures. SEM surface morphology of oxidized TiAlN coating is shown in Figure 6-6 revealed that TiAlN coating exhibited a higher oxidation resistance when compared to its binary TiN counterpart. It is found that oxide scales were formed on the entire surface. These oxides were observed to be block-like and at higher temperature they became flake-like with noticeable porosity. The EDS analysis (Figure 6-7) shows that the oxides consisted mainly of Ti, Al and O. Atomic percent of oxygen were 54.09 and 56.22 at% after oxidation at 900°C and 1000°C, respectively. XRD pattern for the as-deposited and the tested coating are shown in Figure 6-8. Several oxides phases of Ti and Al were found on the surface with rutile TiO₂ phase as also observed in a similar study [87]. Anatase TiO₂ was not detected because the investigative temperature in this study exceeded the 500 – 700°C anatase-to-rutile transformation temperature range [58,98]. The incorporation of Al in the TiAlN coating enhanced the oxidation resistance through the formation of dense and protective Al₂O₃ scales. This oxide plays a significant role in retarding the high rate of diffusion of the reacting species at coating/oxide boundary thereby ensuring a transition from the linear to majorly parabolic growth rate at 900°C. However, the poor protective property of rutile TiO₂ formed and consequent upon its porous nature, oxidation continued to occur at 1000°C, since oxygen diffusion through TiO₂ is much higher than in Al₂O₃ as reported in previous studies [87,193]. The presence of Al₂O₃ oxide confers the improved oxidation resistance performance of TiAlN above TiN coating. Al₂O₃ contribution in oxidation resistance was more appreciable at the lower temperature as compared to the oxidation at 1000°C. Oxygen diffusivity increases as temperature increases, thus a more stable and protective oxide free from defects and porous phases is required for enhanced resistance.

The non-protectiveness observed in TiN coating can be attributed to the fact that at these temperatures it is certain that anatase TiO_2 would have completely transform to rutile TiO_2 with significant volume shrinkage which resulted into pores and cracks as noted by Hollerweger et al. [97].

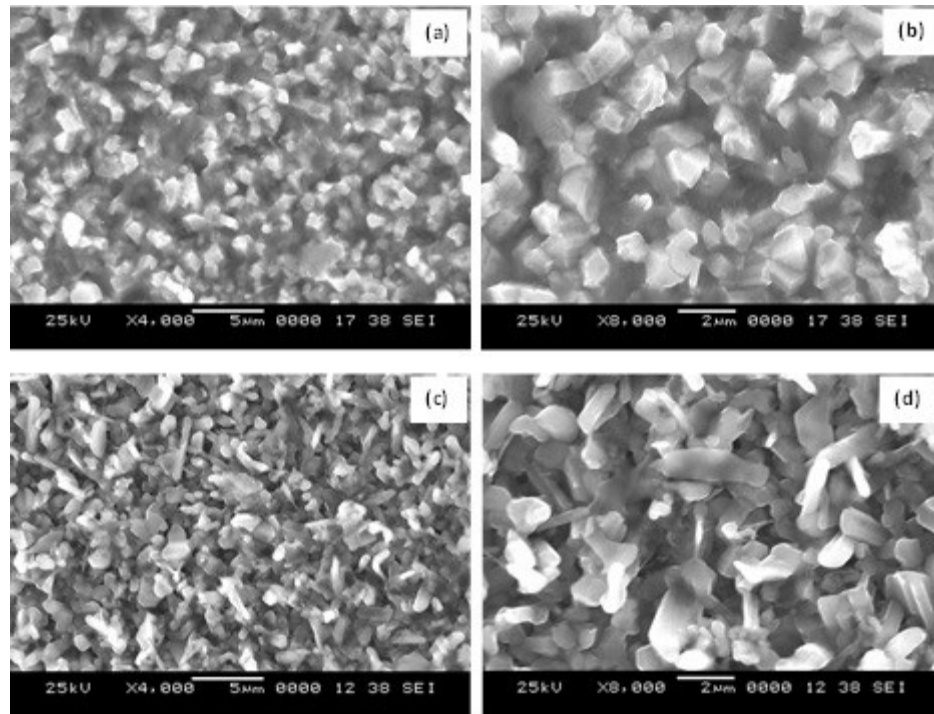


Figure 6-6: SEM Surface morphology of TiAlN Coatings after oxidation for 5 hrs at (a) & (b) 900 °C and (c) & (d) 1000 °C.

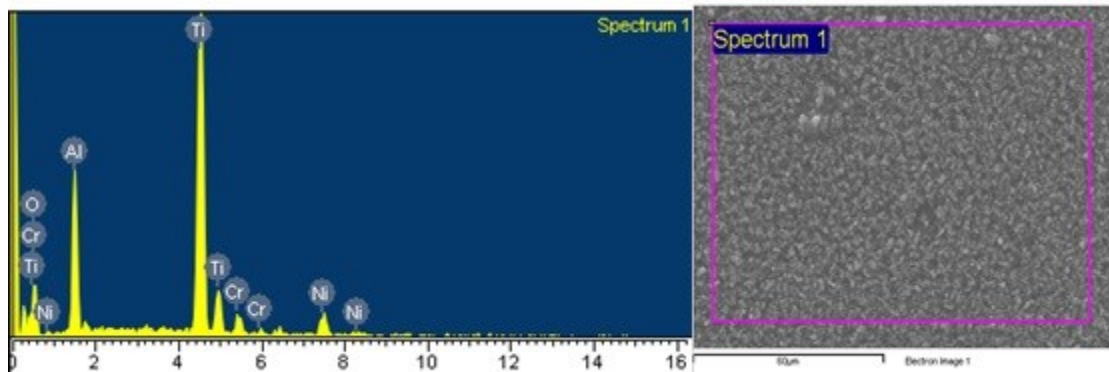


Figure 6-7: EDS of TiAlN Coating after oxidation at 900 °C for 5 hrs.

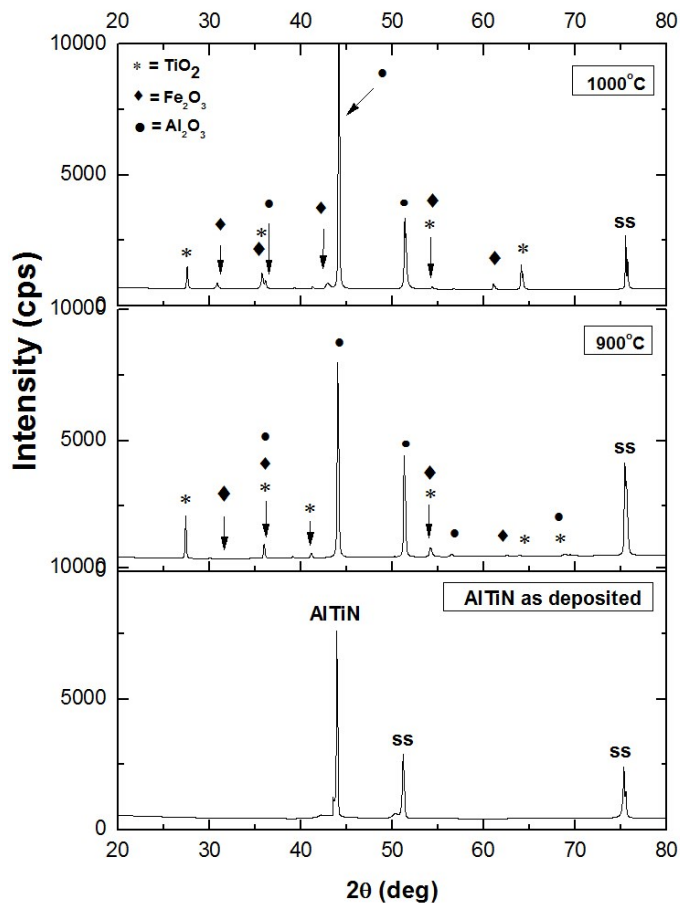


Figure 6-8: XRD pattern of TiAlN coating as deposited and after oxidation at different temperatures.

CrN and AlCrN coatings' SEM surface morphology images are shown in Figure 6-9 and Figure 6-12, respectively. The SEM images of oxidized CrN coatings show the gradual growth of oxide layer as temperature increased. EDS analysis of oxidized CrN coating shown in Figure 6-10 revealed that atomic percentage of oxygen was 51.19, 46.64 and 46.40 at% at oxidation temperatures of 800°C, 900°C and 1000°C, respectively. The oxygen content is almost constant at the higher temperatures. The coatings can be said to be fully oxidized as no traces of nitrogen were detected and the process of the nitride-to-oxygen transformation is similar to Equation 1 if Ti replaces Cr as indicated by Mayrhofer et al [194]. XRD pattern as shown in Figure 6-11 confirmed the presence of chromium

oxides (Cr_2O_3 and Cr_2O) on the oxidized coatings. The presence of these oxides does not prevent or decelerate oxidation, possibly because the oxide does not attain sufficient coverage to hinder further oxidation owing to the slow oxidation formation or scale thinning due to the evaporation of CrO_3 . With further increase in temperature, there is attendant increase in evaporation of CrO_3 coupled with the increase in the diffusivity of oxygen, thus oxygen diffuse into the coating aggressively and react with the substrate. This results in the formation of iron oxides. This also explains the increase in iron oxide peaks observed at 1000°C in the XRD analysis. However, with the addition of Al, the AlCrN coating shows more enhanced oxidation resistance compared to CrN coating with the oxygen contents as 3.30, 9.59, and 34.44 at.% for oxidation temperatures of 800, 900 and 1000°C , respectively. In addition, significant amount of nitrogen was found in the EDS analysis (Figure 6-13) for both samples oxidized at 800°C and 900°C and the nitrogen percent detected were 30.34 and 24.85 at.%, respectively, compared with the as-deposited nitrogen content of 49.2 at.% (Table 5-7). But at 1000°C , a complete nitride-to-oxygen transformation was observed. This behavior supports the fact that AlCrN coating forms oxides that are very dense and protective which provides resistance to oxidation of the coating at temperature as high as 900°C .

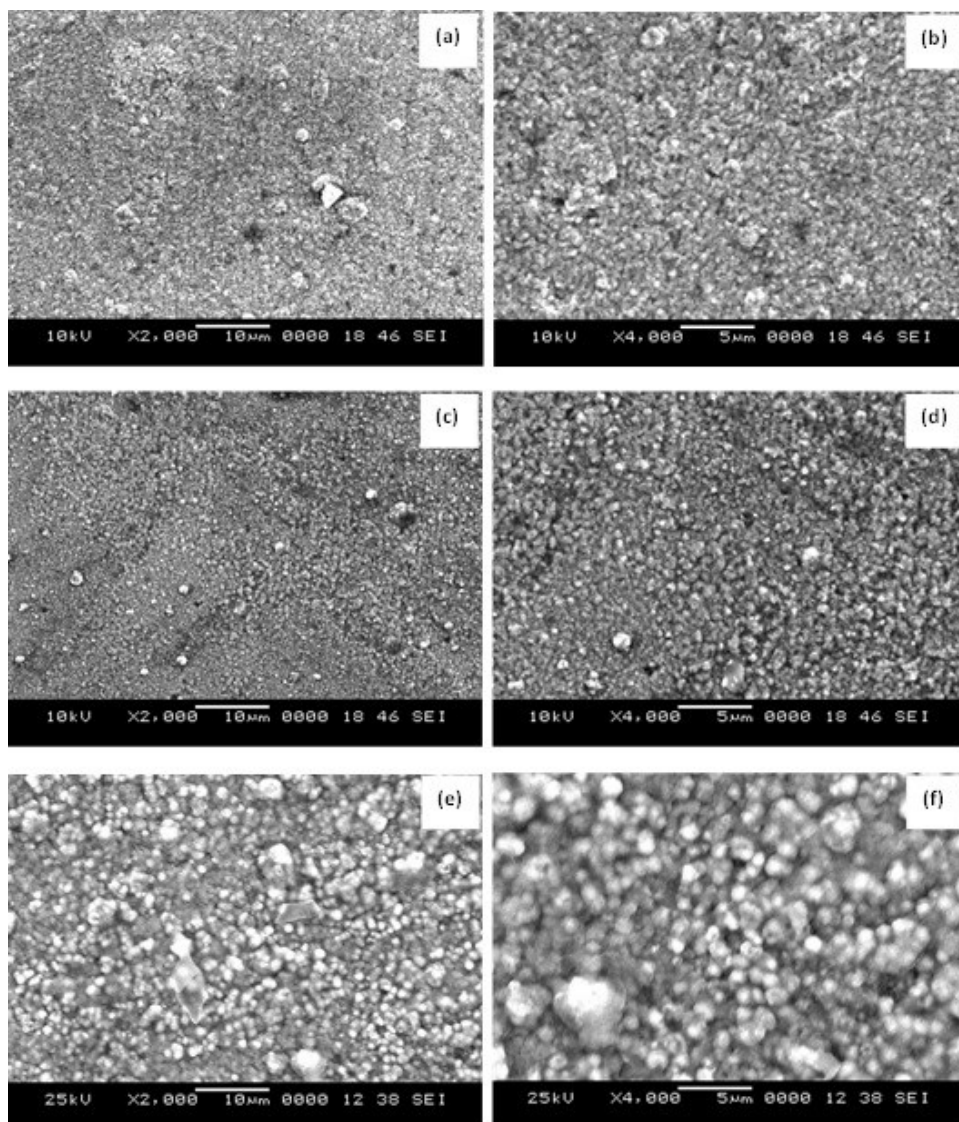


Figure 6-9: SEM Surface morphology of CrN Coatings after oxidation for 5 hrs at (a) & (b) 800 °C, (c) & (d) 900 °C, (e) & (f) 1000 °C.

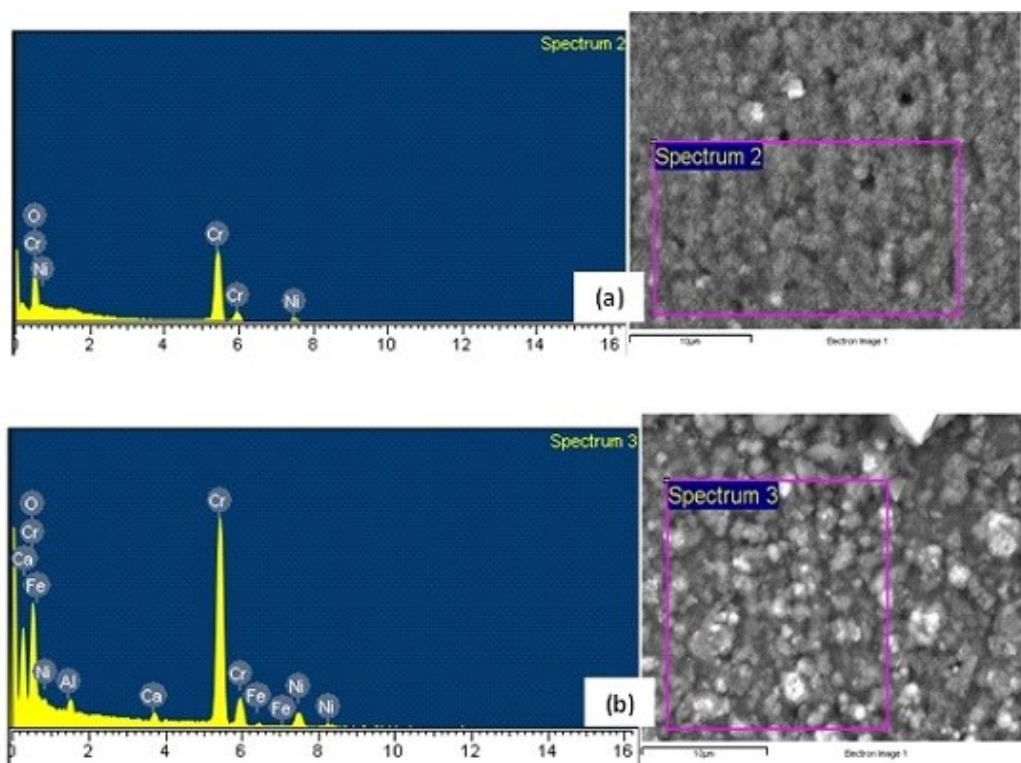


Figure 6-10: EDS of CrN Coating after oxidation at (a) 800 °C and (b) 1000 °C for 5 hrs.

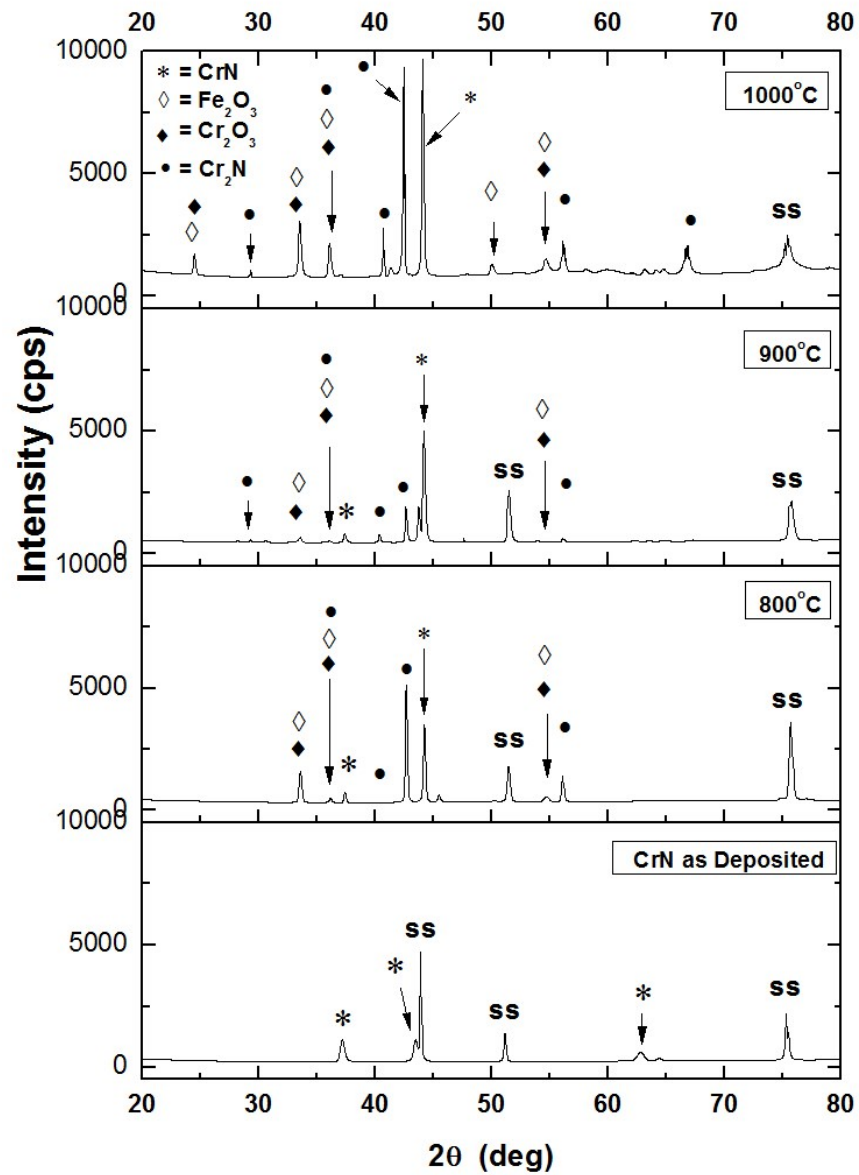


Figure 6-11: XRD pattern of CrN coating as deposited and after oxidation at different temperatures.

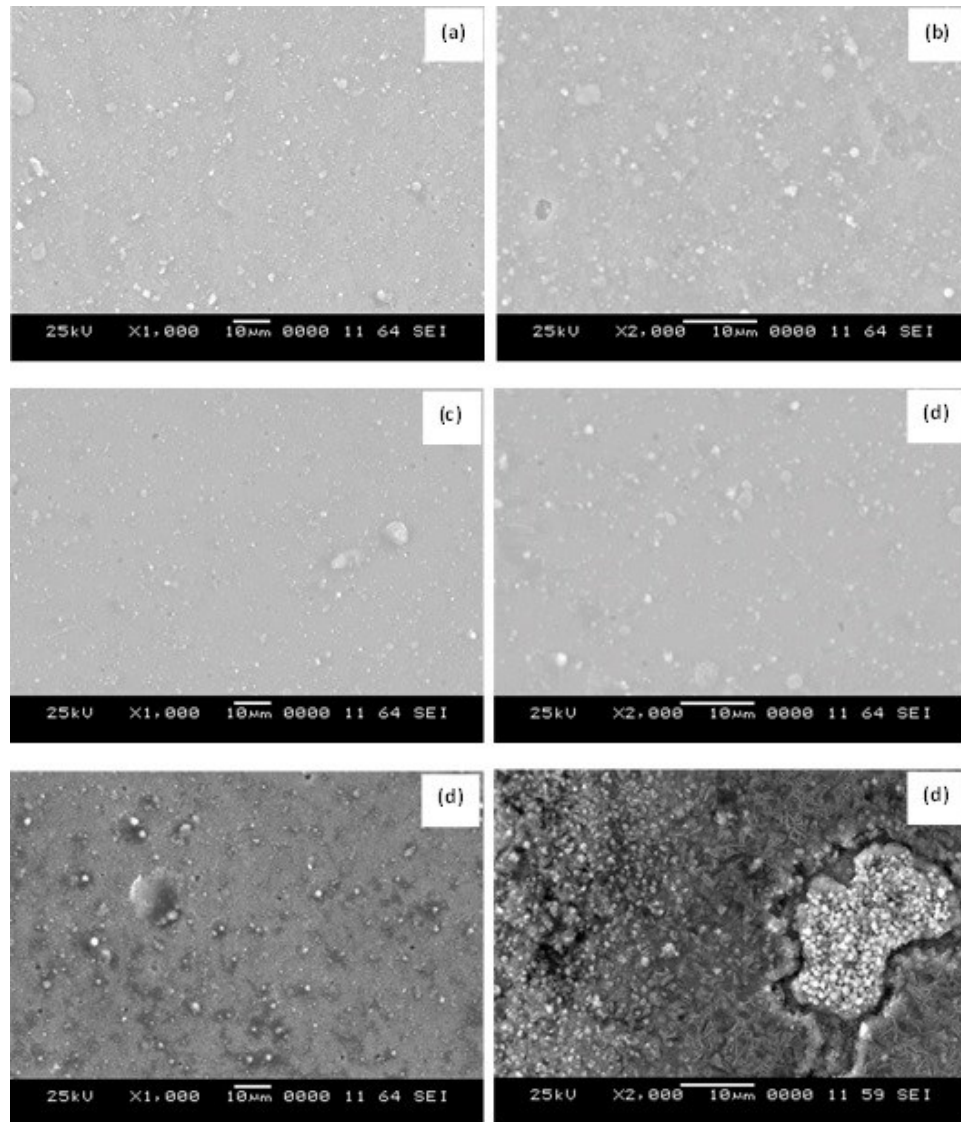


Figure 6-12: SEM Surface morphology of AlCrN Coatings after oxidation for 5 hrs at (a) & (b) 800 °C, (c) & (d) 900 °C, (e) & (f) 1000 °C.

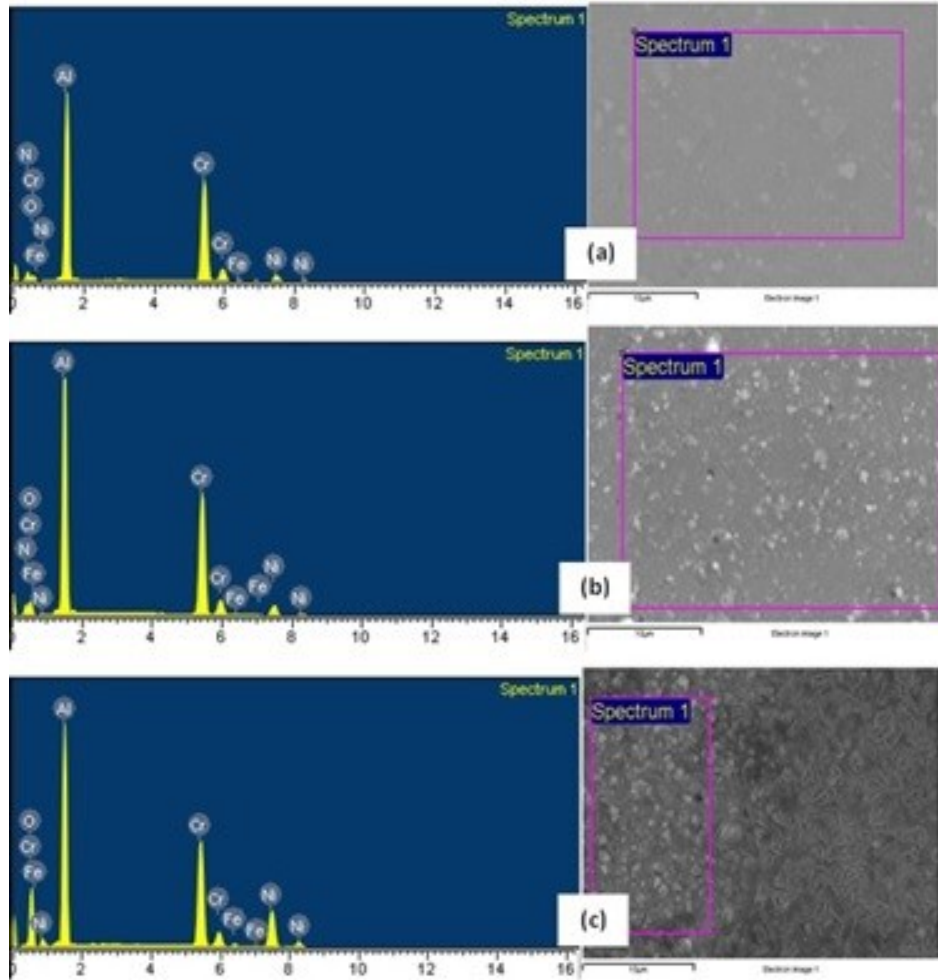


Figure 6-13: EDS of AlCrN Coating after oxidation for 5 hrs at (a) 800 °C (b) 900 °C and (c) 1000 °C.

The XRD pattern as shown in Figure 6-14 revealed that Al_2O_3 and Cr_2O_3 were the main oxides formed during the oxidation. Both oxides are known for their dense, protective and adherent nature to steel substrates as well as having good thermal stability. This explains the observed enhanced oxidation resistance behavior of AlCrN up to 1000°C for the 5hrs oxidation duration. Peaks of AlCrN were found and matched up to 900°C confirming the EDS analysis which detected significant percentage of nitrogen at this temperature. SEM images of these coatings at elevated temperatures of 800°C and 900°C show no major

difference with the as-deposited coating. Similar conclusion can be made from the percentage of diffused oxygen at the end of isothermal oxidation period. No oxides of iron were noticed in both EDS and XRD analysis of these coating for the oxidation temperature evaluated. Hence the substrate was completely protected for the oxidation conditions studied. Similar observation have been reported in the literatures for the oxidation resistance behavior of AlCrN coatings [3,17,34]. Comparatively, the oxygen weight percentage (wt %) of all coatings are shown in Figure 6-15, and it is seen that AlCrN coatings exhibited the lowest oxygen weight percentage. CrN coatings show decreasing trend for oxygen content. This is due to oxygen migration and escape into the interface and subsequent reaction with the substrate as temperature increased. The escape oxygen was unaccounted for by the EDS spectra. TiN and TiAlN show similar oxygen content. However, TiN coatings were completely delaminated from the substrates. TiAlN coating exhibited considerable oxidation resistance as diffused oxygen enhanced the formation of protective alumina oxide.

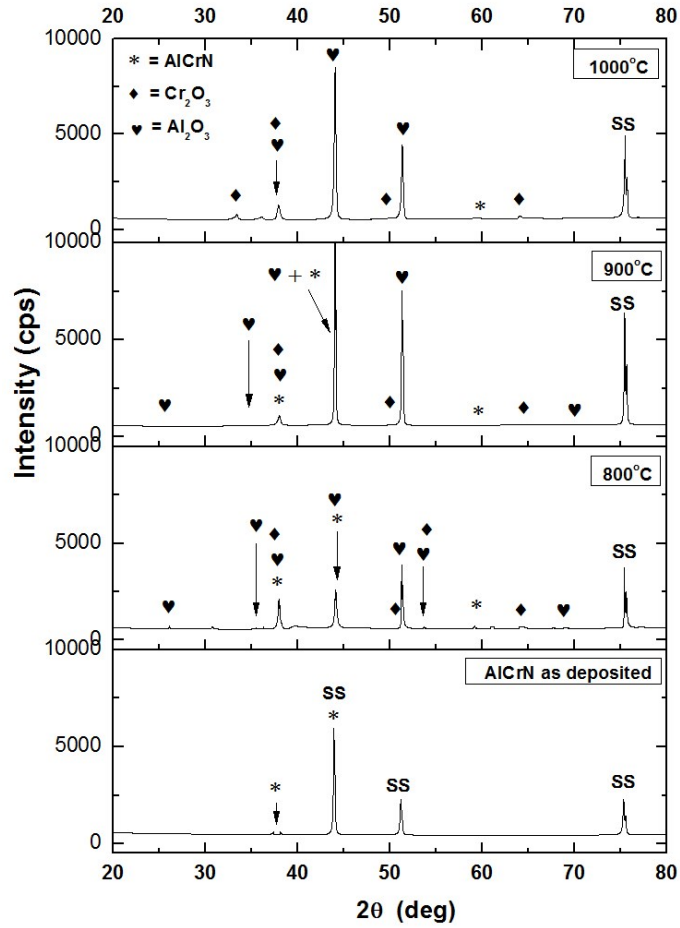


Figure 6-14: XRD pattern of AlCrN Coating as deposited and after oxidation at different temperatures.

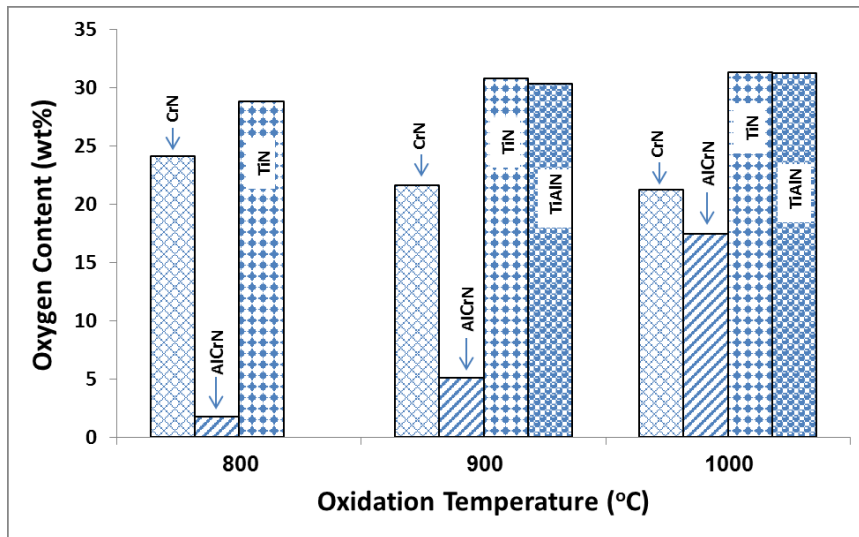


Figure 6-15: Oxygen content in the coatings after isothermal oxidation for 5 hrs at different temperatures.

6.1.2.2 Cross-section characterization

Since the oxidation test was conducted without detaching the coating from the substrate, the cross-sectional analysis will offer the opportunity to evaluate the coating/substrate interface. This is necessary as inward diffusing oxygen may penetrate the coating then react with elements of the substrate to form new phases at the interface which is deleterious to the coating/substrate system. Cross sectional analysis was not carried out for TiN tested coatings because the TiN coating was completely detached from the substrate for the evaluated temperatures. However, CrN, TiAlN and AlCrN coatings, which were obviously still intact and adherent to the substrate, were cross-sectioned for examination. The cross-section SEM images of CrN are shown in Figure 6-16 for the temperatures considered. The thickness of the coatings after oxidation test can be measured from the SEM images to be between 1.5 and 2 μm . At 900°C and 1000°C new phase features were observed to have formed at the interface, however, no such features were noticed at 800°C. This can be attributed to the diffusion of oxygen and subsequent reaction with the substrate. EDS mapping reveals that the interface of sample oxidized at 800°C is lean while interfaces at 900°C and 1000°C are oxygen-rich. It was observed that the interface become enriched with both oxygen and chromium at the expense of nitrogen. Hence, it can be said that the increased kinetics of diffusing species at higher temperatures are responsible for the observed features. Figure 6-17 and Figure 6-18 respectively show the cross-section SEM images of heat treated TiAlN and AlCrN coatings. Analysis indicated that the composition at the interface of these ternary coatings is similar to that of the bulk substrate and no interfacial damages or formation of new phases were observed. The ability of these coatings to effectively hinder the complete diffusion of oxygen at high temperatures can

be associated with the formation of Al_2O_3 oxides. According to the Ellingham diagram, Al has the lowest free energy of formation of oxides among the elemental constituents of the coatings and thus most stable, therefore compared to the oxides of Cr and Ti, Al_2O_3 will first formed. Thus, the early formation of a dense and protective Al_2O_3 layer effectively produced a good barrier against oxygen penetration.

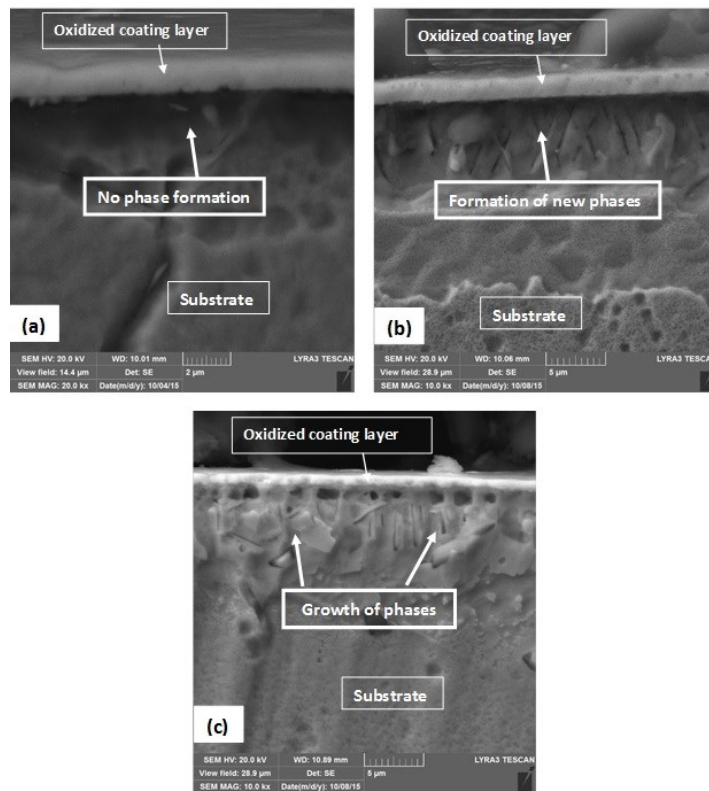


Figure 6-16: Cross-section SEM images of CrN coating tested at (a) 800 °C (b) 900 °C and (c) 1000 °C for 5 hrs isotherm.

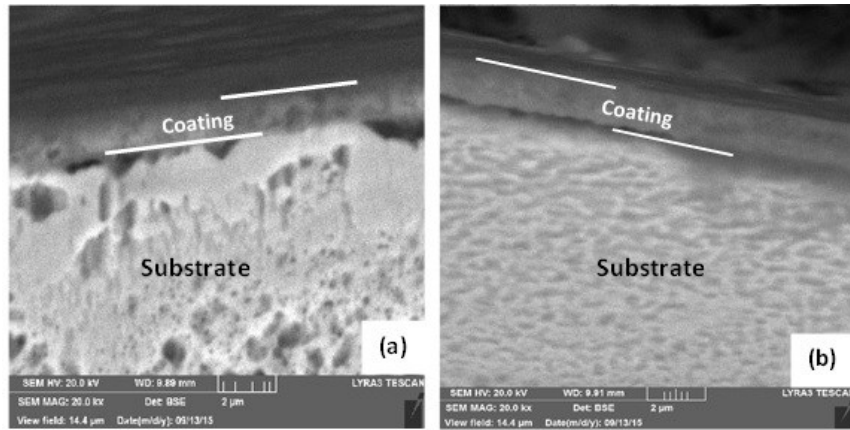


Figure 6-17: Cross-section SEM images of TiAlN coating tested at (a) 900 °C and (b) 1000 °C for 5 hrs isotherm at different magnifications.

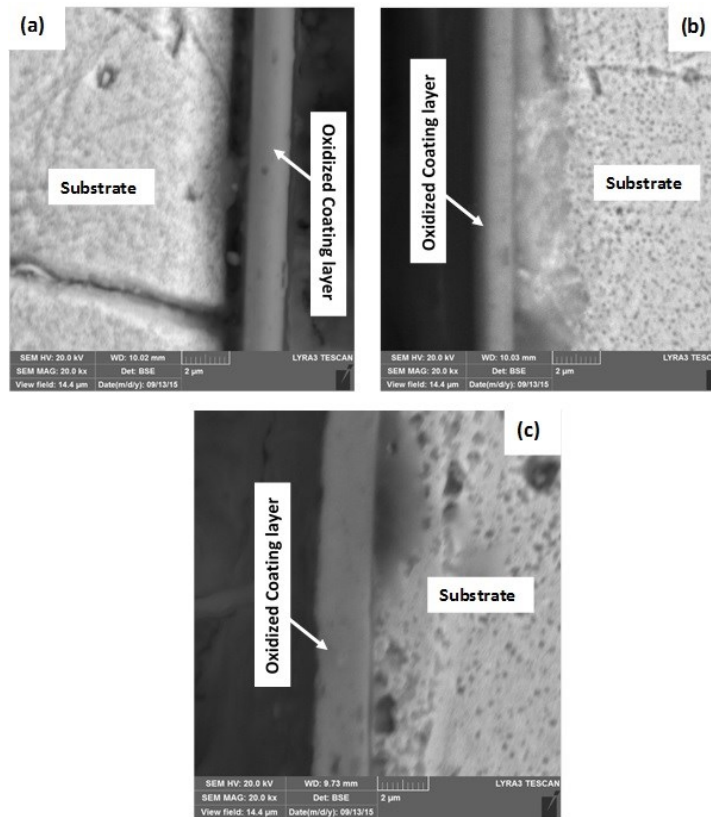


Figure 6-18: Cross-section SEM images of AlCrN coating tested at (a) 800 °C (b) 900 °C and (c) 1000 °C for 5 hrs isotherm.

6.1.2.3 Mechanical Analysis

The microhardness of the coatings as a function of temperature after oxidation test is shown in Figure 6-19. It is observed that all coatings exhibited considerable drop in their hardness after 5hrs isothermal oxidation test. TiN coating has the highest drop in hardness from 16 GPa at room temperature to 8 and 3 GPa when oxidized and annealed at 800 °C and 1000 °C, respectively. This corresponds to about 50 to 80% drop in hardness. This significant drop can be attributed to the fact that the coating has been delaminated from the substrate, thus, the measured hardness reflects typical hardness of the substrate. In the same manner, the hardness of TiAlN coating dropped from around 20 GPa as-deposited to 15 GPa after having been oxidized at 900 °C. However, at 1000 °C, the hardness drastically reduced to around 9 GPa. Comparatively, it is observed that the hardness of TiN rapidly degenerated to more than 50% at 800 °C unlike TiAlN which experienced only about 30% drop in hardness up to 900 °C oxidation temperature. The drop in hardness can be attributed to the soft and porous rutile TiO₂ oxides formed on both TiN and TiAlN coatings as observed from XRD results. As for TiAlN, TiO₂ oxides reduce the hardness by acting as a weak spot for deformation in the hard Al₂O₃ oxide matrix. As for the chromium-based coatings, the hardness of the as-deposited CrN coating dropped from 12 to 10, 9 and 5 GPa after oxidation test at 800, 900 and 1000 °C, respectively. AlCrN coating however retained its hardness substantially at 800°C (from 24 to 22 GPa) which is less than 10% reduction in hardness. However, the hardness deteriorated further at higher temperatures. The hardness, at 900°C and 1000°C, were 18 and 13GPa corresponding to about 25 and 45% drop, respectively. This shows that besides the improved oxidation resistance, the coating retained considerably its mechanical properties at elevated temperature. A similar hardness

trend has been reported by Chim et al. [77] for AlCrN. In all, the chromium-based coatings respectively retained their hardness when compared with their titanium based counterparts. Also, it is found that the ternary coatings exhibited improved hardness sustainability better than their binary counterparts.

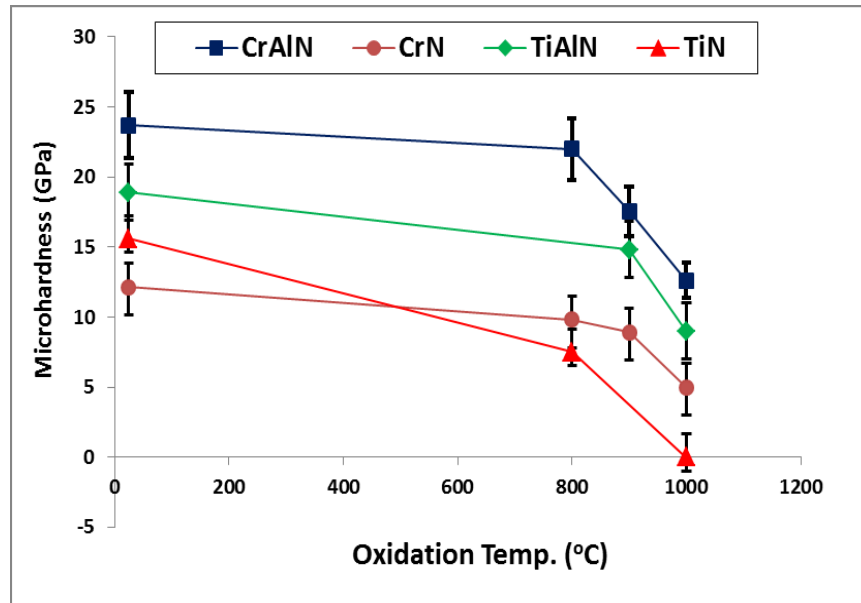


Figure 6-19: Microhardness of the coatings after isothermal oxidation for 5 hrs at different temperatures.

6.1.2.4 Thermogravimetric Analysis (TGA)

Figure 6-20 (a - d) respectively shows the specific weight gain curves for TiN, TiAlN, CrN and AlCrN coatings subjected to different isothermal temperatures of 800, 900 and 1000 °C for 5 hrs (the oxidation test for TiAlN coating at 800 °C could not be conducted). The curves show the specific weight gain variation over the isothermal duration. The trend in the curves depicted the oxidation resistance behavior of the coatings and provide insight into the mechanism and the kinetics for the formation of the characteristic oxides. It is observed that the TGA curves for the coatings exhibited a combination of oxidation rate

law as described elsewhere [97,194,195]. The TGA curve of TiN coating at 800 °C indicated that at the initial stage the coating exhibited a linear growth rate, followed by a parabolic growth rate where the rate of weight gain gradually reduced. This stage continued for about 120 min before the onset of a third stage with linear growth rate. The first two stages represent the growth of an oxide layer and subsequent diffusion retardation after the layer attained sufficient thickness thereby decelerating the diffusion process. The last stage is characterized with an increased weight gain indicating saturation of the oxide and a gradual breakdown of the protective oxides due to prolonged isothermal heating. Coating tested at 900°C and 1000°C oxidation temperatures also show similar trend however they show a quick transition between the first two stages. It is observed that the duration of parabolic regime decreased as the temperature increased from 800 to 1000 °C and the last stage duration thereby increased accordingly.

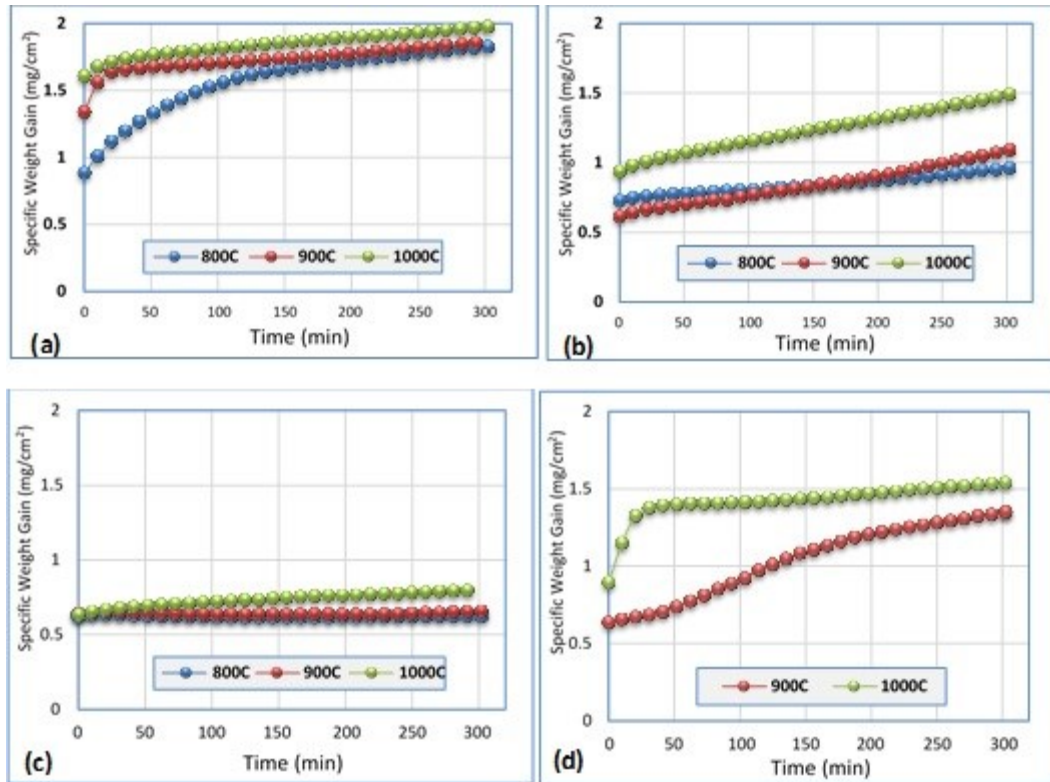


Figure 6-20: Specific weight gain vs time curve for (a) TiN (b) CrN (c) AlCrN (d) TiAlN coatings.

At 900 and 1000 °C, the last stage with linear growth rate became significant and the predominant regime; this indicates that the initially formed oxides possibly degraded over a short period thus could not protect the substrate for the duration. The non-protective nature of the oxide can be attributed to the porous nature of rutile TiO_2 as found in the XRD analysis and its eventual breakdown as observed from the surface morphology. Hence, at higher temperature, the TiO_2 formed were extremely degraded resulting in an increased oxidation which led to subsequent damage to the substrate. The specific weight gains of TiN coating tested at 800, 900 and 1000 °C at the end of the isothermal duration were 1.83, 1.87 and 1.98 mg/cm², respectively. Figure 6-20(b) shows the specific weight gain rates for CrN coating at the different temperatures. It is found that they mainly

exhibited the linear growth rate with the rate increasing as the temperature increased. This trend shows the continuous and steady oxidation of the coating throughout the isothermal period. Unlike in TiN coating, visual observation of the coating after the completion of the heating cycle indicated that the coating remained intact with no clear damage to the coating. CrN coatings show lesser oxidation compared with TiN with 0.97, 1.07 and 1.54 mg/cm² specific weight gain at 800, 900 and 1000 °C oxidation temperatures, respectively. It is found that as the temperature increased, the weight gain increased due to higher thermal activity of outward and inward diffusing of Cr and O, respectively. The interfacial damage especially at high temperature as seen in the SEM cross-section images substantiate the non-protective nature of oxides due the reasons earlier stated in section 3.2.2. This also explains the observed linear growth and the relatively low oxygen percentage at the surface as measured from the EDS surface analysis. TGA analysis of AlCrN coating is shown in Figure 6-20(c). At 800°C and 900°C tested temperatures, the oxides formed during the early stage completely halted further oxidation of the coating as can be seen with the fixed weight gain for the entire isothermal duration. This implies that inward diffusion of oxygen, nitride-to-oxygen transformation and subsequent reaction with the coating species were almost completely stopped resulting in approximately constant specific weight gain recorded during the period. Thus, this substantiate the presence of nitrogen in the coating that were detected in the EDS analysis test at these temperatures. However, at 1000 °C the TGA curve shows a slightly linear growth. This suggests that there is a continuous growth of the oxides with time. This can be attributed to the continuous growth of both Al₂O₃ and Cr₂O₃ oxides throughout the isothermal duration due to increased activities of Al, Cr and O at this temperature. Figure 6-22 show the schematics of the oxide growth with time. This

is in accord with the EDS and XRD analysis that shows that there is complete nitrogen-to-oxygen transformation. These oxides are dense and protective thus their improved oxidation resistance. It is also impressive to note that the AlCrN coating after tested at 1000 °C, showed neither crack nor any other form of damage. As for TiAlN coating, it is observed that the TGA curve (Figure 6-20(d)) of isothermal temperature 900 °C shows that the coating portrayed mainly parabolic growth rate. This indicates that the incorporation of Al into TiN coating alters the oxidation behavior from a predominantly linear growth to parabolic growth behavior at 900 °C. This change in the growth behavior can be attributed to the formation of the dense and protective Al₂O₃ oxide for the considerable isothermal duration. However, at higher temperature of 1000 °C, the coating experienced combination of higher and lower linear growths. The higher linear growth was observed briefly within the initial period of the isothermal duration while the lower linear growth, which was preceded by a transition parabolic kinetics regime, became predominant afterward. This behavior can be attributed to the fast oxidization of the coatings during the initial higher linear rate to form Al₂O₃ oxide which results in diffusion retardation and consequently decelerate oxidation. This is substantiated by the fact that the majority of the weight gain i.e. about 80% of the total weight gain at 1000 °C, was during the initial linear growth. The oxide formed during this stage acted as a barrier against further oxidation thus altering the kinetics. However, with increased isothermal heating at the same temperature, weight gain was found to increase though at a lower rate. This could be due to the formation of porous TiO₂, as observed from XRD results, consequent upon longer duration and higher temperature. The formation of TiO₂ require the diffusion of both Ti and O outwardly and inwardly respectively through the already formed Al₂O₃ scales. Hence TiO₂ phases are

formed and dispersed in Al_2O_3 oxides as shown schematically in Figure 6-23 and also illustrated elsewhere [99]. The specific weight gain at the end of the isothermal heating was 1.34 and 1.54 mg/cm^2 at 900 and 1000 $^\circ\text{C}$, respectively.

Figure 6-21 compares the TGA curves of the four coatings at the tested isothermal temperatures. It can be clearly seen that TiN coating were highly oxidized as compared to the other coatings at all temperatures. This severe oxidation led to significant buildup of compressive stresses which results in the cracking and delamination of the oxides, thus exposing the substrates. CrN coatings seems to perform better considering the lower weigh gain, however the consequent effects at the substrate/coating interface indicated the limitation of the coating. While TiAlN was relatively thermally stable up to about 1000 $^\circ\text{C}$ without obvious cracking and defects rather only the formation of porous TiO_2 dispersed in dense Al_2O_3 , AlCrN shows the least oxygen uptake and no obvious effect on the coating and its interface. The specific weights gain of these coatings are compared in Figure 6-24. It is observed that the weight gain increased with oxidation temperature for all coatings. AlCrN coating exhibited the least weight gain of 0.63, 0.66 and 0.78 mg/cm^2 at 800, 900 and 1000 $^\circ\text{C}$, respectively, and hence exhibited the highest oxidation resistance. CrN coating shows a linear oxidation behavior at 900 and 1000 $^\circ\text{C}$ with weight gain similar to that of TiAlN, however interfacial damage was observed due to oxygen reaching with the substrate. TiAlN show improved oxidation resistance compared to TiN evident from the reduced weight gain and its protection of the substrate. It is observed that as the temperature increased the difference in the specific weight gain among the coatings also increased.

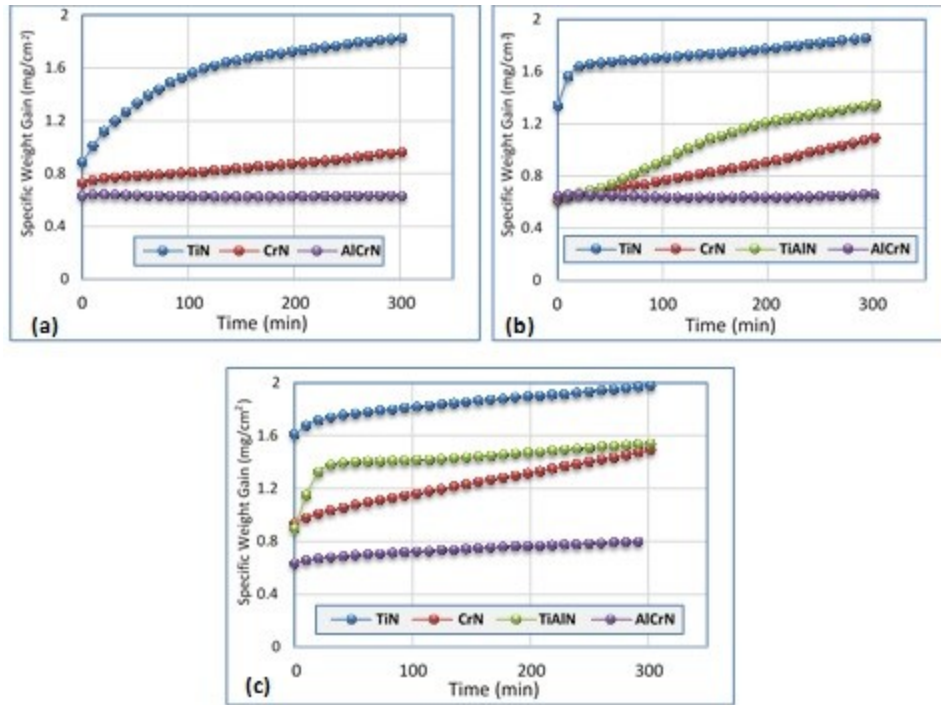


Figure 6-21: Specific weight gain vs time curve at different isothermal temperatures; (a) 800 °C (b) 900 °C (c) 1000 °C.

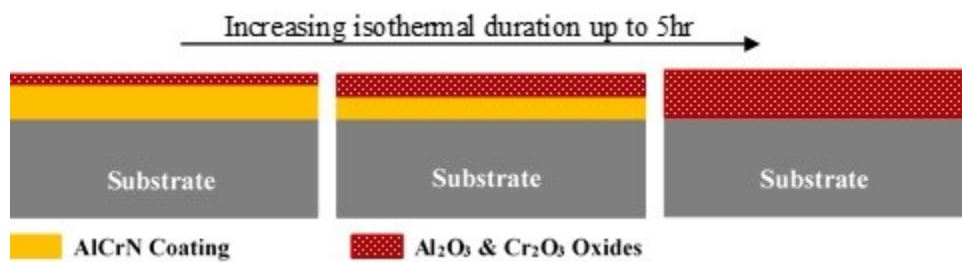


Figure 6-22: Schematics of Al_2O_3 and Cr_2O_3 oxides growth in AlCrN coating at 1000 °C.



Figure 6-23: Schematics of TiO_2 dispersed in Al_2O_3 oxides in oxidized TiAlN coating.

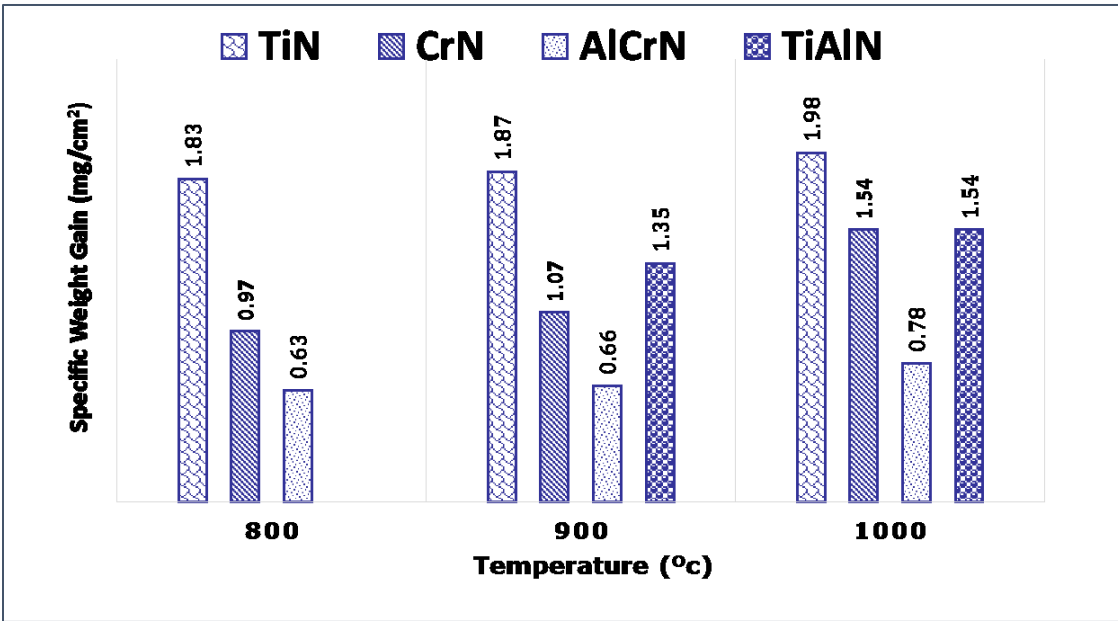


Figure 6-24: Weight gain after oxidation at different temperatures for 5 hrs.

6.2 Effect of Vacuum Annealing on the Corrosion Behavior of Cathodic Arc CrAlN and TiAlN Coatings

6.2.1 Surface characterization of as-deposited and annealed coatings

The coatings surface morphologies are shown in Figure 6-25(a-b) exhibiting similar morphology as typical CA-PVD coatings. Characteristic surface defects including micrometer sized droplets (macroparticles), shallow micrometer sized craters (pits) and shallow micrometer sized protrusions, as classified by Harlin et al. [196], can be observed. Macroparticles were significantly higher in CrAlN as compared to TiAlN while micro sized craters are higher in TiAlN coating. The origin of these defects is inherent in the deposition process where molten metal droplets solidify en route from the target to the substrate often due to the low melting point elements via stationary and quasi-stationary processes or explosive emission [172,173]. Boxman and Goldsmith et al. [172] described the comprehensively the theory of defects on CA-PVD coatings and its generation, transport, effect on coating and control of macroparticles. The cross-sectional SEM images of the coatings are presented in Figure 6-26 (a-b). It shows the uniformity, thickness, and the dense and fine structure of the coatings. The cross-section images also show that the coatings are continuous and free from internal defects and that the observed defects shown in Figure 6-26 are limited to the surface. Average thickness and the chemical composition of the coatings are shown in Table 6-2. The non-stoichiometry formula of the coatings is $\text{Cr}_{0.34}\text{Al}_{0.67}$ and $\text{Ti}_{0.50}\text{Al}_{0.49}\text{N}$ while the weight ratios Cr/Al and Ti/Al are 1.12 and 1.73 in the coatings, respectively. From the roughness parameters shown in Table 6-3, it is obvious that CrAlN coating has higher surface roughness than TiAlN coating as also found by Chawla [167]. The higher roughness of CrAlN coating is obviously due to the large amount

of macroparticles which are consequent upon increase in droplets emitted from low melting Al element. Ding et al. [68] found that increasing Al content increased the roughness of CA-PVD coatings. CrAlN (atomic ratio Al/Cr =1.74) contains 35 wt.% Al as compared to 26 wt.% of Al in TiAlN (atomic ratio Al/Ti =1) and similar roughness were also reported for both coatings with the same atomic ratios [68].

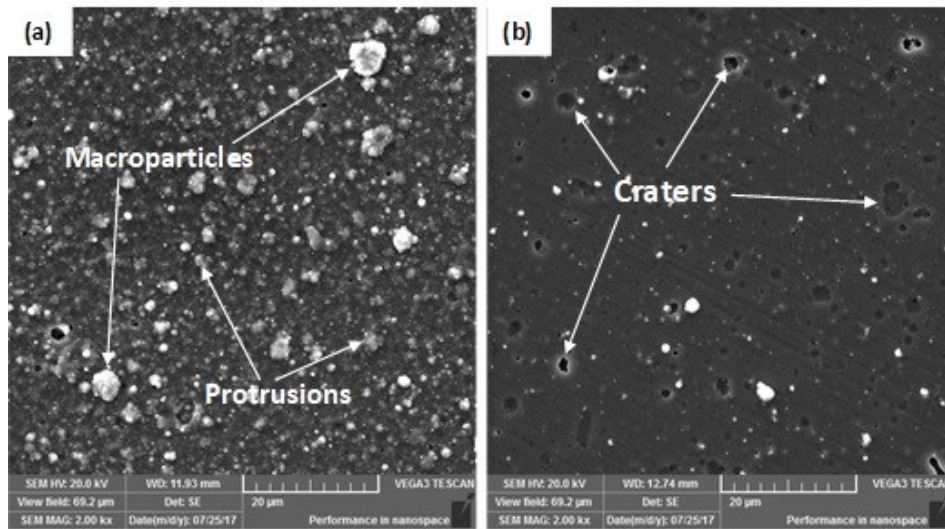


Figure 6-25: Surface morphology of as-deposited (a) CrAlN and (b) TiAlN coatings.

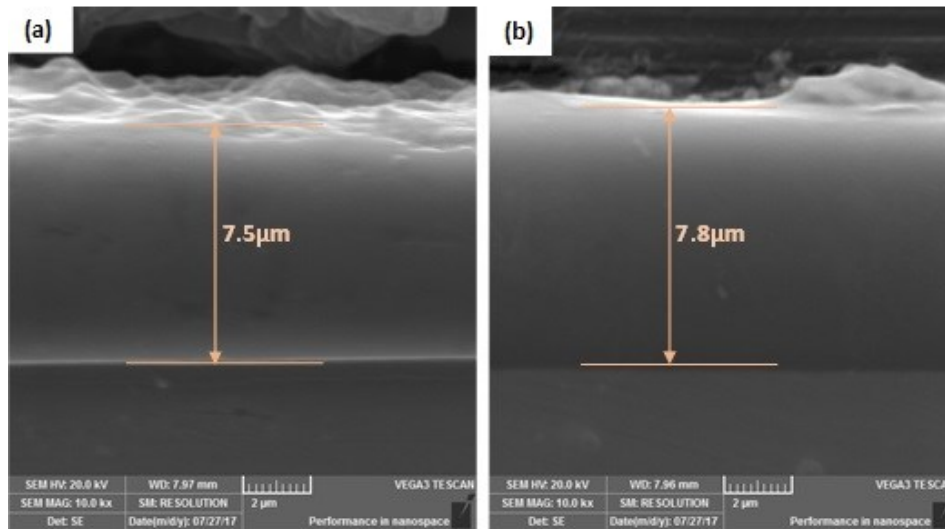


Figure 6-26: Cross section SEM images showing the thickness of as-deposited (a) CrAlN (b) TiAlN coatings.

Table 6-2: Chemical composition and thickness of as-deposited coatings.

Coating	N	Al	Cr	Ti	Thickness (μm)
CrAlN	45.7	29.3	17		7.5 ± 0.5
TiAlN	50.2	25.2		24.6	7.8 ± 0.3

Figure 6-27 and Figure 6-28, respectively, show the surface morphologies of the CrAlN and TiAlN coating after annealing at different temperatures. No significant surface morphological alternation is observed between the annealed coatings in comparison to the as-deposited coating. However, the surface roughness differs as can be observed from surface roughness parameters in Table 6-3. CrAlN coatings annealed at 700, 800 and 900 °C exhibited similar R_a and RMS roughness values of 0.1 and 0.2 μm respectively as the as-deposited coating. However, after annealing at 1000 °C the surface roughness increased considerably to R_a and RMS values of 0.5 and 0.8 μm respectively. The roughness gradually increased with annealing temperature up to 900 °C in the case of TiAlN coatings but still marginally lower than the roughness of the as-deposited coating. However, after annealing temperature at 1000 °C, the R_a roughness increased by about 100% as compared to as-deposited and other annealed coatings. The increase in roughness at higher annealing temperature may be associated to coalescence of existing surface features and grains caused by increased mobility/diffusion thus forming larger crystallites with high peaks in between large valleys [197]. Others have attributed the increase to the process of recrystallization of the coating and formation of new crystals [198].

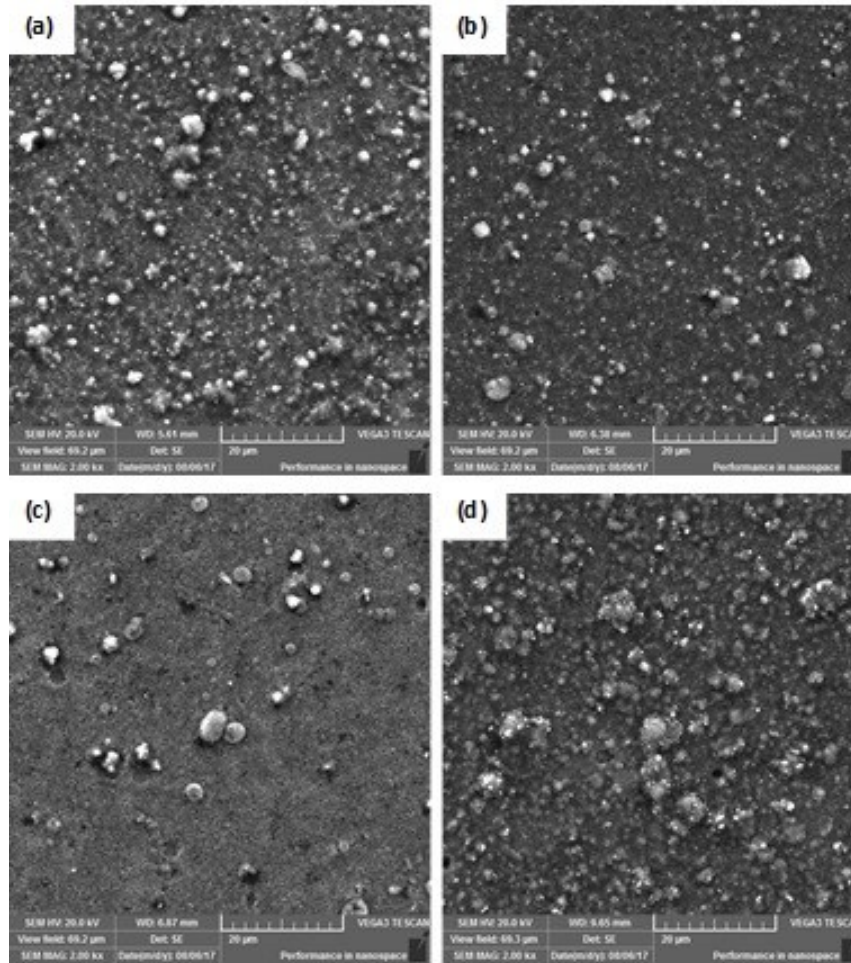


Figure 6-27: SEM surface morphology of CrAlN coatings annealed at (a) 700 °C (b) 800 °C (c) 9000 °C and (d) 1000 °C.

Table 6-3: Roughness parameters of as-deposited and annealed coatings.

Coatings	Parameters (µm)	Annealing Temperature (°C)				
		As-dep.	700	800	900	1000
CrAlN	R _a	0.11	0.12	0.11	0.14	0.52
	RMS	0.16	0.19	0.17	0.19	0.80
	PV	9.64	23.29	11.06	14.18	26.78
TiAlN	R _a	0.053	0.046	0.048	0.051	0.10
	RMS	0.086	0.074	0.074	0.075	0.14
	PV	6.89	6.56	6.15	4.82	7.19

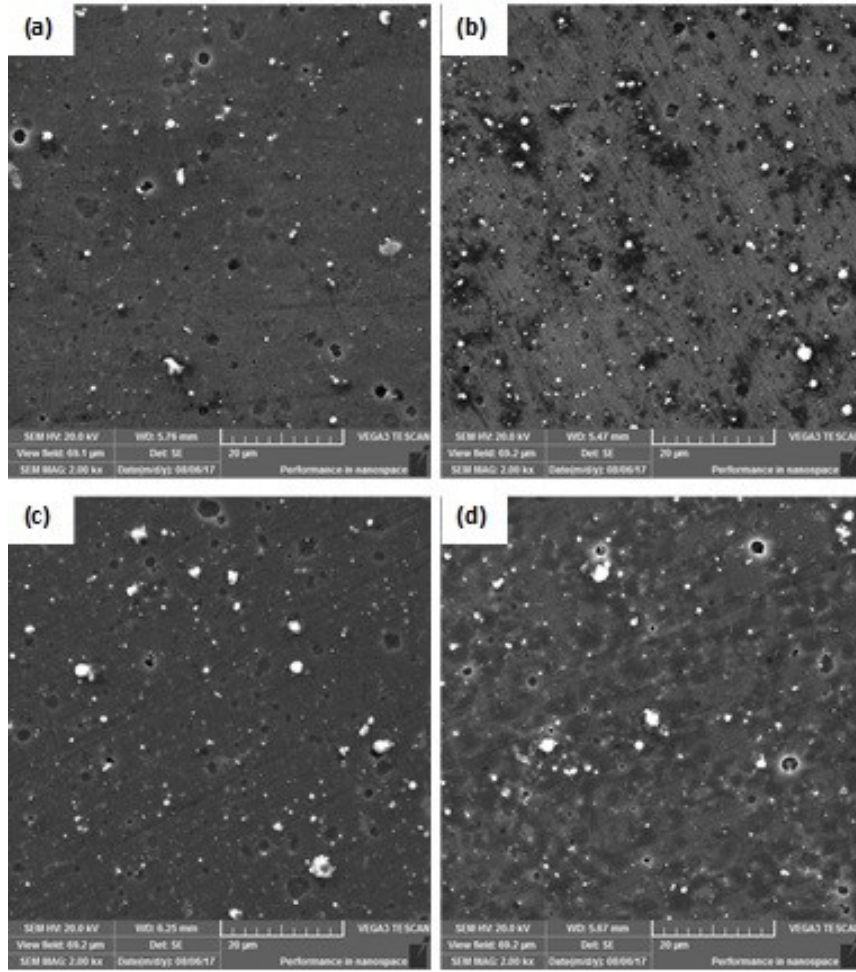


Figure 6-28: SEM surface morphology of TiAlN coatings annealed at (a) 700 °C (b) 800 °C (c) 9000 °C and (d) 1000 °C.

6.2.2 Characterization of as-deposited and annealed coatings

X-ray diffraction spectra of the coatings are shown in Figure 6-29. As-deposited CrAlN and TiAlN coatings crystallized into the B1-NaCl cubic structure with major diffraction peaks. Two major diffraction peaks of CrAlN as-deposited are identified at $2\theta = 37.8^\circ$ and 43.75° corresponding to the (111) and (200) planes [199]. The peaks were slightly shifted to higher diffraction angles after annealing to 800 °C which may indicate that there is a decrease in the lattice parameter caused by recovery and stress relaxation processes [98].

At 900 °C, these peaks were diminished and almost vanished while new peaks of c-CrN and c-AlN appeared [117]. This indicates that at 900 °C, the coating began to decompose. Further annealing to 1000 °C shows an increase in the intensity of the newly formed peaks in addition to the formation of h-AlN phase, which illustrates the complete formation of the new phases via segregation of the solid solution CrAlN. The major peaks for TiAlN as-deposited were detected at $2\theta = 37.2^\circ$ and 43.1° corresponding to (111) and (200) planes, respectively, as also reported in [40,200]. However, Solid solution decomposition began much earlier in TiAlN coating as can be observed with the formation of shoulder peaks for both c-TiN and c-AlN after annealing at 700 °C as shown in Figure 6-29 (TiAlN). Similar to CrAlN coating, the main peaks shifted to higher diffraction angle with annealing temperature in addition to decreasing crystallinity due to peak diminishing. At 900 °C the TiAlN peaks completely vanished while the peak intensity of c-TiN and c-AlN increased and h-AlN peaks were also detected. Interestingly, at 1000 °C, the peaks of c-TiN and c-AlN diminished again indicating further reduction in the crystallinity of the coating. The decomposition of TiAlN has also been reported at 700 °C [111,201].

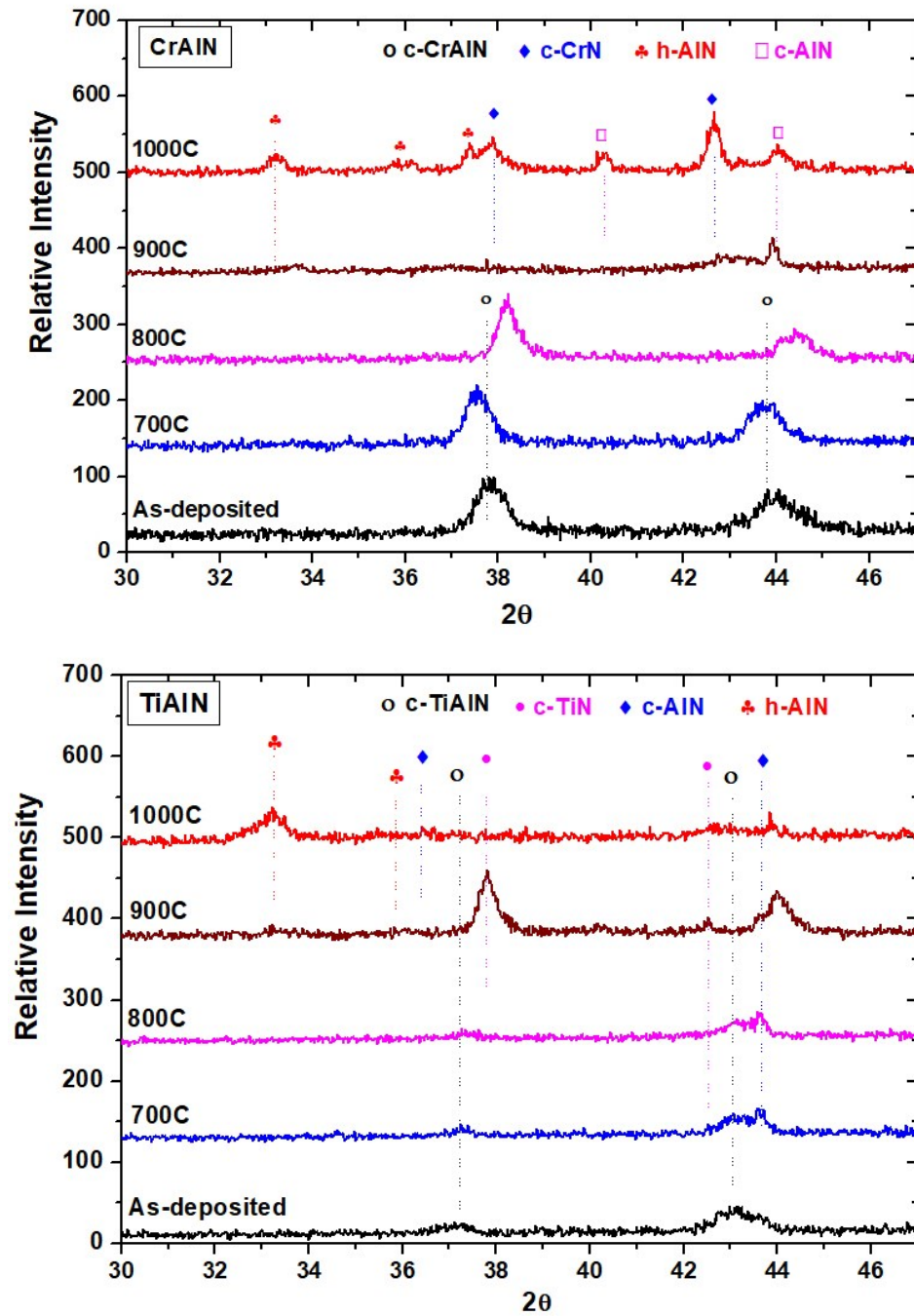


Figure 6-29: XRD spectra of the as-deposited and annealed coatings.

Figure 6-30 shows the room temperature mechanical properties of the coatings after various annealing temperatures. The hardness of the as-deposited CrAlN and TiAlN coatings are 33 ± 4 and 34 ± 4 GPa, respectively. CrAlN coating hardness decreased sharply with increase in the annealing temperature to 22 GPa at 900 °C, then slightly increased to 26 GPa after annealing at 1000 °C as shown in Figure 6-30 (a). The hardness at 700 and 800 °C are respectively 26.7 and 25.3 GPa. The sharp drop in the hardness is attributed to recovery and stress relaxation [98,117]. The slightly hardness increase after 1000 °C might be due partial recrystallization. The hardness of TiAlN coating increased with annealing temperature from 700 to 900 °C before decreasing at 1000 °C. At all annealing temperatures, TiAlN exhibited higher hardness as compared to CrAlN. The continuous increase in the hardness of TiAlN might be related to the early age hardening process via spinodal decomposition into c-TiN and c-AlN which does not occur in CrAlN coating [98,117,202]. However, with the growth of softer h-AlN phases at 1000 °C [202], the hardness dropped to 35 GPa which is still higher than the as-deposited coating. Figure 6-30 (b) shows the corresponding elastic modulus of the coatings. As-deposited and annealed coatings of CrAlN and TiAlN showed a typical elastic modulus for CA-PVD coatings which ranges between 400 to 500 ± 25 GPa as reported by Koller et al. [109]. The elastic modulus remains relatively constant at elevated annealing temperature because the crystallized phases such as AlN, CrN, TiN at such temperature possessed similar elastic modulus or higher [203,204]. Variant range of elastic modulus have also been reported depending whether it is filtered or non-filtered CA-PVD process [205,206].

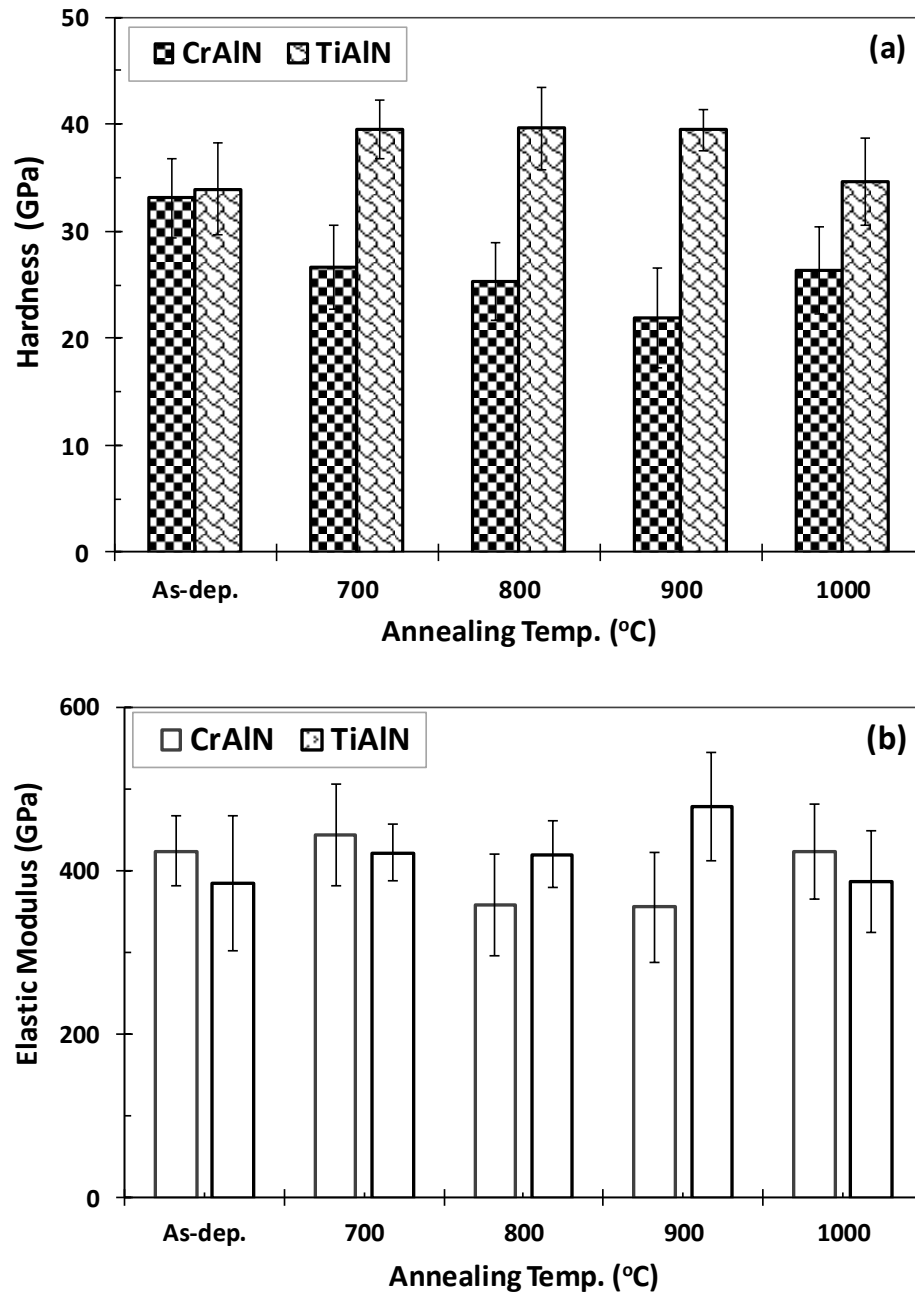


Figure 6-30: Mechanical properties (a) hardness and (b) elastic modulus of the as-deposited and annealed coatings.

6.2.3 Corrosion behavior of as-deposited and annealed coatings

6.2.3.1 Corrosion properties measurements

Measurement of the corrosion properties of the bare sample, as-deposited and annealed coatings was conducted using the EIS and PDP tests and the findings were comparatively evaluated. Figure 6-31 and Figure 6-32 show the EIS spectra in 1M HCl solution after 1hr immersion time for as-deposited and annealed CrAlN and TiAlN coatings, respectively, in comparison to the bare 304 SS. It can be observed that the bare sample revealed a single time constant behavior related to the capacitive nature of the double layer (C_{dl}) originating from the metallic corrosion. However, the as-deposited and annealed coatings exhibited a double time constants as can be noticed from the slight inflection and broadening at the low frequencies of the bode plots (Figure 6-31(a), (b) and Figure 6-32 (a), (b)) of the EIS spectra. This is expected to become more obvious if exposed for longer duration. CrAlN coating exhibited a continuous increase at low frequency in the Z_{mod} (Figure 6-31(a)) with annealing temperature while it decreased after attaining maximum value at 700 °C in TiAlN coating (Figure 6-32(a)). Figure 6-31(b) and Figure 6-32(b) revealed that the phase angles of as-deposited and annealed coatings are higher (above 80°) than the bare sample (about 60°) which showed that the coatings have strong capacitive response [207]. However, at 900 and 1000 °C annealing temperatures, the phase angle dropped indicating an effect in the dielectric properties of the coating and the coating became less capacitive. Nyquist plots shown in Figure 6-31(c) and Figure 6-32(c) depicted the significantly enlarged semi-circles of the as-deposited and annealed coating as compared to the bare (magnified and shown in the right top corner of Figure 6-31(c)). Localized inhomogeneity in the dielectric material resulting in frequency dispersion, surface roughness and porosity etc. are examples of

factors that can affect semicircle of the Nyquist plot [208]. It is thus important to use constant phase element (CPE) in the equivalent circuit to cater for surface heterogeneity which causes the surface to deviate from ideal dielectric material. The equivalent circuits shown in Figure 6-33 (a) and (b) were used to fit the EIS data of the bare and coatings, respectively. The circuits consist of CPE_{dl} , to accounts for the double layer surface properties of the metal at the metal/electrolyte interface (metal/coating interface in the case of coated samples), is connected in parallel with the charge transfer resistance R_{ct} , (which accounts for the resistance to ionic transfer at the coating/substrate interface in the case of coated samples), both are then arranged in series with the solution resistance R_s , (Figure 6-33). In addition to these elements, CPE_f , double layer capacitance of the coatings, pore resistance R_f which accounts for the coating resistance to porosity due to the ionic pathways through the coating and Warburg W elements were added to the equivalent circuit used to fit the coatings (Figure 6-33 (b)). These elements are typical in fitting the EIS data of PVD coatings [69,152] while the incorporation of W have been reported to improve the fitting accuracy [209]. The CPE is employed due to the inhomogeneous microscopic nature of the surface consisting of localized pits and charge heterogeneously distributed, two- and three-phase regions, adsorbed species and variation in compositions [210] and it is defined by $Z_{CPE} = Y_o^{-1} (j\omega)^{-n}$, where Z_{CPE} is the impedance of the CPE_{dl} , j is the imaginary number ($j^2 = -1$), ω is the angular frequency (in radian per second), Y_o is the frequency dependent proportionate parameters and n is also frequency dependent parameter that accounts for the surface roughness and defects which lead to the uniform distribution of the current at the interface [165,211].

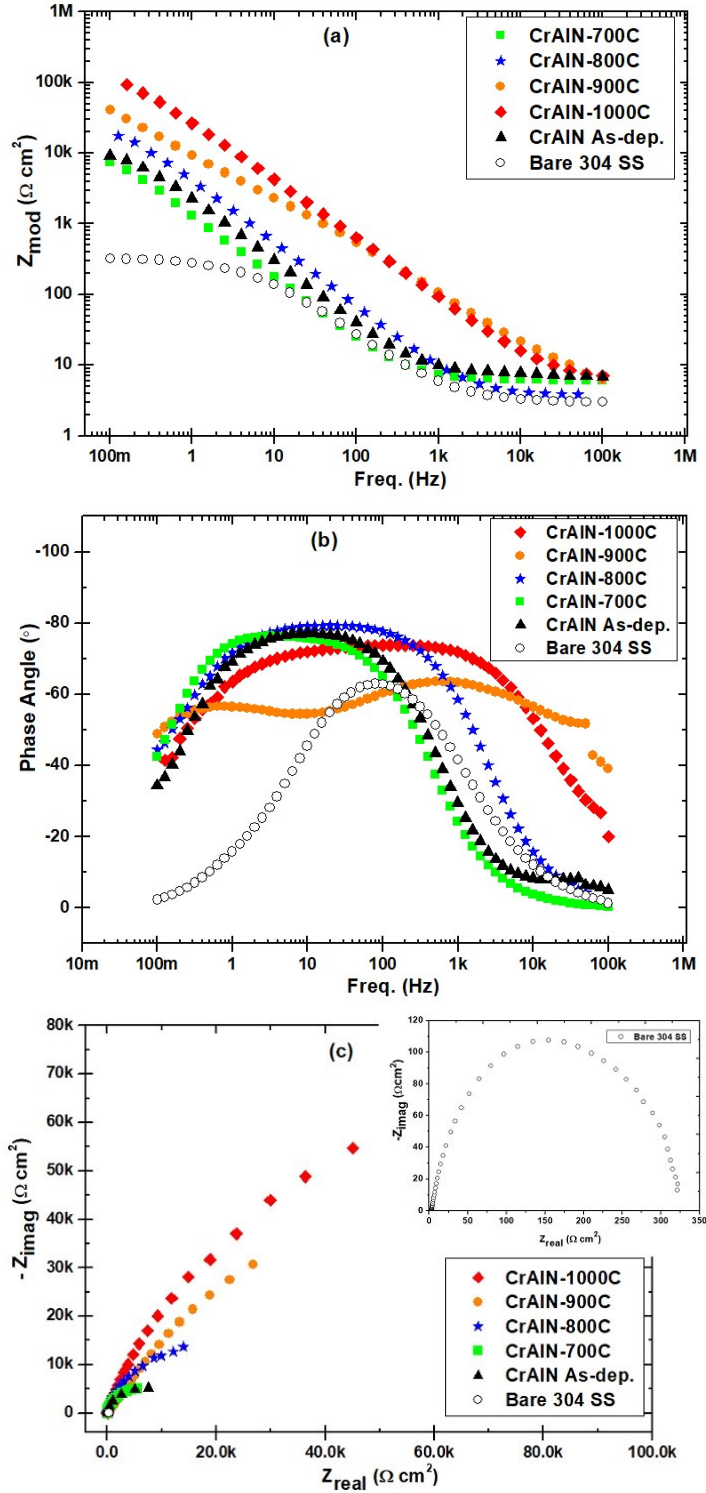


Figure 6-31: EIS spectra showing (a) modulus (b) phase angle and (c) nyquist plots for the as-deposited and annealed CrAlN coatings.

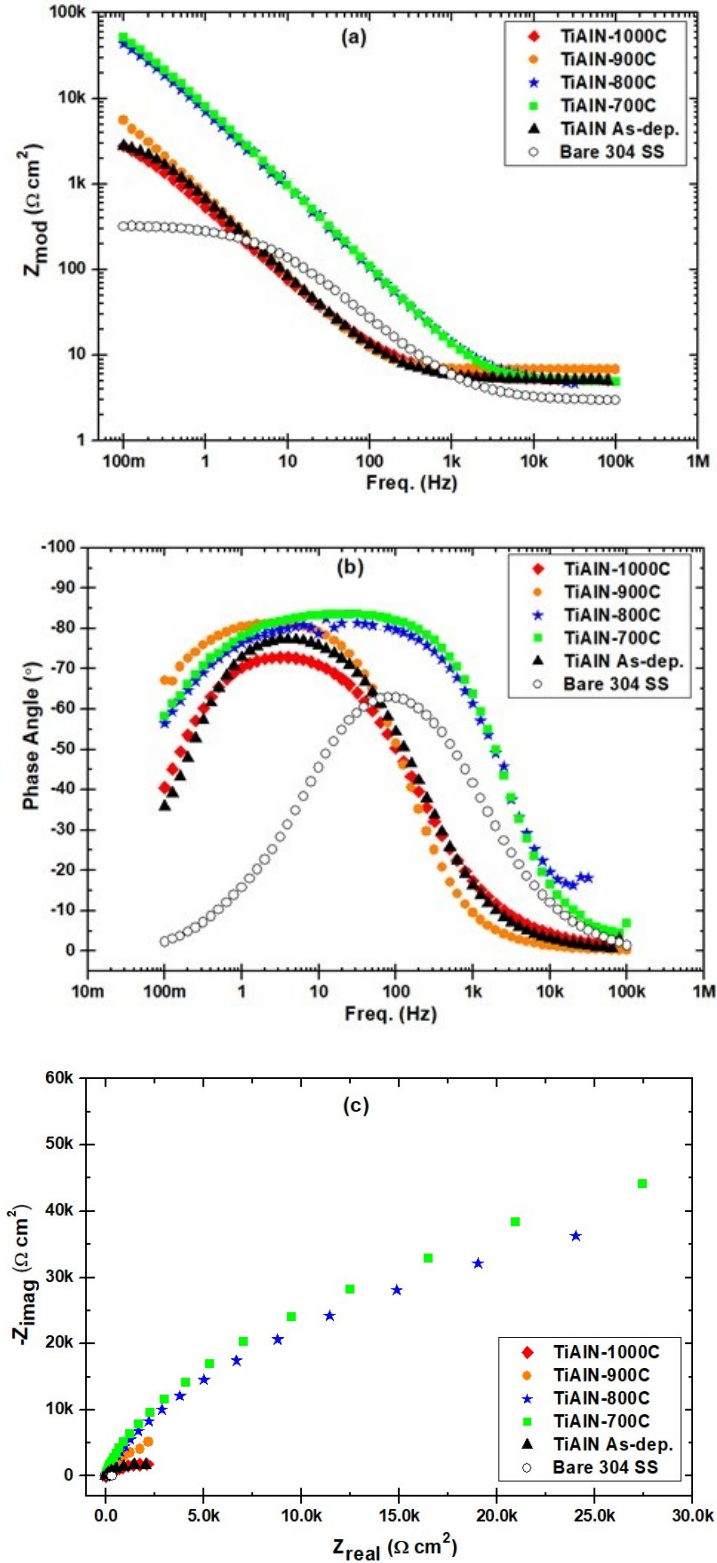


Figure 6-32: EIS spectra showing (a) modulus (b) phase angle and (c) nyquist plots for the as-deposited and annealed TiAlN coatings.

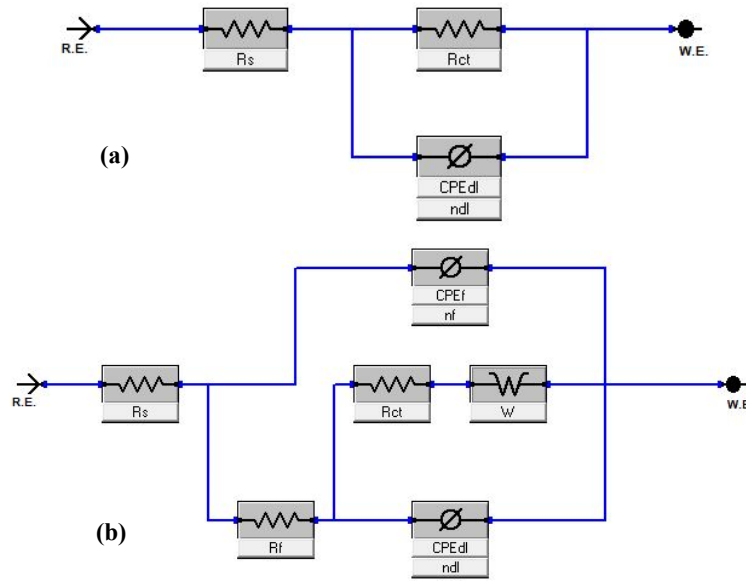


Figure 6-33: Equivalent circuit used in fitting the EIS curves for (a) bare and (b) coatings.

Optimum EIS parameters obtained from curve fitting is presented in Table 6-4 and Table 6-5 for CrAlN and TiAlN coatings, respectively. From Table 6-4 it is obvious that the R_{ct} values of as-deposited and annealed CrAlN coatings are greater than that of the bare and the value increased with increasing annealing temperature to the peak value of $156 \text{ k}\Omega\cdot\text{cm}^2$ at 1000°C . It also shows that the resistance R_f to electrolytic penetration via pores or pinholes present in the coating increased with annealing temperature and attained maximum value at 900°C . However, R_{ct} is of several orders of magnitude higher than R_f . Stress relaxation, recovery and formation of thin oxides layers could be responsible for the increasing charge transfer and pore resistances of the annealed coatings [117]. The EIS parameters for TiAlN coating as tabulated in Table 6-5 shows that the R_{ct} values for as-deposited and annealed coatings at all annealing temperatures were higher than the bare. However, the R_{ct} value dropped rapidly to 5.23 and $4.63 \text{ k}\Omega\cdot\text{cm}^2$ after annealing at 900 and 1000°C , respectively. Higher R_{ct} at 700 and 800°C can be attributed to the decomposition

of TiAlN into cubic TiN and metastable AlN phases which upon further annealing decomposes to stable h-AlN phase as observed from the XRD spectra (Figure 6-29). This spinodal decomposition as described in details by Johnson et al. [212] results in age-hardening of the coating and similar findings were reported for TiAlN annealed coatings by Chen et al. [111]. Further annealing at higher temperatures of 900 and 1000 °C decreased the corrosion resistance of the coating and similar trend is also observed in the PDP test.

Table 6-4: EIS parameters for the bare, as-deposited and annealed CrAlN coatings.

Samples	R_s (Ωcm^2)	R_{ct} ($\text{k}\Omega\text{cm}^2$)	Q_{dl} ($\mu/\text{cm}^2\text{s}^n\Omega$)	n_{dl}	R_f (Ωcm^2)	Q_f ($\mu/\text{cm}^2\text{s}^n\Omega$)	n_f	W (cm^{-2} $\sqrt{s}\Omega^{-1}$)	χ^2 ($\times 10^{-6}$)	E_{eis} (%)
Bare 304 SS	3.01	0.32	215.0	0.799	-	-	-	-	579	-
CrAlN-As-dep.	5.957	11.11	68.7	0.901	2.4	11.3	0.864	9.08E-4	99	97.12
CrAlN-700C	6.169	12.43	25.0	0.879	3.0	119	0.887	1.78E-1	264	97.43
CrAlN-800C	3.806	22.86	2.25	0.946	36.3	41.4	0.899	1.40E-4	94	98.60
CrAlN-900C	2.358	39.26	0.176	0.999	117.2	16.4	0.711	1.89E-5	1644	99.18
CrAlN-1000C	4.276	155.60	6.07	0.817	4.4	1.57	0.872	1.417	599	99.79

Table 6-5: EIS parameters for the bare, as-deposited and annealed TiAlN coatings.

Samples	R_s (Ωcm^2)	R_{ct} ($\text{k}\Omega\text{cm}^2$)	Q_{dl} ($\mu/\text{cm}^2\text{s}^n\Omega$)	n_{dl}	R_f (Ωcm^2)	Q_f ($\mu/\text{cm}^2\text{s}^n\Omega$)	n_f	W (cm^{-2} $\sqrt{s}\Omega^{-1}$)	χ^2 ($\times 10^{-6}$)	E_{eis} (%)
Bare 304 SS	3.01	0.32	215.0	0.799	-	-	-	-	579	-
TiAlN-As-dep.	5.192	3.58	89.50	0.898	16.5	183	0.920	3.03E-3	362	91.06
TiAlN-700C	4.812	62.10	6.26	0.971	1.9	15.10	0.925	2.42E-5	145	99.48
TiAlN-800C	3.266	58.80	14.6	0.952	3.5	10.70	0.853	3.03E-5	3350	99.46
TiAlN-900C	6.832	5.23	2150	0.613	4.6	246	0.933	1.57E-3	202	93.88
TiAlN-1000C	5.263	4.63	185	0.845	5.8	186	0.867	1.41E-1	210	93.08

Figure 6-34 and Figure 6-35 presents the PDP curves of bare, as-deposited and annealed coatings in 1 M HCl solution. As shown in Table 6-6 and Table 6-7 the corrosion density i_{corr} of as-deposited coatings is lower than that of the bare 304 SS. The i_{corr} is $2.22 \mu\text{A}/\text{cm}^2$ for CrAlN and $2.64 \mu\text{A}/\text{cm}^2$ for TiAlN, against $92 \mu\text{A}/\text{cm}^2$ for the bare, this indicates considerable protection with the coatings of about 98 and 97%, respectively. The i_{corr} of annealed CrAlN coating decreased with annealing temperature from $1.8 \mu\text{A}/\text{cm}^2$ at 700°C to $0.4 \mu\text{A}/\text{cm}^2$ at 1000°C . This trend agrees with the EIS results. Similarly, the corrosion resistance of annealed TiAlN coatings increased after annealing at 700 and 800°C with almost the same i_{corr} of approximately $0.1 \mu\text{A}/\text{cm}^2$. However, after annealing at 900 and 1000°C , the i_{corr} increased slightly to $0.186 \mu\text{A}/\text{cm}^2$ and then sharply to $3.75 \mu\text{A}/\text{cm}^2$, respectively. However, with higher annealing temperature of 900 and 1000°C , thermal migration of absorbed atoms, grain size coarsening and crystal clustering leading to the reduction in the amorphous phase have been attributed to cause the observed decrease in the corrosion resistance of TiAlN coating after annealing at 900°C [111].

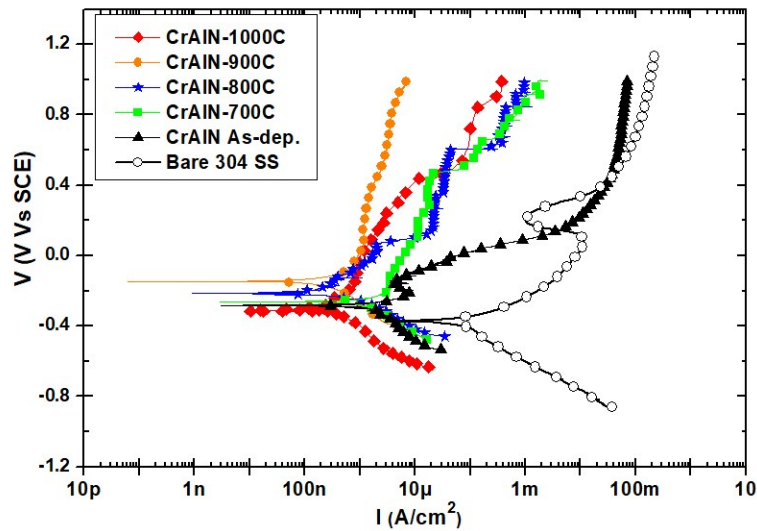


Figure 6-34: PDP curves of bare, as-deposited and annealed CrAlN coatings.

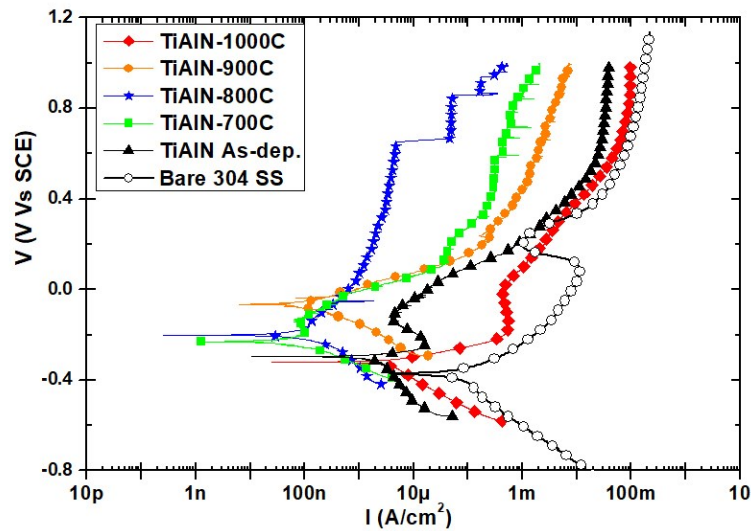


Figure 6-35: PDP curves of bare, as-deposited and annealed TiAlN coatings.

Table 6-6: PDP parameters for bare, as-deposited and annealed CrAlN coatings.

Samples	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	CR (mpy)	E_{pdp} (%)	P (%)
Bare 304 SS	-373	91.90	119.8	250.3	53.46	-	-
CrAlN-As-dep.	-282	2.220	85.9	344.6	0.85	97.58	0.501
CrAlN-700C	-262	1.790	139.3	255.7	0.68	98.05	0.305
CrAlN-800C	-206	0.614	322.6	165.6	0.23	99.33	0.056
CrAlN-900C	-146	0.507	275.1	325.9	0.19	99.45	0.010
CrAlN-1000C	-301	0.395	642.5	247.4	0.15	99.57	0.052

Table 6-7: PDP parameters for bare, as-deposited and annealed TiAlN coatings.

Samples	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	CR (mpy)	E_{pdp} (%)	P (%)
Bare 304 SS	-373	91.9	119.8	250.3	53.46	-	-
TiAlN-As-dep.	-296	2.64	45	398	1.008	97.13	2.025
TiAlN-700C	-230	0.119	340.9	105	0.045	99.87	0.033
TiAlN-800C	-201	0.114	242.9	83.2	0.044	99.88	0.020
TiAlN-900C	-63.9	0.186	91.4	125.3	0.071	99.80	0.016
TiAlN-1000C	-320	3.75	45	163.6	1.430	95.92	2.495

6.2.3.2 Porosity and corroded surface of as-deposited and annealed coatings

Porosity P in ceramic PVD coatings is defined as the fraction of the substrate surface exposed to the electrolyte [213]. EIS is a systematic and informative tool in evaluating the porosity of PVD coatings and has been extensively examined by a number of researchers [214–217]. Porosity estimation is fundamentally based on the assumption that the coating is electrochemically inert at low anodic polarization and expressed as in Equation 6-2 [213], which can be approximated to the ratio of the current density at a fixed potential since the second term of Equation 6-2 is negligible.

$$P = \frac{i_{a,c-s}}{i_{a,s}} - \frac{K_c}{K_s} \exp \left[E \left(\frac{1}{\beta_{a,c}} - \frac{1}{\beta_{a,s}} \right) \right] \quad 6-2$$

Where $i_{a,c-s}$ and $i_{a,s}$ are respectively the corrosion densities of the coating-substrate system and the substrate, K_c and K_s are respectively the rate constants of the coating and substrate, and $\beta_{a,c}$ and $\beta_{a,s}$ are the anodic Tafel coefficients of the coating and substrate respectively. Thus, P can be estimated using the relation in Equation 6-3 [168,169,218]; a derivative of Equation 6-2.

$$P (\%) = \left[\left(\frac{R_{p,s}}{R_{p,c-s}} \right) \times 10^{-\left(\frac{|\Delta E_{corr}|}{\beta_{a,s}} \right)} \right] \times 100 \quad 6-3$$

Where $R_{p,s}$ and $R_{p,c-s}$ are the polarization resistance of the substrate and coating-substrate system respectively and ΔE_{corr} is the difference between the corrosion potentials. R_p represents the total polarization resistance which is the summation of the R_{ct} and R_f .

Figure 6-34 and Figure 6-35 presents the PDP curves of bare, as-deposited and annealed coatings in 1 M HCl solution. As shown in Table 6-6 and Table 6-7 the corrosion density

icorr of as-deposited coatings is lower than that of the bare 304 SS. The icorr is 2.22 $\mu\text{A}/\text{cm}^2$ for CrAlN and 2.64 $\mu\text{A}/\text{cm}^2$ for TiAlN, against 92 $\mu\text{A}/\text{cm}^2$ for the bare, this indicates considerable protection with the coatings of about 98 and 97%, respectively. The icorr of annealed CrAlN coating decreased with annealing temperature from 1.8 $\mu\text{A}/\text{cm}^2$ at 700 $^{\circ}\text{C}$ to 0.4 $\mu\text{A}/\text{cm}^2$ at 1000 $^{\circ}\text{C}$. This trend agrees with the EIS results. Similarly, the corrosion resistance of annealed TiAlN coatings increased after annealing at 700 and 800 $^{\circ}\text{C}$ with almost the same icorr of approximately 0.1 $\mu\text{A}/\text{cm}^2$. However, after annealing at 900 and 1000 $^{\circ}\text{C}$, the icorr increased slightly to 0.186 $\mu\text{A}/\text{cm}^2$ and then sharply to 3.75 $\mu\text{A}/\text{cm}^2$, respectively. However, with higher annealing temperature of 900 and 1000 $^{\circ}\text{C}$, thermal migration of absorbed atoms, grain size coarsening and crystal clustering leading to the reduction in the amorphous phase have been attributed to cause the observed decrease in the corrosion resistance of TiAlN coating after annealing at 900 $^{\circ}\text{C}$ [111].

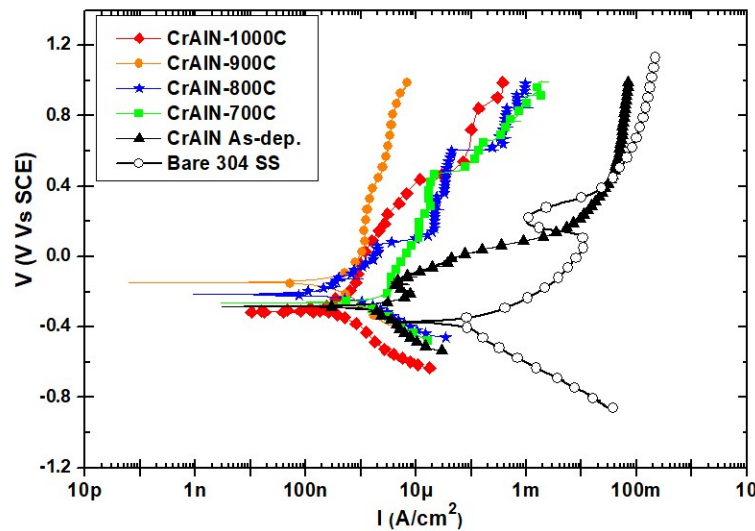


Figure 6-34: PDP curves of bare, as-deposited and annealed CrAlN coatings.

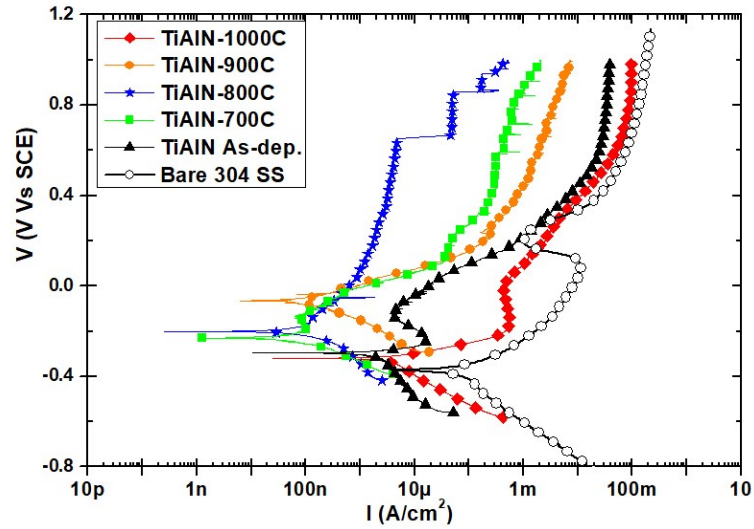


Figure 6-35: PDP curves of bare, as-deposited and annealed TiAlN coatings.

Table 6-6 and Table 6-7 also show the porosity of the as-deposited and annealed coatings. In both TiAlN and CrAlN coatings, it is obvious that the porosity decreased with increasing annealing temperature up to 900 °C. For CrAlN, the as-deposited coating porosity is 0.5% and after annealing at 700, 800, 900 and 1000 °C the porosity reduced by 39, 89, 98 and 90 %, respectively. It is noticed that there is slight rise in the porosity after annealing at 1000 °C in comparison to annealed coating at 900 °C. This can be related to the increased coating activity resulting from elevated annealing temperature as seen from the E_{corr} . As for TiAlN coating, the porosity of as-deposited coating is 0.36 % and after annealing at 700, 800 and 900 °C it reduced by 98, 99, and 99 %, respectively. This reduction in the porosity with annealing temperature might be attributed to increased ionic mobility which resulted in sealing off pores in the coating [111]. However, after annealing at 1000 °C, a sharp increase in the porosity is observed by about 23 %. This illustrates that structural changes in the coating at higher annealing temperature as depicted by the XRD analysis (Figure 6-29)

may result in enlargement and/or formation of new pores beyond the optimum annealing temperature.

The wide field SEM images of the area of the coatings exposed to 1M HCl solution are shown in Figure 6-36 and Figure 6-37 for CrAlN and TiAlN coatings, respectively. The as-deposited CrAlN coating (Figure 6-36 (a)) show severe corrosion attack and significant amount of pitting with over 90% of the exposed area pitted with different severity. The exposed of CrAlN annealed at 700 and 800 °C showed very few number of pits which can be seen in Figure 6-36 (b) and (c), respectively. For annealed coating at 900 and 1000 °C no pitting was observed but some changes in the coating surface as can be observed at 1000 °C as in Figure 6-36 (e) and (f). This alteration in the coating might be due the interaction of the corrosive HCl solution with different crystal phases as seen in the XRD spectra (Figure 6-29).

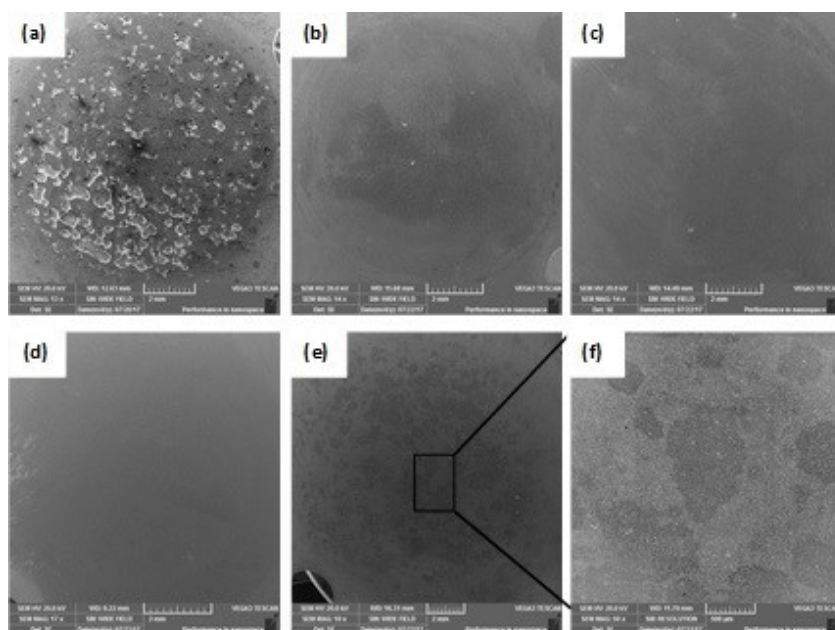


Figure 6-36: SEM wide field view of the exposed area to 1M HCl solution for CrAlN (a) as-deposited (b) 700 °C (c) 800 °C (d) 900 °C (e) & (f) 1000 °C.

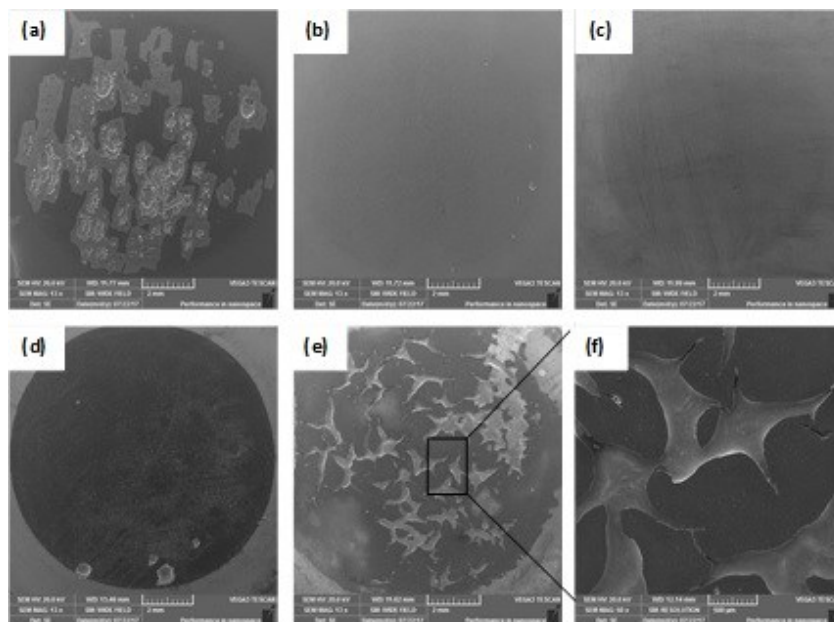


Figure 6-37: SEM wide field view of the exposed area to 1M HCl solution for TiAlN (a) as-deposited (b) 700 °C (c) 800 °C (d) 900 °C (e) & (f) 1000 °C.

In Figure 6-37(a) and (e), the wide field SEM image of as-deposited and annealed at 1000 °C TiAlN coatings are shown. Damages to the coatings are clearly apparent and it is more severe with TiAlN annealed at 1000 °C. For annealed coating at 700 and 900 °C, few pits were obvious on the exposed area while TiAlN annealed at 800 °C is pit free. This behavior is in accordance with the measured i_{corr} of both coatings. In Figure 6-38, porosity and corrosion current densities were plotted against the annealing temperature. It can be noticed that i_{corr} decreases with an attendant decrease in the porosity in both coatings. This illustrates that the corrosion resistance behavior of these coatings depends on the density of porosity in the coating. The i_{corr} of TiAlN annealed at 1000 °C sharply increase due to rapid increase in the porosity. The porosity of TiAlN diminishes with increasing annealing temperature to an optimum temperature of 900 °C, and similar findings have also been reported by Chen et al. [111]. However, the porosity of CrAlN coating after annealing at 800, 900

and 1000 °C are almost similar and one order of magnitude lower than the porosity of the as-deposited and annealed at 700 °C coatings.

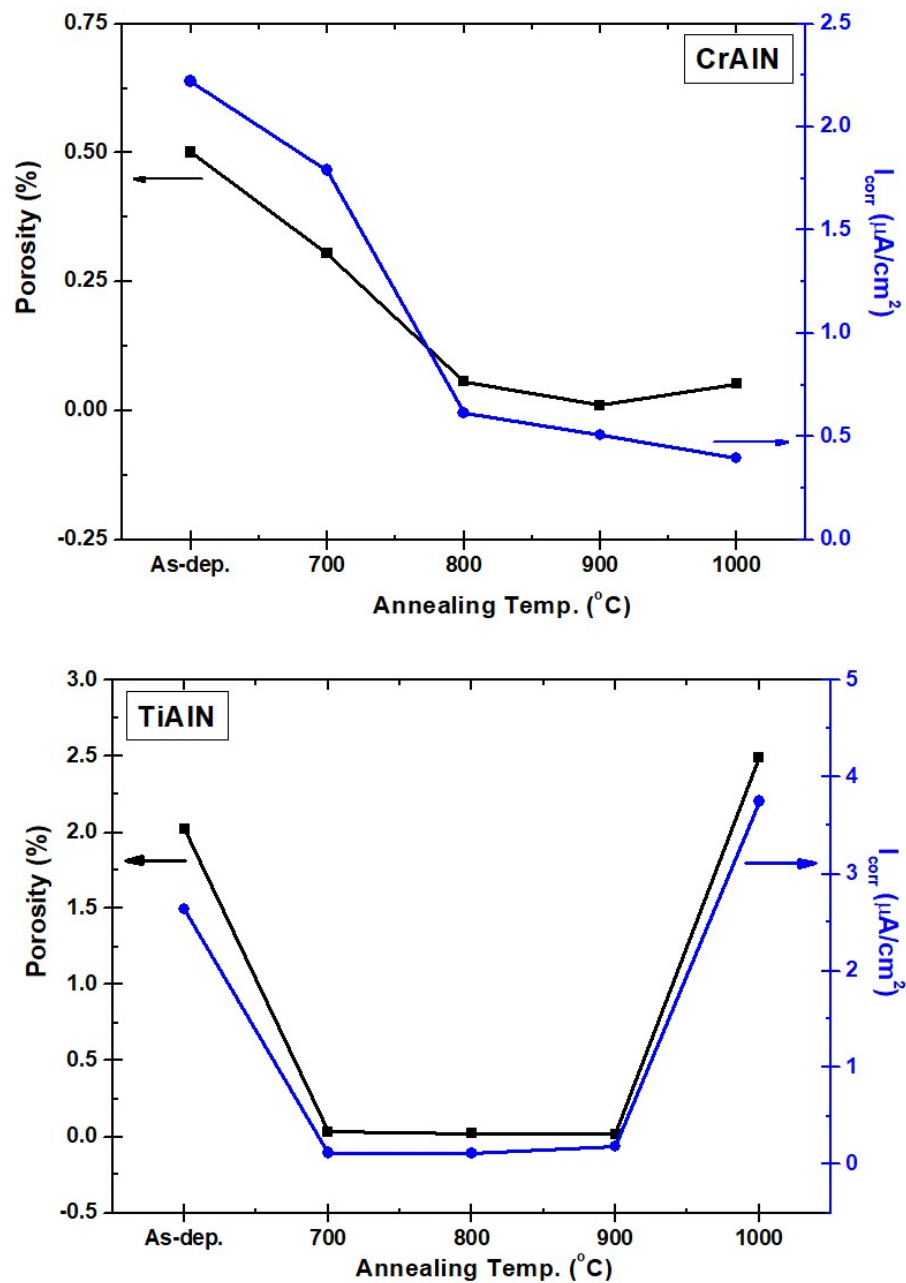


Figure 6-38: Porosity and corrosion current density variation with annealing temperature.

CHAPTER 7

EVALUATION OF AlCrN COATED FSW TOOL

In this chapter, the tribological performance of AlCrN coating was compared with newly developed FSW tool material, W-25%Re-HfC composite, for welding high strength materials such as steels and Ti alloys. Furthermore, preliminary FSW test using AlCrN coated steel tool on welding Al alloy was conducted. The wear resistance performance of the coated tool was compared with the uncoated tool.

7.1 AlCrN Coated W-25%Re-HfC Composite for FSW

Ball-on-disc wear and scratch tests were used to evaluate the tribological properties of the AlCrN coated W-25%Re-HfC. The mechanical properties and wear resistance behavior of the coated sample was compared with the uncoated sample. This investigation serves as preliminary study to illustrate the possible use of AlCrN coated composite tools to reduce tool wear during FSW of high strength materials.

7.1.1 Characterization of coated sample

The surface morphology of the as-deposited AlCrN coating on W-25%Re-HfC is shown in Figure 7-1. Micro particles and pore defects which are typical of cathodic arc PVD coatings can be observed. The roughness parameters of the coating as obtained from optical profilometer are presented in Table 7-1. The values of the arithmetic mean (R_a), root-mean-square (RMS) and the peak-to-valley (PV), presented in Table 7-1, show that the coating possessed low surface roughness.

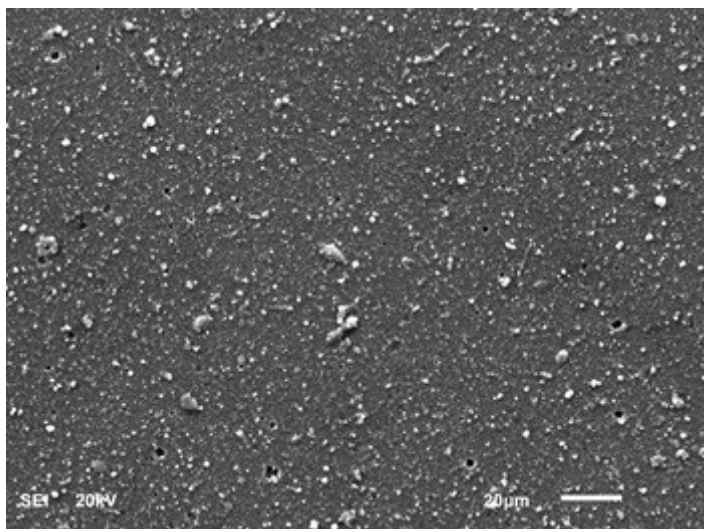


Figure 7-1: Surface morphology of the as-deposited AlCrN coating on W-Re-HfC substrate.

The elemental composition of the coating shown in Table 7-1 corresponds to a non-stoichiometric $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ coating with 1.77 Al/Cr ratio. This is similar to reported value elsewhere [153]. The XRD patterns of the substrate and coated sample are presented in Figure 7-2. The peaks of the W-Re alloy and HfC reinforcement were detected in the composite substrate material and they matched with JCPDS PDF No. 03-065-8387 and 00-039-1491, respectively. The XRD pattern of AlCrN coated sample indicate the presence of the substrate material though the peaks have been significantly depressed. The AlCrN coating crystallized into cubic CrN (00-011-0065) and cubic AlN structures with (111) and (200) strong peaks. These peaks correspond to the peaks of CrN with JCPDS PDF No. 00-011-0065 and of AlN with JCPDS PDF No. 00-046-1200. The estimated average grain size of the coating calculated based on the (111) and (200) peaks using the Scherrer equation is about 9.30 nm. Considering that the instrumental broadening and possible micro strain were not decomposed from the observed peaks, the calculated average grain size is the minimum grain size obtainable in the coating.

Table 7-1: Composition and surface properties of AlCrN-coated W-25%Re-HfC sample.

Coating Chemical Composition			
Elements	Al	Cr	N
Composition (at. %) (wt.%)	33.3 (35.4)	18.6 (38.1)	48.1 (26.5)
Surface Roughness			
Roughness parameters (μm)	R_a	RMS	PV
Values	0.15 ± 0.02	0.23 ± 0.01	8.85 ± 0.13

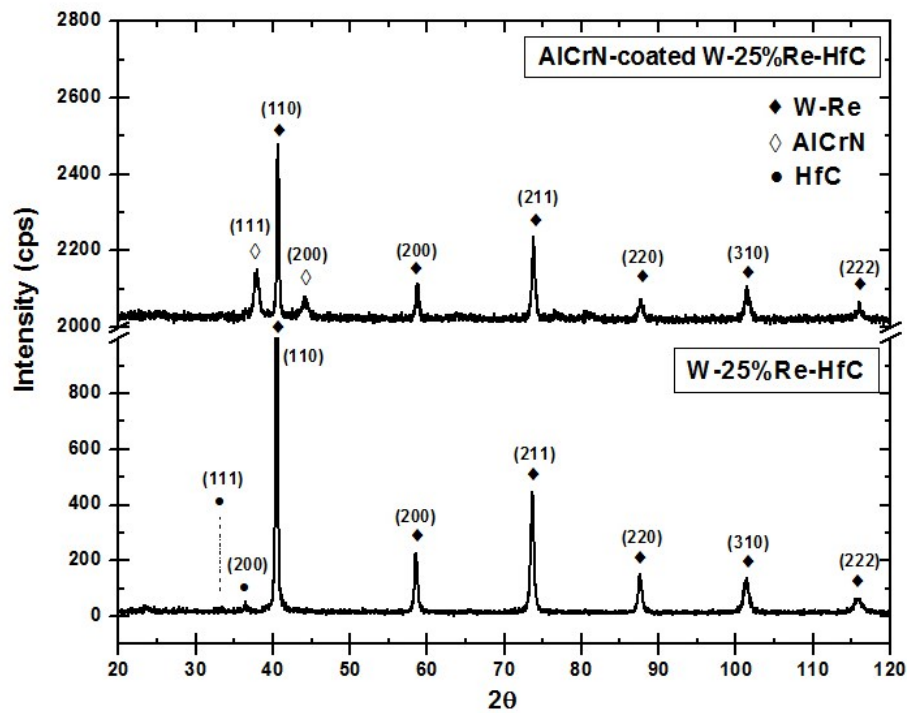


Figure 7-2: X-ray diffraction patterns of W-25%Re-HfC and AlCrN coated sample.

7.1.2 Micromechanical and scratch properties

Table 7-2 shows the micromechanical properties of the coated sample from an average of twelve measurements. The coating possessed higher hardness value as compared to the hardness values of the substrate material. The Vickers hardness value of the coating was 2563 HV_{2mN} against 717 HV_{2N} of the composite substrate. Wear resistance behavior of the coating can be described by the relationship between the hardness and elastic modulus. The

elastic strain to failure (H/E) and plasticity index (H^3/E^2) parameters are often used to index the wear resistance of coatings [178,179]. The coating in this study exhibited relatively high H/E and H^3/E^2 values of 0.1 and 0.3, respectively. These values were similar to that obtained from a previous study [153]. This confirms that the measured mechanical properties of the coating were not influenced by the substrate.

Table 7-2: Mechanical properties of AlCrN-coated W-25%Re-HfC sample.

Samples	Hardness (GPa)	Vickers (HV)	Elastic Modulus (GPa)	H/E	H^3/E^2 (GPa)
Uncoated W-25%Re-HfC	7.6 ± 0.2	717 ± 15	224.1 ± 4.3	0.034	0.0087
AlCrN Coated sample	27.2 ± 8.1	2563 ± 763	264.2 ± 54.6	0.101	0.306

Scratch test was used to determine the cohesion and adhesion strengths of the coating. Figure 7-3 shows the AE signal and the COF as a function of the applied normal load. The AE signal was used to estimate the cohesion force of the coating, denoted as L_{c1} , while the change in the COF was utilized to estimate the adhesion force, denoted as L_{c2} , as shown in Figure 7-3. The coating showed high cohesion and adhesion strengths of 9.5 and 25 N, respectively. This is an indication of the coating good adhesion to the composite tool material. The AE signal is suitable for detecting the initiation of crack within the coating by detecting the acoustic (elastic) waves radiated due to irreversible changes in the internal structure of the coating caused by a crack. This is reflected as a sudden increase in the AE signal as shown in Figure 7-3. The crack consequently increased as the applied load is increased until a sudden increase in the COF as illustrated in Figure 7-3 indicating a major failure in the coating. The COF is observed to be constant after the coating failure, this indicate a change in the counterface-substrate interaction.

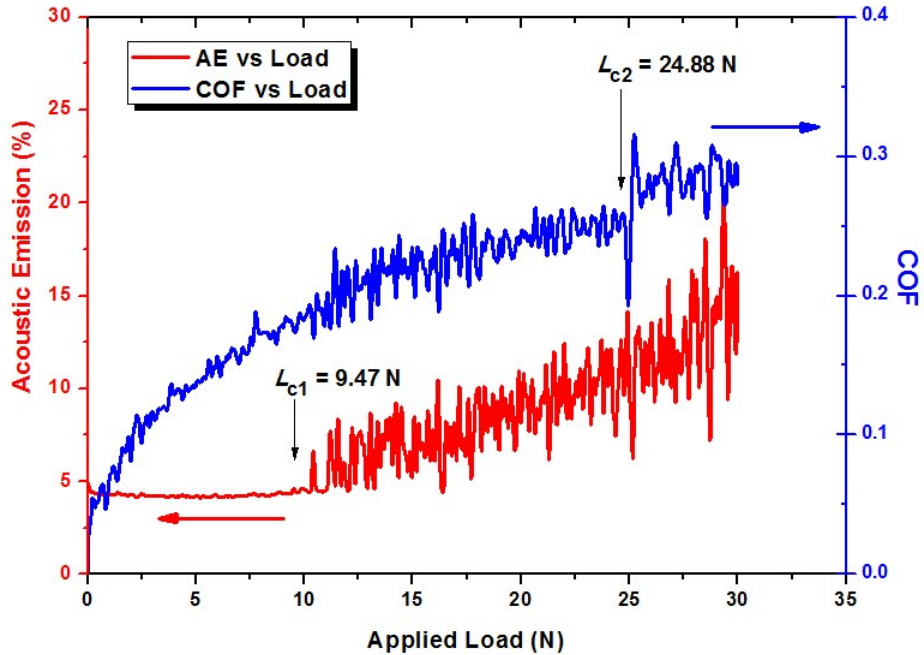


Figure 7-3: Scratch acoustic emission and COF as a function of the applied load.

Figure 7-4 shows optical images of the scratch track and the excerpts X and Y show the micrographs around the point of cohesive and adhesive failures, respectively. The failure mechanism shows recovery spallation behind the indenter at both sides of the track with very small coating chipping. It is observed that no delamination of the coating occurred inside the scratch track even up to the maximum applied load, rather, tensile crack failure was evident. Figure 7-5 shows the SEM image of the track and the compositional analysis within the track. It is interesting to note that the coating was present after the adhesive failure. This confirms that the mode of failure of the coating inside the track is not by delamination of the coating, rather the coating failure mechanism was tensile cracking and thinning. Thus, the coating combines between recovery spallation at the edges of the track and tensile cracking within the track. These failure modes are typical of PVD nitride coatings deposited on tough substrates and thus necessitate a high adhesion of the coating

as illustrated by Bull [189]. W-25%Re-HfC is a tough and easily machinable composite material and this can be observed from the large groove in the SEM image of the scratch track in Figure 7-5.

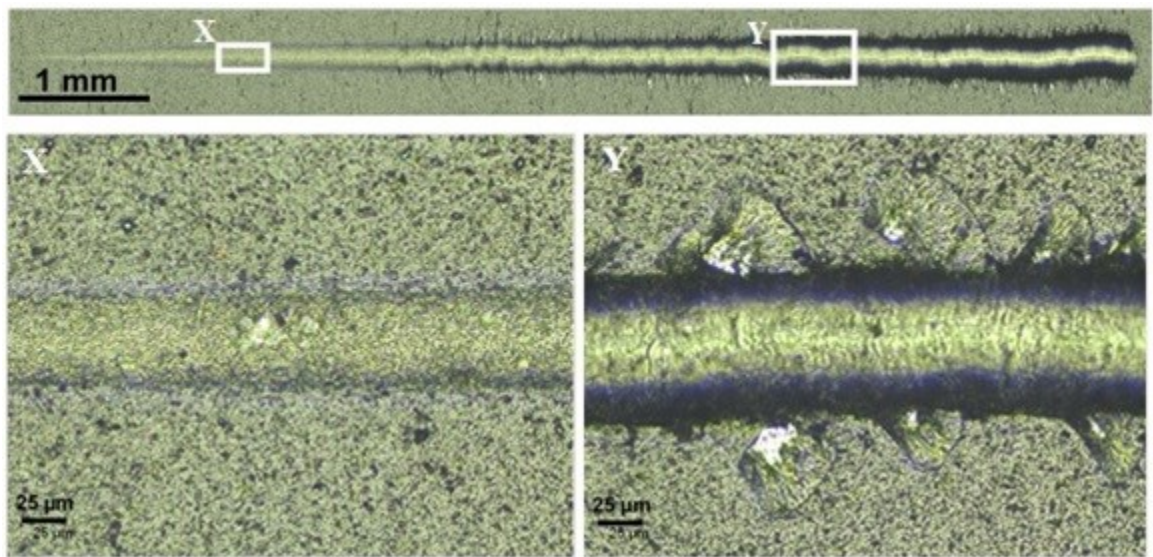


Figure 7-4: Optical micrographs of the scratch track and excerpts X and Y showing micrograph around cohesive and adhesive failures respectively.

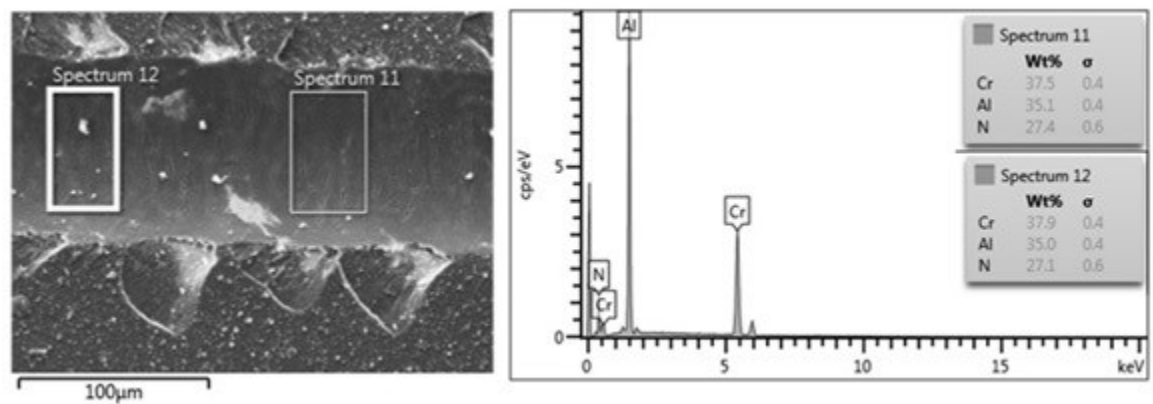


Figure 7-5: SEM images of the scratch track and the composition analysis of the track after adhesion failure.

7.1.3 Wear test analysis

Ball-on-disc wear test configuration was used for the wear resistance evaluation. The initial Hertzian contact pressure was about 1 GPa. High contact pressure is an advantage of ball-on-disc test configuration. However, after run-in the contact area is enlarged by wear thus reducing the contact pressure as the test progresses. Figure 7-6 shows the COF over the total sliding distance of 500 m. It is found that AlCrN coated sample exhibited lower COF, the curve is steadier and with minimal fluctuation compared to the uncoated sample. The COF of uncoated and coated samples in the steady state regime is about 0.68 and 0.47, respectively. The COF of the uncoated sample is over 30% higher during the steady state regime. High COF is undesirable as it results in significant wear of the materials.

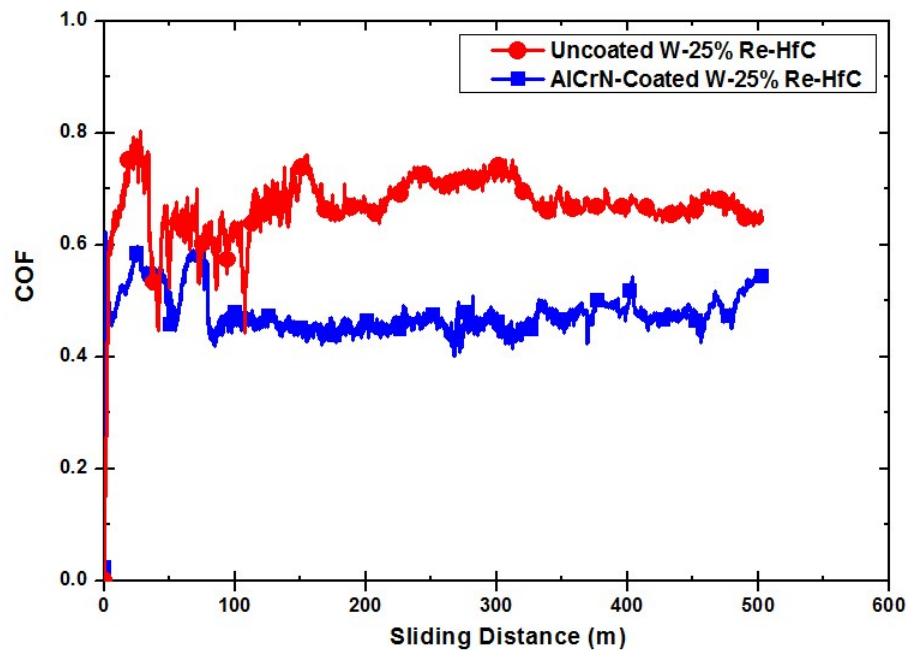


Figure 7-6: COF as a function of the sliding distance.

Figure 7-7 and Figure 7-8 respectively, show the 3D profilometer images and the depth profile across the wear track. It can be observed that the wear track of the coated sample is rougher as compared to the smooth wear track of the uncoated sample. This is an indication of the difference in the wear mechanism for the samples. Also, it can be observed that the wear volume differs significantly. The uncoated sample experienced high wear as compared to the coated sample. The maximum wear track depth of the coated sample was around $1.35\text{ }\mu\text{m}$, which is about 90% lower than the depth of the uncoated sample with a wear track depth of about $12\text{ }\mu\text{m}$. The depth profile indicates that the coating experienced very low wear and that the substrate was protected for the sliding distance considered. The corresponding volume of the wear track was estimated to be around 4.8 and $177.8\text{ }\mu\text{m}^3$ for coated and the uncoated samples, respectively. The contribution of the coating is obvious in reducing the volume of wear. Interestingly, the volume of material loss due to wear for the uncoated sample is 97% higher than that of the coated sample. The specific wear rate of the samples and the weight loss of the respective counterface steel ball are shown in Figure 7-9. AlCrN coated sample possessed lower wear rate of 42.83 mg/kNm compared to the uncoated sample with 443.33 mg/kNm specific wear rate. The use of the AlCrN coating resulted in the reduction in the wear rate of the composite material by about 90%. Similarly, the steel ball counterface against the coated sample was not severely worn as compared to the steel ball counterface against the uncoated composite sample. Figure 7-10 shows the worn ball surfaces and it is found the ball scar diameter is about 1 and 1.58 mm when used against coated and uncoated samples, respectively. The ball scar diameter against the uncoated sample is about 1.5 times larger than ball scar against the coated composite sample. This indicates that the interface between the ball and the uncoated

composite sample experienced higher plastic deformation required to overcome the high interfacial forces.

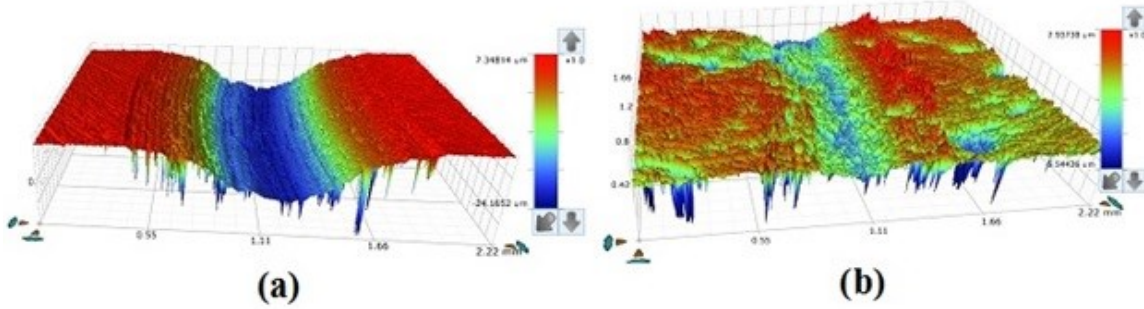


Figure 7-7: Optical 3D micrograph showing the wear track and wear depth of (a) uncoated W-25% Re-HfC and (b) AlCrN-coated W-25%Re-HfC.

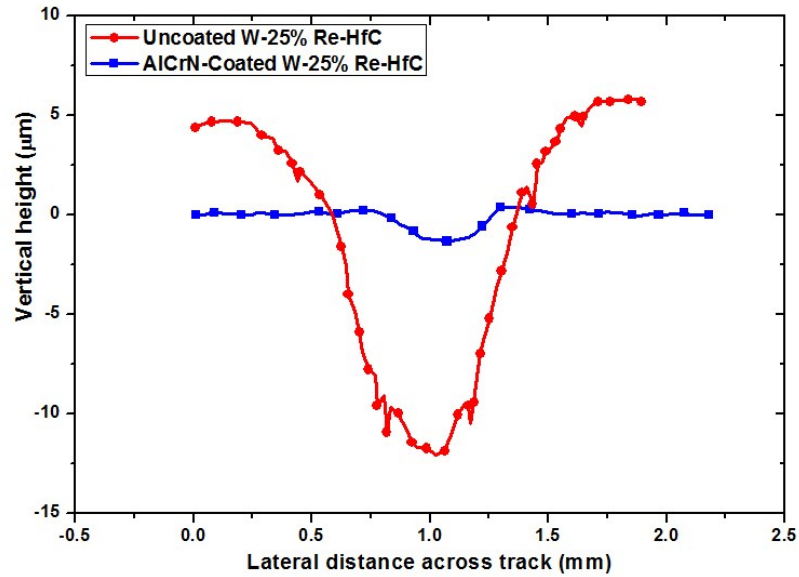


Figure 7-8: Wear track depth for the uncoated and coated samples.

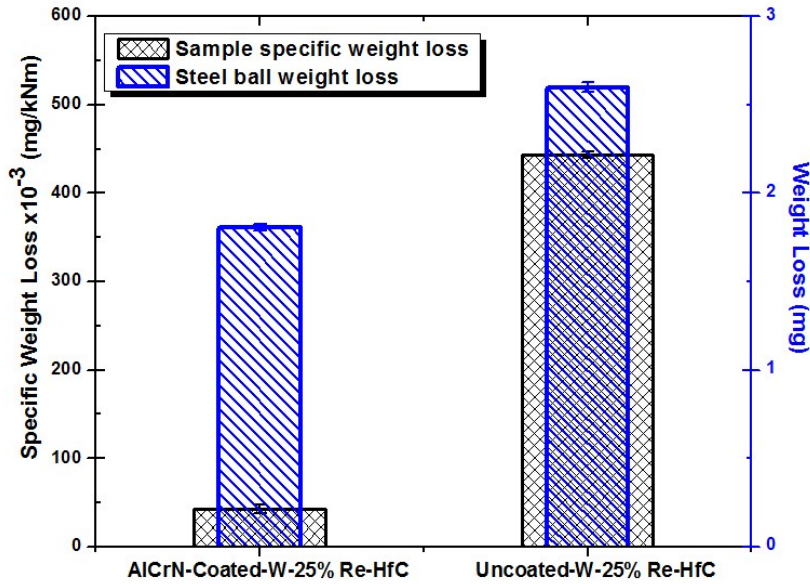


Figure 7-9: Specific weight loss for the samples and the ball counterface.

A close observation of the steel ball surface after wear test as seen in Figure 7-10(a) shows significant grooves along the sliding direction due to plastic deformation. This substantiates the fact that the wear mechanism of the uncoated sample is abrasive wear by plastic deformation. In this type of wear mechanism, the asperities undergo severe plastic deformation leading to subsurface strain hardening. This sequence is followed by plowing of the material resulting in wear through a series of grooves.

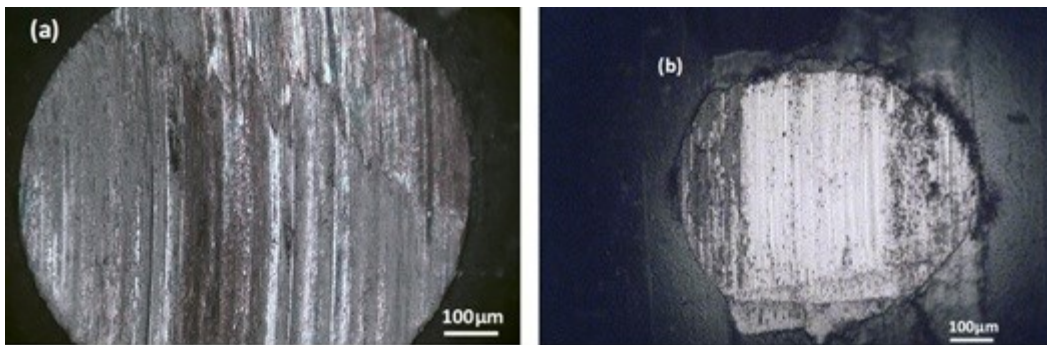


Figure 7-10: Optical images of the ball scar after wear test against (a) uncoated and (b) coated composite samples.

The magnified SEM micrograph of the wear track is shown in Figure 7-11 while Figure 7-12 shows the EDS analysis of the different section observed in the micrograph. It can be seen that there is formation of an oxidized layer with high composition of iron and chromium which are from the counterface steel ball. This oxide layer, as shown in the EDS spectrum, is basically oxides of iron and chromium. Fractured debris, due to low cycle fatigue, from oxidized layer can be seen in the wear track. EDS analysis of the exposed section revealed that coating is intact though oxidized. The oxidation of the coating is indicated by the reduction in the content of nitrogen in the coating from about 26 wt.% to 17 wt.%, and by the presence of significant amount of oxygen of about 10 wt.%. The content of Al and Cr in the wear track, 32 wt.% and 35 wt.%, respectively, is about the same amount as in the elemental composition of the coating. This suggests that the coating is intact and that it protected the substrate from severe wear. Al_2O_3 and Cr_2O_3 , which are typical oxides formed on AlCrN coating at high temperatures, are known for their excellent mechanical properties, good adhesion and high density thus making them very protective. Mo and Zhu [64] have also reported the formation of these oxides on AlCrN coating and its influence on the tribological properties during sliding. Thus, the wear mechanism of the coated sample is oxidation which is accompanied by low cycle fatigue thus led to fracturing of the oxide layer to form the observed debris.

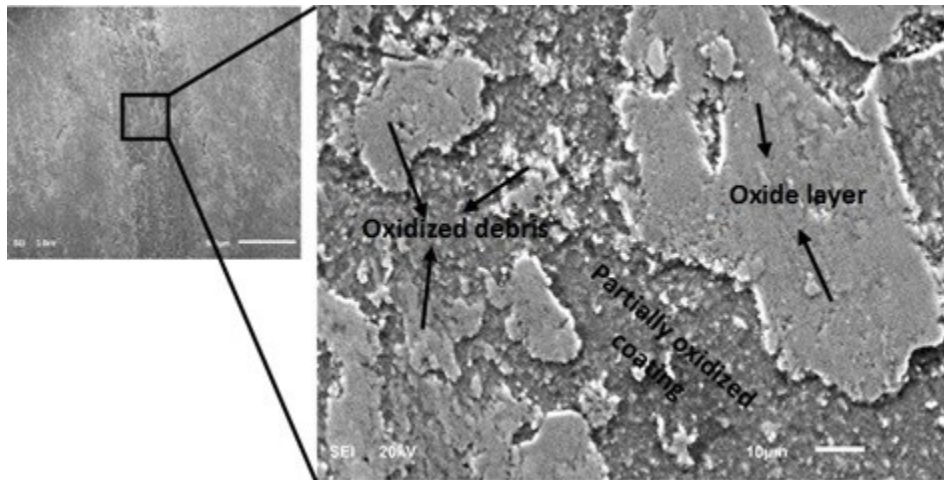


Figure 7-11: SEM micrograph of the wear track showing the oxide layer and wear debris.

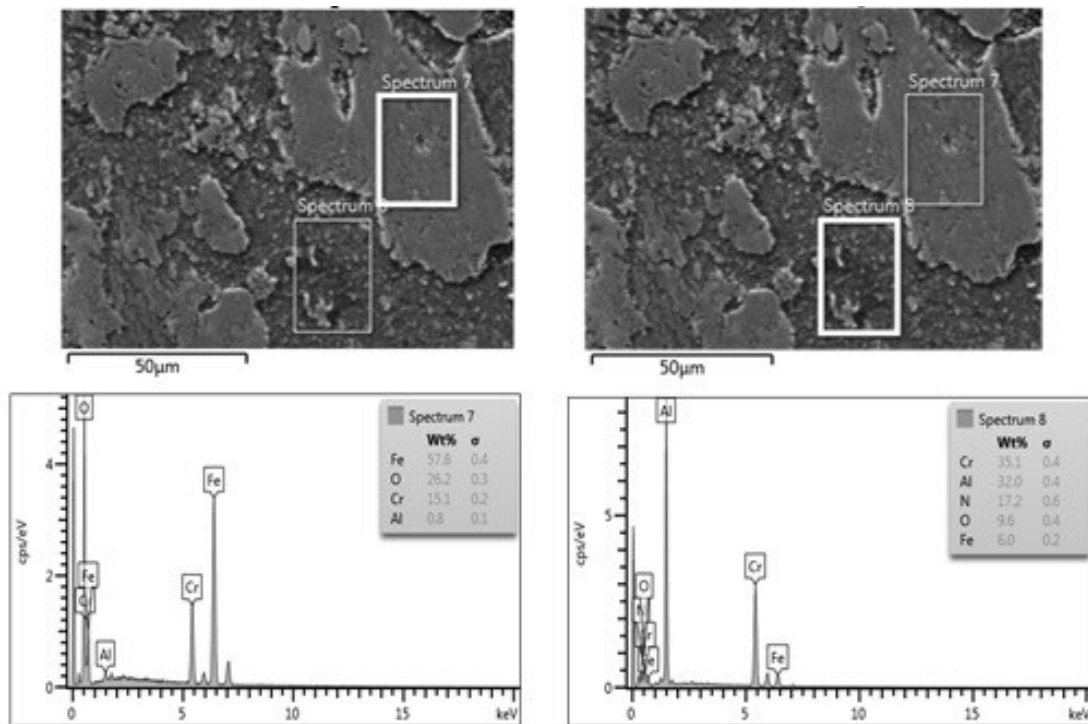


Figure 7-12: EDS analysis of the wear track of AlCrN coated sample showing the wear debris and wear mechanism.

7.2 AlCrN Coated FSW Tool for Welding Al-Alloy

Detail investigation of the preliminary FSW of A6061-T6 alloy using coated tools is presented in this section.

7.2.1 FSW tool design and coating characterization

PVD is a line-of-sight deposition process which makes it practically difficult to deposit PVD coatings on tools with complex geometry or features. Hence, a plain conical pin on a featureless shoulder is considered in this study. The dimension commonly recommended for the tool design is a shoulder to pin ratio of 3:1 and pin length of 0.85 - 0.95 of the thickness of the workpiece. Thus, the tool was manufactured with the following dimension; shoulder diameter of 18 mm, pin diameter is 6 mm at the root and 4 mm at the tip. The shoulder was concaved 2° towards the center to reduce dissipation of frictional heat. The schematic diagram of the tool with the dimension is shown in Figure 7-13. The workpiece was a 6 mm thick 6061-T6 aluminum alloy, thus the pin length was 5.6 mm. The FSW tool was hardened by water quenching and tempering heat treatment to 55-56 HRC hardness. However, the FSW tool to be coated was not tempered, it is expected that it will be tempered during the deposition process. After the coating process, the hardness of the uncoated shank of the tool was approximately 40 HRC.

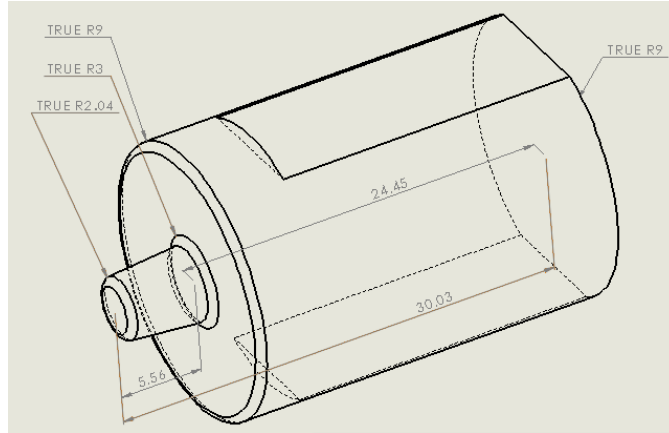


Figure 7-13: Geometry and dimensions of the designed FSW tool (all dimensions in mm).

Figure 7-14 shows the micrograph of the calotester crater from which the coating thickness was measured, while the cross-section SEM images in Figure 7-15 confirm the thickness to be approximately $5.6\mu\text{m}$. From the SEM image it is also observed that the coating is uniform, dense and continuous. The surface morphology of the coating is shown in Figure 7-16. The majority of the micro defects in the coating are less than $1\mu\text{m}$ in diameter as seen from the higher magnification image in Figure 7-16. With high plasma density, effective and efficient deposition of dense coating is attained with reduced micro particles. Micro particles are undesirable because they change the surface roughness and morphology of the coating thereby causing drawbacks such as sticking to workpiece, higher friction, localized coating failure and pitting corrosion [174,175]. The surface morphology, typical 3D profilometer image, of the coating is shown in Figure 7-17. The roughness of the coating is shown in Table 7-3. The low roughness of the coating is a direct result of the reduced micro particles and thus the coating is expected to proffer improved surface against high friction and sticking during FSW.

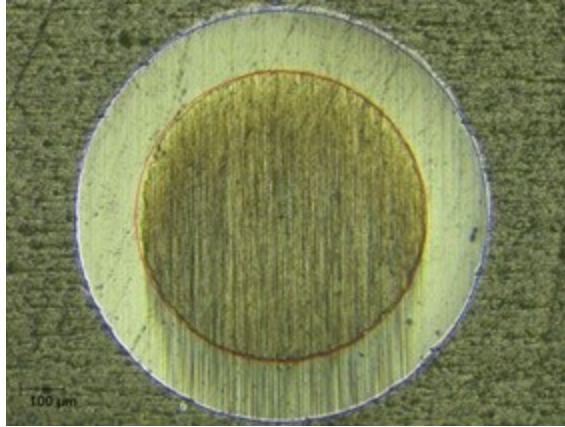


Figure 7-14: Typical crater image for thickness measurement using calotester; inner diameter = 649 μm , outsider diameter = 928 μm . Layer thickness = 6 μm .

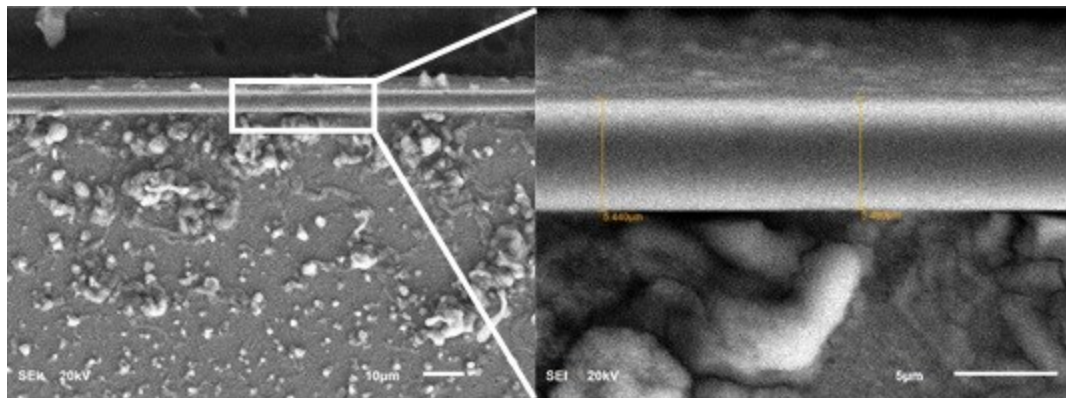


Figure 7-15: Cross section SEM images of AlCrN coating showing the thickness.

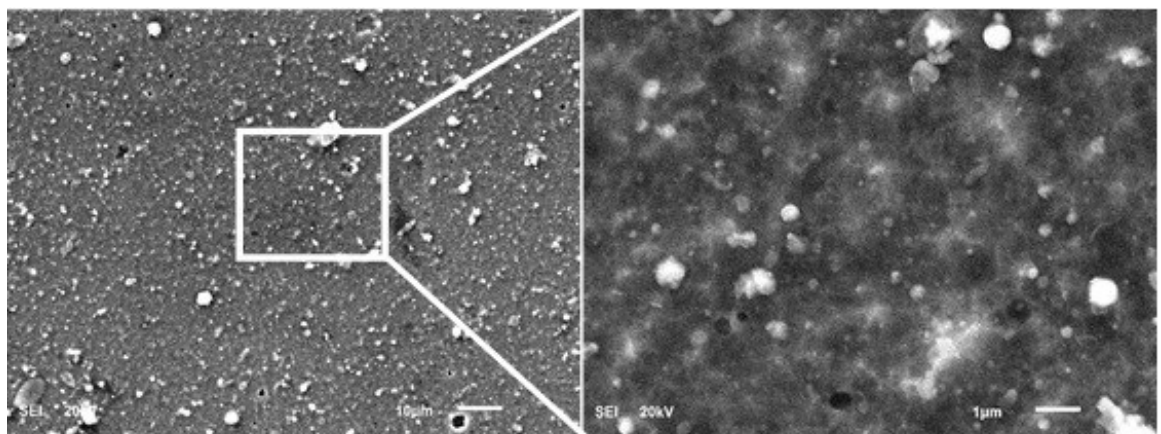


Figure 7-16: SEM images of the surface morphology of AlCrN coating.

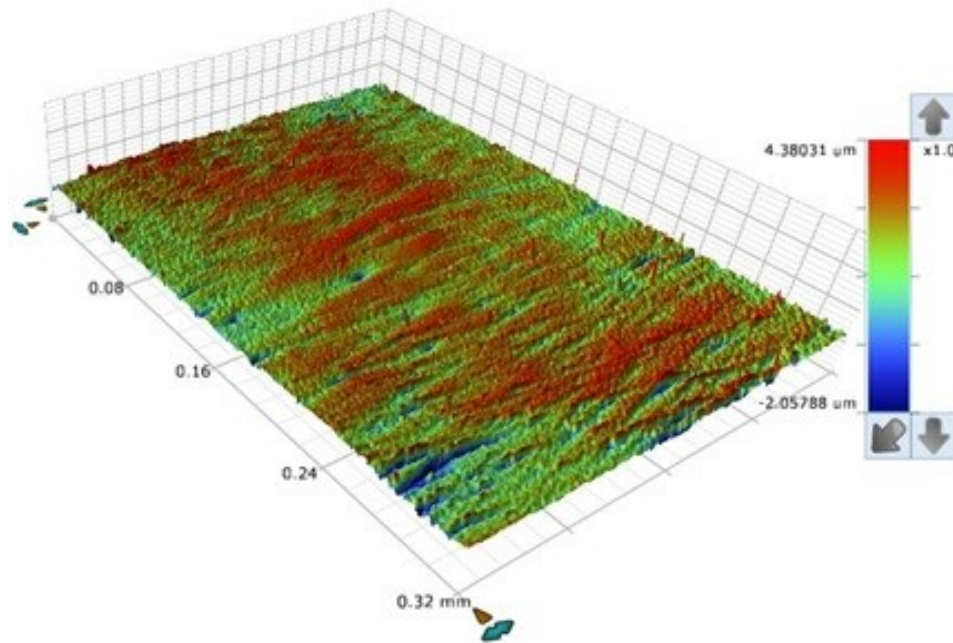


Figure 7-17: Surface morphology of AlCrN coating (Roughness parameters; $R_a = 97$ nm, RMS = $0.14 \mu\text{m}$, PV = $6.4 \mu\text{m}$).

Table 7-3: Mechanical properties, surface roughness parameters and chemical composition of the AlCrN coated 4140 FSW tool.

Mechanical Properties		Surface Roughness	
Hardness (GPa)	37.78 ± 7.57	R_a (nm)	98.47 ± 4.18
Elastic Modulus (GPa)	392.85 ± 108.70	RMS (μm)	0.140 ± 0.01
Coating Thickness (μm)	5.56 ± 0.05	PV (μm)	7.109 ± 1.79
Max. Penetration Depth (μm)	0.29 ± 0.02		
Coating Chemical Composition			
Elements	Al	Cr	N
Composition (at. %)	31.6	18.2	50.2

Elemental composition of the coating is shown in Table 7-3. The chemical composition corresponds to $\text{Al}_{0.63}\text{Cr}_{0.36}\text{N}$ with Al/Cr ratio of 1.75. As indicated in the XRD pattern shown in Figure 7-18; the coating crystallized into characteristic fcc-CrN and fcc-AlN

phases with strong (111) and (200) planes, respectively. This agrees with what was reported elsewhere [56,112,219]. The peaks of the fcc-AlN correspond to JCPDS card no 00-046-1200. Other reflections of CrN were also detected including (200), (220) and (311). These reflections for CrN correspond to JCPDS card no 00-011-0065 [220]. The diffraction pattern is preferentially oriented in the direction of (111) and (200) planes. Due to the coating thickness, peaks attributable to the substrate were not detected. The estimated average grain size from the Scherrer's equation using the (111) peak of CrN was about 12 nm. This value is only an indication of the size of the grains and should be considered as a lower limit since both micro-strain and instrumental broadening are not accounted for in the Scherrer's equation (Equation 4-1). The mechanical properties of the coating are summarized in Table 7-3. The hardness and elastic modulus are about 38 and 393 GPa, respectively. The hardness was measured at an average maximum penetration depth of 0.3 μm which is reasonably below one-tenth of the coating thickness so as to avoid the substrate effect. The high hardness of the coating can be associated with solid solution strengthening due to lattice distortion and densification of grain boundaries due to the nano-crystalline size of the coating [221].

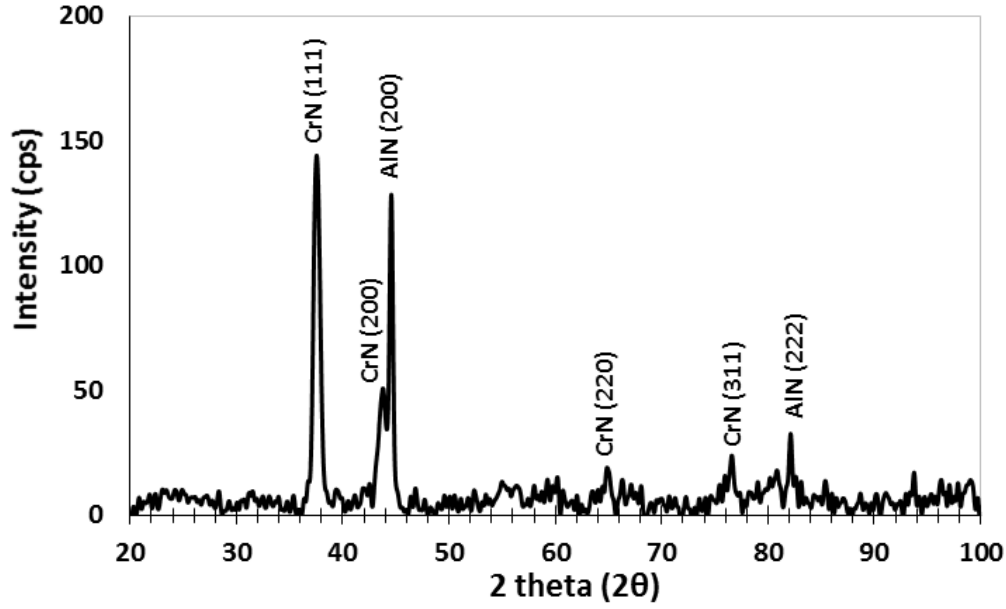


Figure 7-18: XRD pattern of AlCrN coating.

Figure 7-19 shows typical $F\mu$ and AE curves during the scratch test from which the critical loads were determined. The critical loads were determined by mutual observation of the penetration depth, optical images of the scratch track, $F\mu$ and AE curves. The critical loads as shown in Figure 7-20 indicated that the coating exhibited excellent cohesive (lower critical load L_{c1}) and adhesive (upper critical load L_{c2}) strength to the tune of 11 and 19 N, respectively. The coating possesses higher critical loads than those reported for TiAlN coating elsewhere [49]. The L_{c1} is related to the load at the initiation of crack within the coating while L_{c2} is related to the load at the complete delamination of the coating. The higher the values of both L_{c1} and L_{c2} , the more difficult for a crack to initiate and propagate to the interface before delamination of the coating occurs.

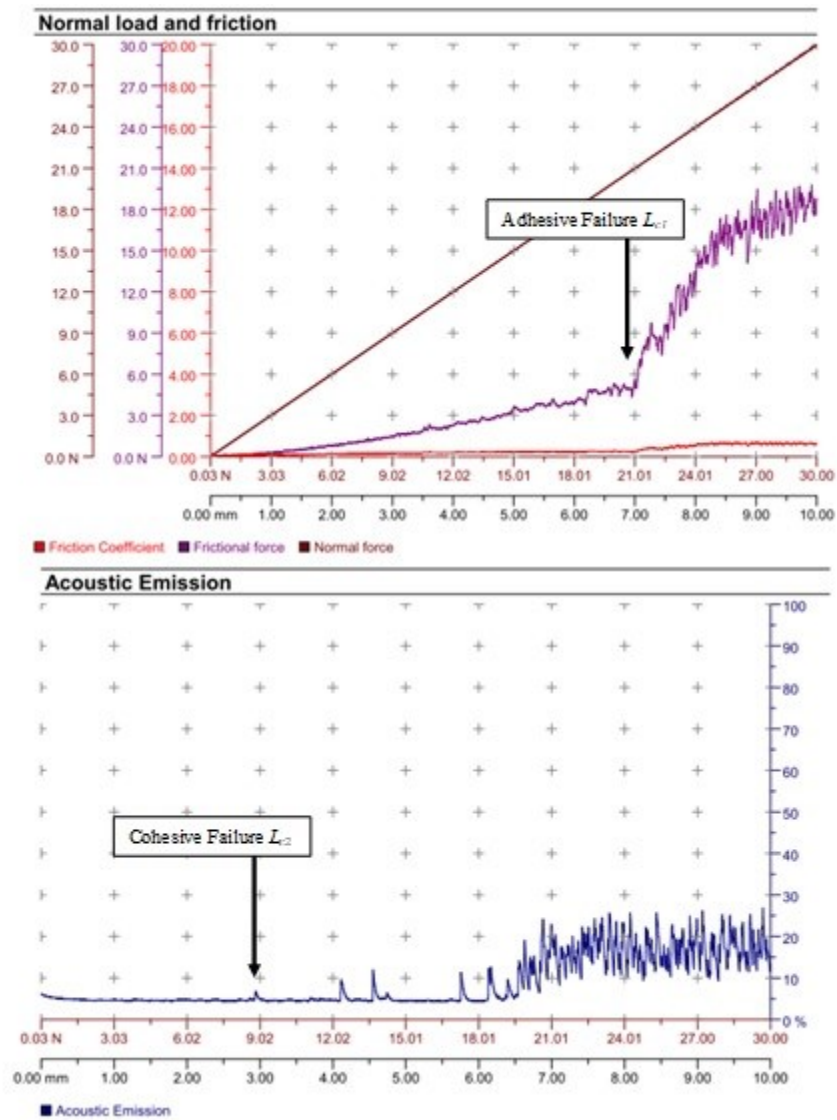


Figure 7-19: Typical friction and acoustic emission signals of the AlCrN coating during scratch test.

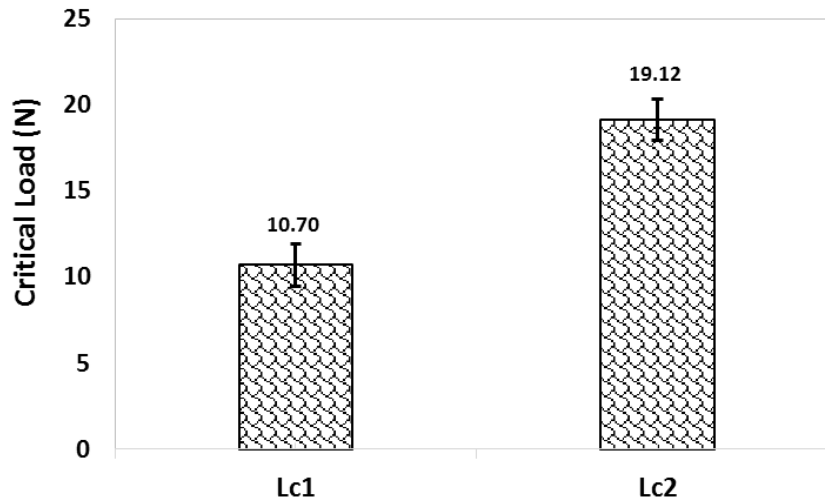


Figure 7-20: Measured critical loads of the AlCrN coating.

7.2.2 Wear and friction test

The COF curves are shown in Figure 7-21 as a function of the sliding distance for both the coated and uncoated samples. The uncoated sample was tested for a total of 500 m sliding distance. The COF is divided into the run-in and the steady-state wear regime. As observed in Figure 7-21, the run-in stage is characterized with sharp increase in the COF to about 0.6 in both cases. As for the uncoated sample the COF decreased significantly to about 0.4 within 100 m and then increased to about 0.68 for the rest of the sliding distance. However, the COF of the coated sample maintained a steady and regular increment during the entire steady-state regime attaining a COF of about 0.75. Although the COF of the coated sample is much higher than the uncoated sample, it is more stable, steady and less fluctuating. The specific wear rate for the coated and uncoated samples are presented in Figure 7-22. The weight loss of the coated and uncoated samples was 0.05 and 0.38 mg, respectively. The loss from the uncoated samples is about 87% higher than the coated samples despite that the wear test was conducted for a lesser sliding distance of 500 m. Consequently, the

specific wear rate follows a similar trend, the uncoated sample wear rate was 38×10^{-3} mg/kNm while that of the coated sample was 3.57×10^{-3} mg/kNm. It is interesting to note that the uncoated sample wear at a rate of about ten times the coated sample. The excellent mechanical properties of the coating, as illustrated in Table 7-3, in comparison to the properties of the uncoated hardened 4140 steel, is responsible for the remarkable wear resistance.

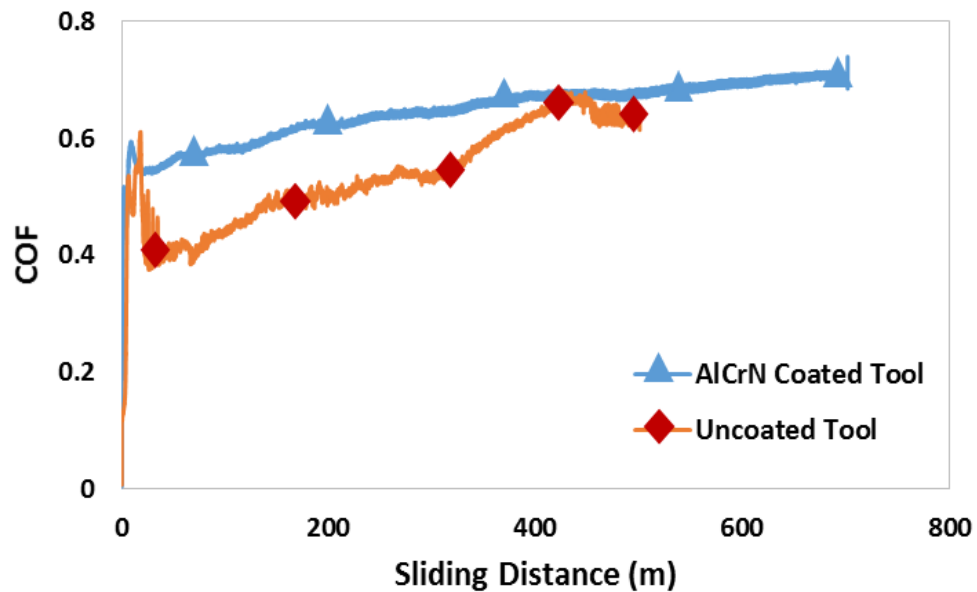


Figure 7-21: COF verses sliding distance curves.

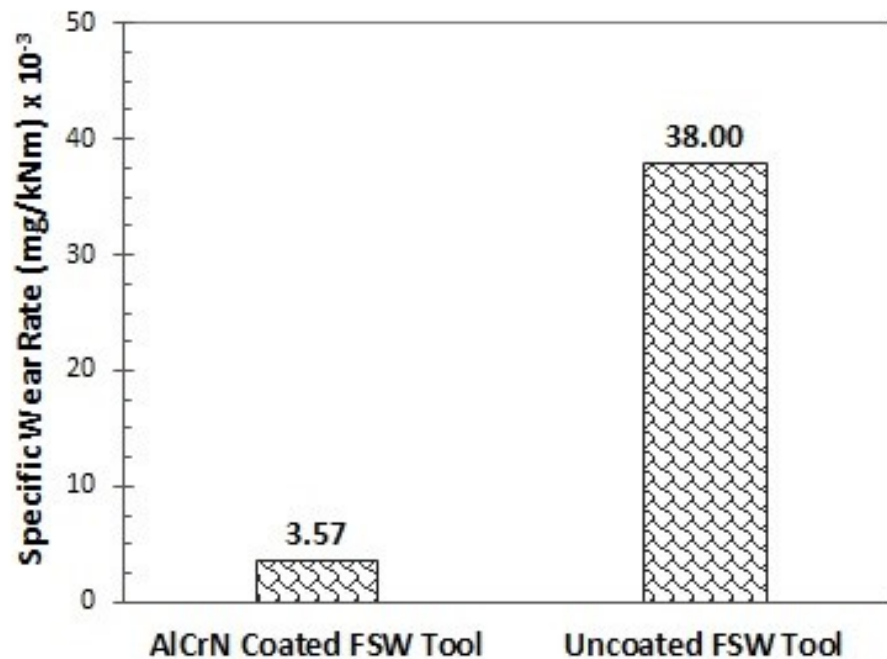


Figure 7-22: Specific wear rate of coated and uncoated FSW tool.

7.2.3 Weld quality of FSW test

Weld quality evaluation involves macrostructure and microstructure analysis as well as compositional characterization. Figure 7-23 shows typical bead-on-plate weld produced with the coated FSW tool. Each weld pass consisted of a plunge, 150 mm traverse length and a retraction. It is observed that both tools produced a full penetration bead on plate weld with no defects. The cross-section macrostructures of the welded region showing the nugget or dynamic recrystallized region and defect-free full penetration weld is shown in Figure 7-24.

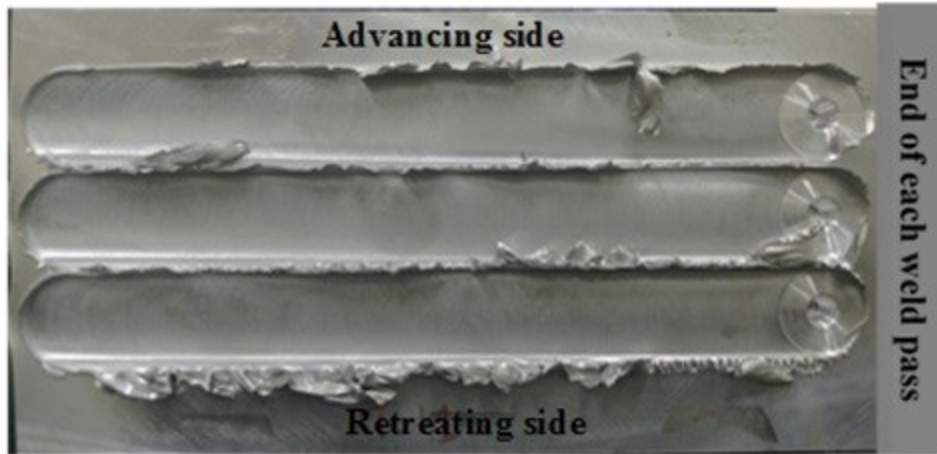


Figure 7-23: Weld conducted with AlCrN coated FSW tool showing the three passes and plunges.

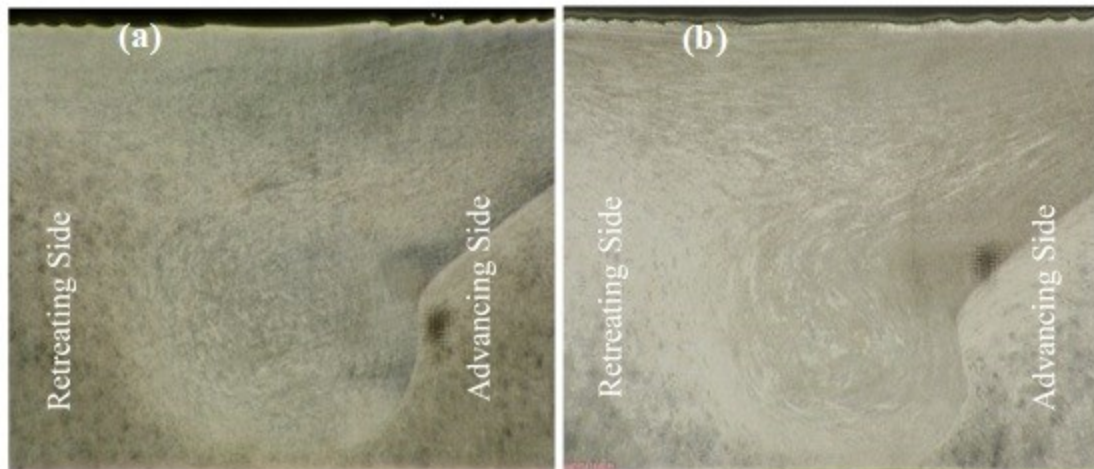


Figure 7-24: Macrograph of the cross section of the weld produced by: (a) Uncoated FSW tool and (b) AlCrN coated FSW tool.

The microstructural evolution of different zones of the weld produced by AlCrN coated FSW tool is presented in Figure 7-25. Similar microstructural evolution is also observed for the weld produced by the uncoated tool. The heat affected zone (HAZ) microstructures is shown in Figure 7-25 (a) and Figure 7-25 (i) for the retreating side (RS) and advancing side (AS), respectively. Also, the thermomechanical affected zone (TMAZ)

microstructures is shown in Figure 7-25 (b/c) and Figure 7-25 (g/h) for RS and AS, respectively. The nugget microstructures where recrystallization had occurred is shown in Figure 7-25 (d) and Figure 7-25 (e) for RS and AS, respectively. Higher magnification SEM images of the nugget produced by both tools, shown in Figure 7-26 (a) and (b), however reveal some distinction in the microstructures. Partial recrystallization may have occurred in the nugget produced by the AlCrN coated tool. This resulted in the formation of crystals as shown in Figure 7-26 (a). This can be associated to localize high temperature caused by low thermal conductivity of the coating, thus, slowed the conduction of frictional heat generated away from the stir zone. The temperature in the stirred zone is thus higher and led to the recrystallization and grain growth, hence the observed crystals.

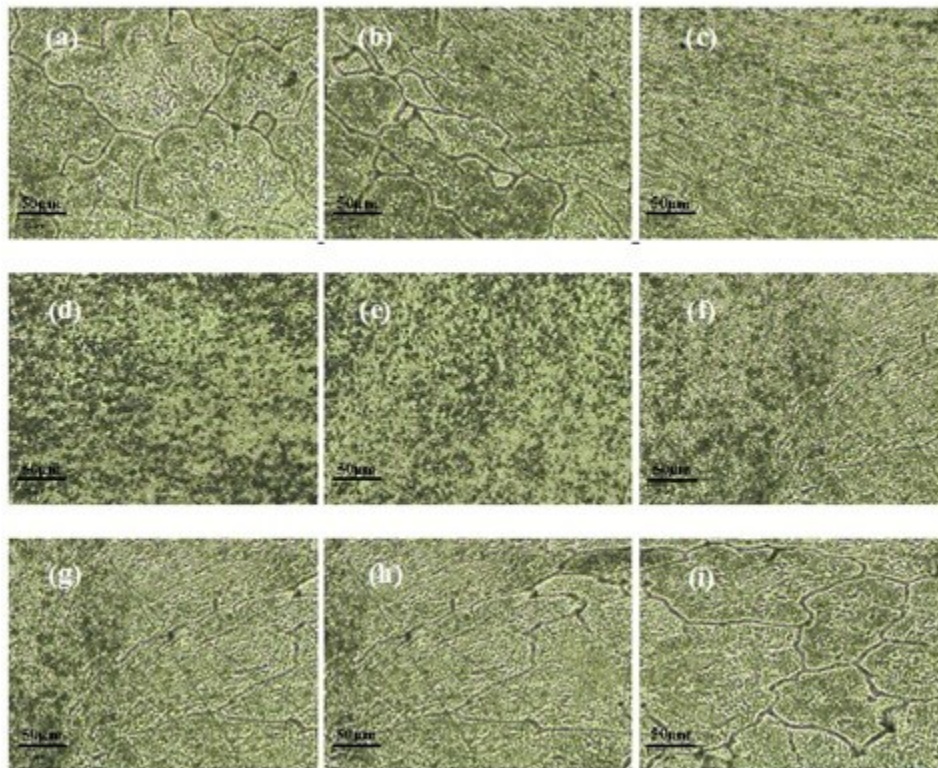


Figure 7-25: Optical images of the microstructural profile of the weld produced by AlCrN coated tool; (a) to (c) HAZ and TMAZ of RS, (d) & (e) nugget and (f) to (i) HAZ and TMAZ of AS.

EDS analysis and back scattered electron (BSE) SEM image show the compositional uniformity between the crystals and the rest of the matrix. This suggests that the crystals are not foreign particles from the coated FSW tool. Conversely, pin-hole weld defect was observed in the weld produced with the uncoated tool as shown in Figure 7-266 (b). This can be attributed to rapid conduction of frictional heat away from the weld zone due to higher thermal conductivity of the uncoated steel tool. Due to the possibility of highly localized melting, rapid solidification at these spots may result in the observed defect. EDS analysis comparing the base material, weld produced by AlCrN coated tool and weld produced by uncoated is given in Figure 7-27 (a), (b) and (c), respectively. These images show that weld produced by both coated and uncoated tool have similar composition with that of the base material. It is observed that the AlCrN coated tool produced good quality weld without being detached from the substrate for the entire process. The weld is defect free and the hardness profile across the welded region as shown in Figure 7-28 revealed that the hardness of the welds are similar. In general, the nugget zones have higher hardness compared to the thermomechanical affected zone (TMAZ) and the heat affected zone (HAZ). The reduced hardness observed in the TMAZ and HAZ is due to self-annealing effect.

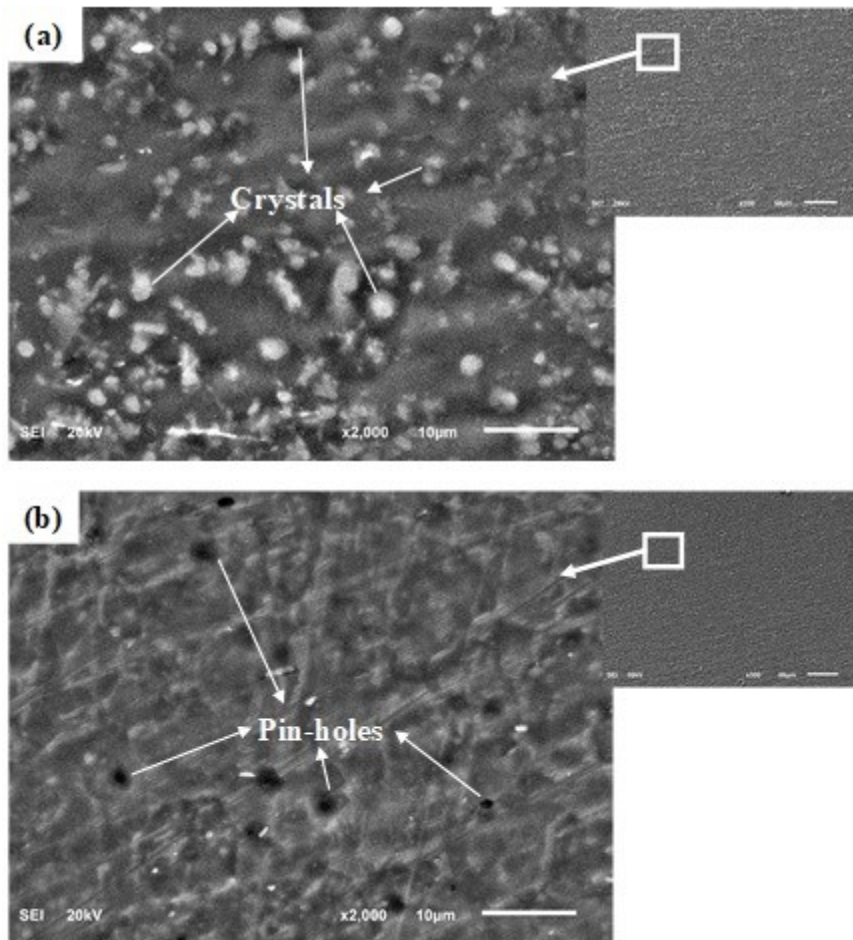


Figure 7-26: Higher magnification SEM image of the nugget zone produced with (a) AlCrN coated and (b) uncoated FSW tool.

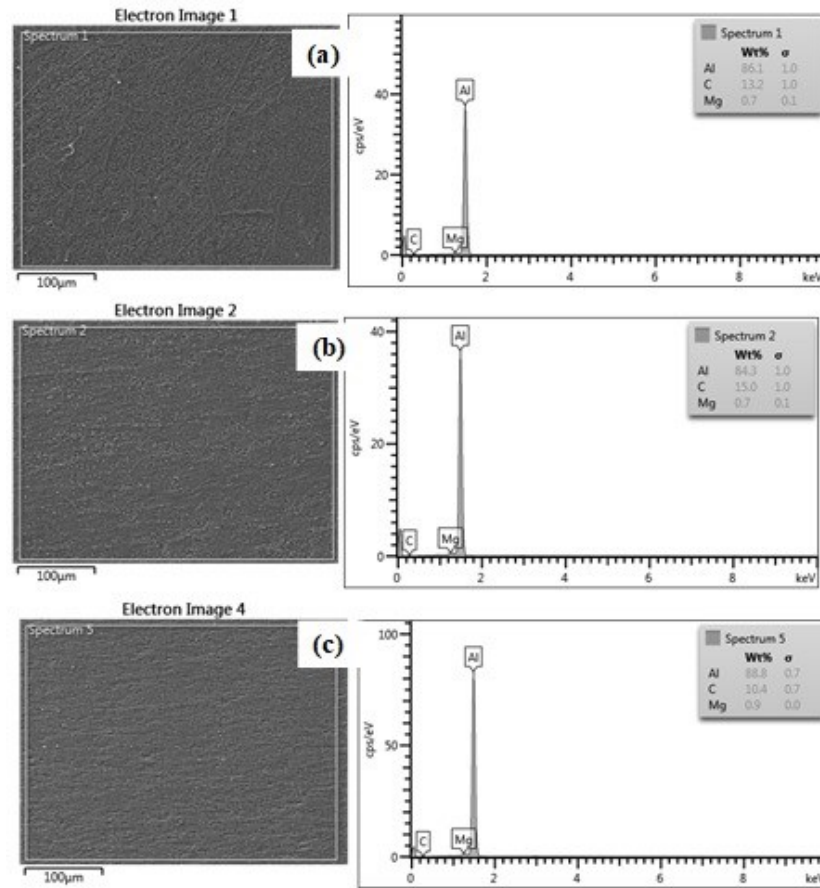


Figure 7-27: EDS analysis of (a) base Al alloy, (b) weld produced by AlCrN coated tool and (c) weld produced by uncoated tool.

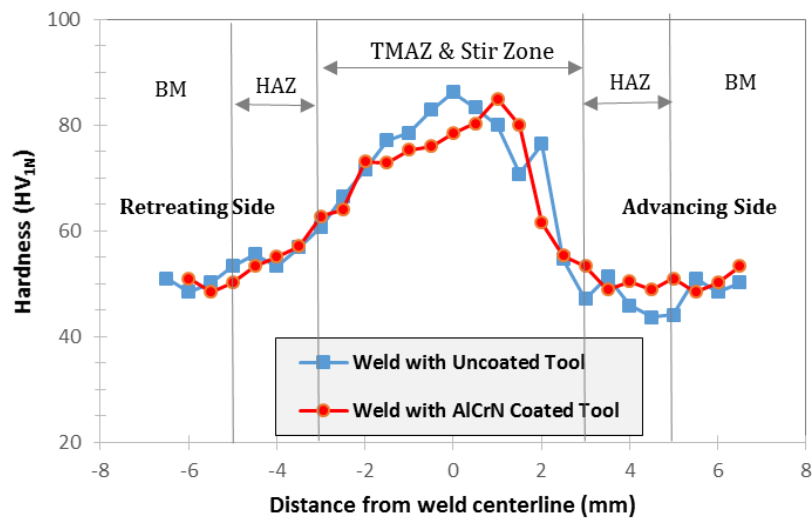


Figure 7-28: Hardness profile across the weld.

7.2.4 Tool wear analysis

The tools performance was examined quantitatively by comparing the tools before and after FSW process. The tool wear was estimated from the percentage variation in the tool dimension after three plunges, passes and the corresponding retractions. The AlCrN coated and uncoated tool before and after the three weld passes are shown in Figure 7-29(a) and (b). The tool performance analysis indicated that the AlCrN coated tool exhibited relatively lesser tool wear and deformation compared to the uncoated tool as evident from the changes in the pin length as shown in Figure 7-30. Approximately 10% variation in pin length was estimated for the uncoated tool compared to negligible change found for AlCrN coated tool. The pin width of both tools was not significantly changed. The variation in pin length is detrimental to the joint quality since it may affect full penetration during welding and results in lack of penetration weld defect. This becomes pronounced with longer weld pass which are typical in practical application. However, tool shoulder and radial wear or deformation were not observed for both uncoated and coated tools.

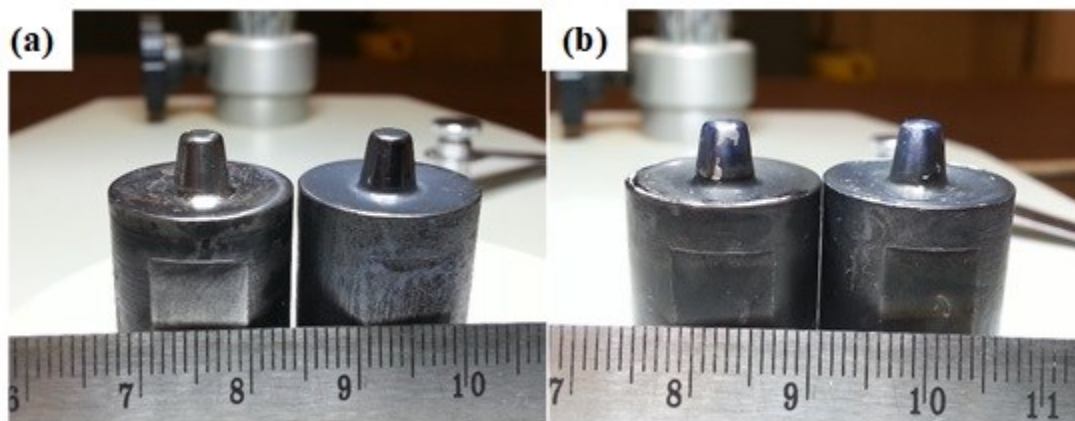


Figure 7-29: FSW tool (a) before FSW process for uncoated (left) and coated (right) tool, and (b) after FSW process for uncoated (left) and coated (right) tool.

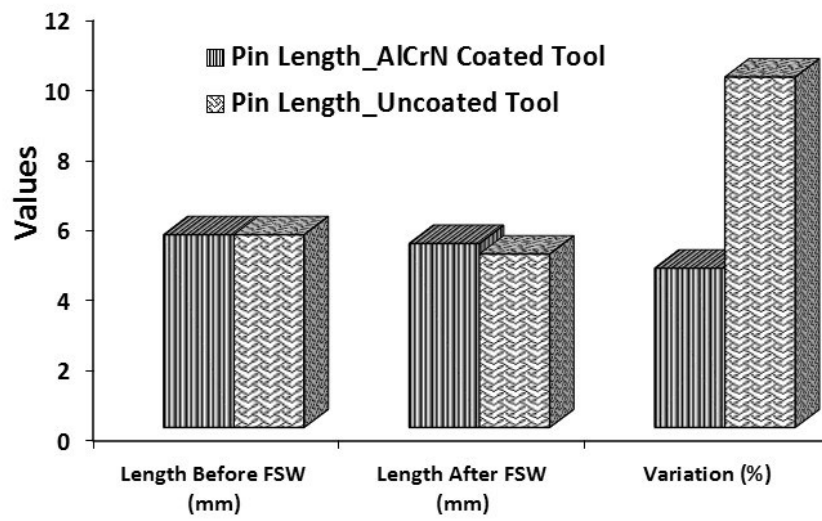


Figure 7-30: Pin dimensions before and after FSW and the percentage variation.

CHAPTER 8

COATED FSW TOOLS FOR A2124/SIC/17P Al-MMC

8.1 Characterization of the Coated H13 Tools

The FSW tool was designed from chromium and molybdenum hot work tool steel H13 grade due to its hot-hardness property, better hardenability and its excellent combination of high toughness and resistance to thermal fatigue. The tool is designed as a featureless frustum-shape tool. Due to the line-of-sight PVD deposition process, it is practically difficult to deposit coatings on tools with complex geometry or features. The tool has a shoulder diameter of 18 mm and pin root diameter of 8 mm tapered to 4 mm. The schematic diagram of the tool showing the dimension and the SEM image of the manufactured tool is shown in Figure 8-1. The H13 FSW tool was then hardened in oil from 1050 °C in argon atmosphere and immediately tempered at 550 °C for about 1hr in a single stage tempering process. The hardness of the tempered H13 tool was 52 – 56 HRC. Similarly, H13 tool steel square samples with dimension 30 x 30 x 8 mm were also prepared and coated under same conditions for mechanical and scratch test.

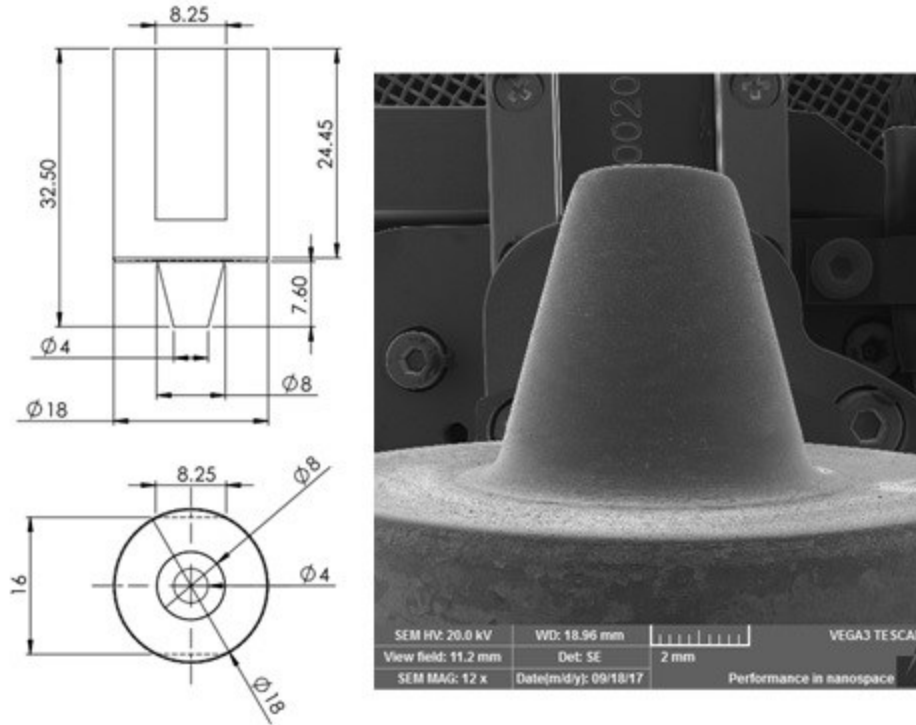


Figure 8-1: Schematic diagram showing the dimensions (in mm) of the FSW tool and the SEM image of the tool.

The surface morphologies of the coated H13 tools is shown in Figure 8-2 (a) and (b). Typical cathodic arc PVD coating morphology is obvious from the micrograph with characteristic micrometer sized droplets (microparticles), shallow micrometer sized craters (pits) and macroparticles as classified by Harlin et al. [196]. They are generally unwanted as they affect the surface roughness and morphology of the coating and can result in high friction, sticking to workpiece, localized coating failure and pitting corrosion [153,174,175]. The cross-sectional SEM images of the coatings are presented in Figure 8-3(a-b). It shows the uniformity, thickness, and the fine structure of the coatings. The average thickness and the chemical composition of the coatings are shown in Table 8-1. The stoichiometry formula of the coatings is $\text{Al}_{0.7}\text{Cr}_{0.3}\text{N}$ and $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ while the weight ratio Cr/Al is 1.12 and Ti/Al is 1.73, respectively.

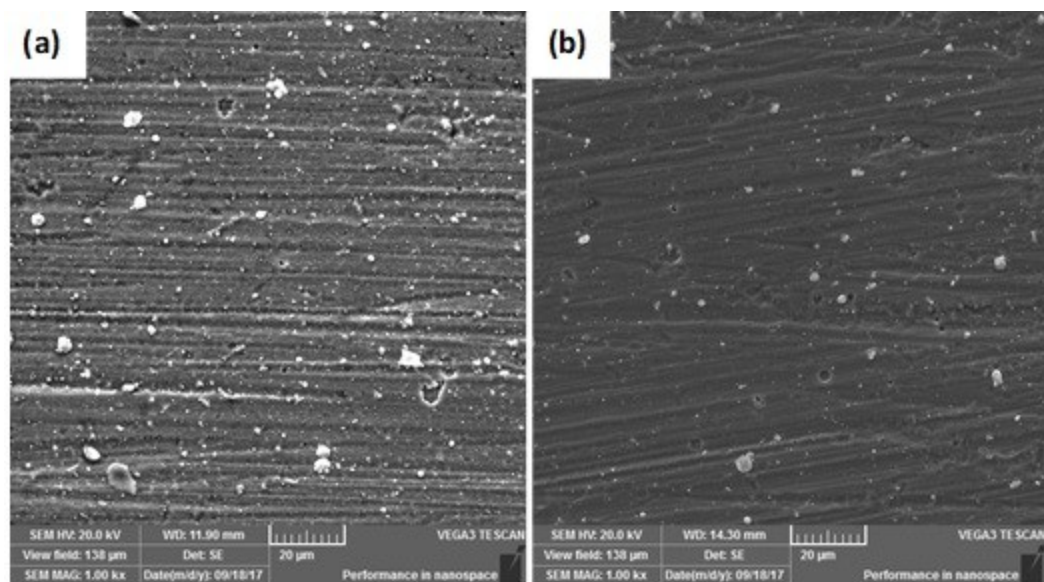


Figure 8-2: Surface morphologies of (a) AlCrN and (b) TiAlN deposited on H13 FSW tool.

Table 8-1: Chemical composition and roughness of coatings deposited on the H13 tool.

Coating	N	Al	Cr	Ti
AlCrN	45.7	29.3	17	
TiAlN	50.2	25.2		24.6

Coating	Roughness Parameters (μm)		
	R_a	RMS	PV
AlCrN	0.17 ± 0.1	0.23 ± 0.01	9.3 ± 1.5
TiAlN	0.21 ± 0.01	0.28 ± 0.01	15.0 ± 5.7

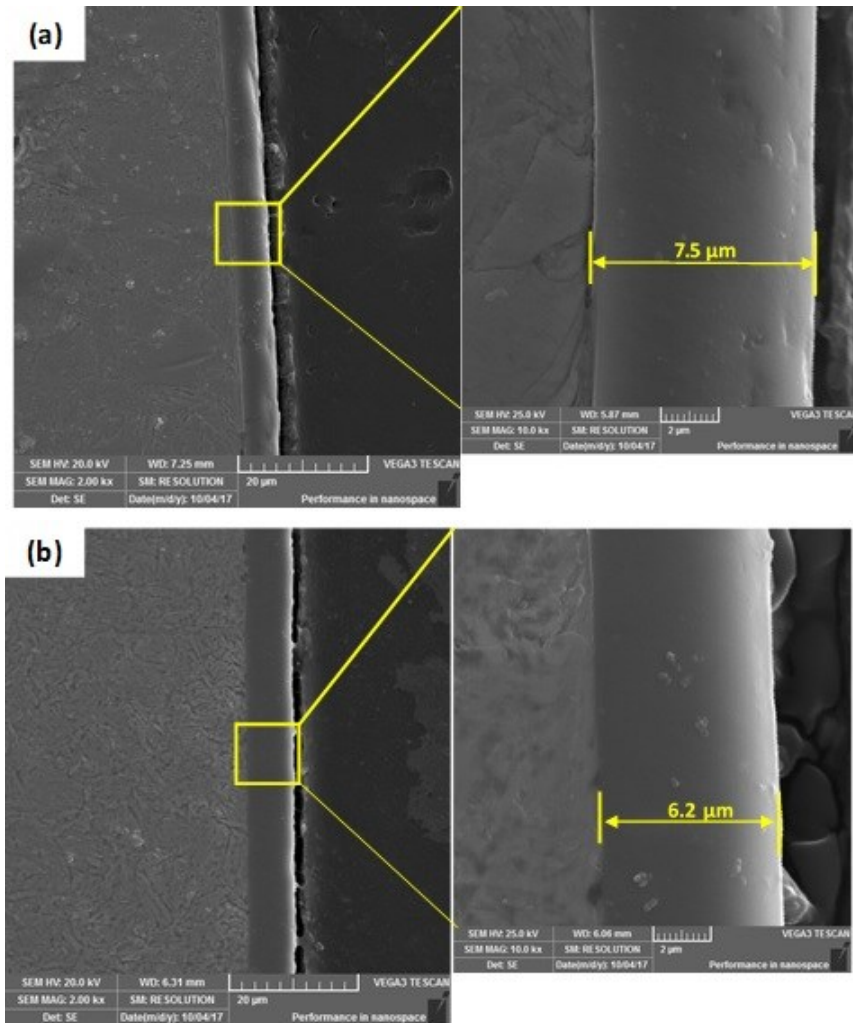


Figure 8-3: Cross-section SEM images showing the thickness of (a) AlCrN and (b) TiAlN coating on H13 FSW tool.

As shown in Table 8-1 it is obvious that both coatings possess relatively low roughness. The low roughness of the coatings (as shown in Table 8-1) illustrates the reduced micro/macro particles and thus the coatings are expected to possess better anti-sticking and low friction properties during FSW. X-ray diffraction spectra of the coatings are shown in Figure 8-4.

AlCrN and TiAlN coatings crystallized into the B1-NaCl cubic structure with major diffraction peaks. Two major diffraction peaks of AlCrN as-deposited are identified at 2θ

= 37.81° and 43.95° corresponding to the (111) and (200) planes. The major peaks for TiAlN as-deposited were detected at $2\theta = 37.22^\circ$ and 43.16° corresponding to (111) and (200) planes, respectively. Several studies [40,199,200] have reported similar diffraction peaks for AlCrN and TiAlN coatings. The estimated average crystallite size from the XRD peaks using the Scherrer's equation is 9.5 and 9.6 nm for AlCrN and TiAlN coatings, respectively. It should be noted that since Scherrer's equation does not account for both micro-strain and instrumental broadening which contribute to peak broadening and thus influence the FWHM, the estimated crystallite size should be considered as the minimal.

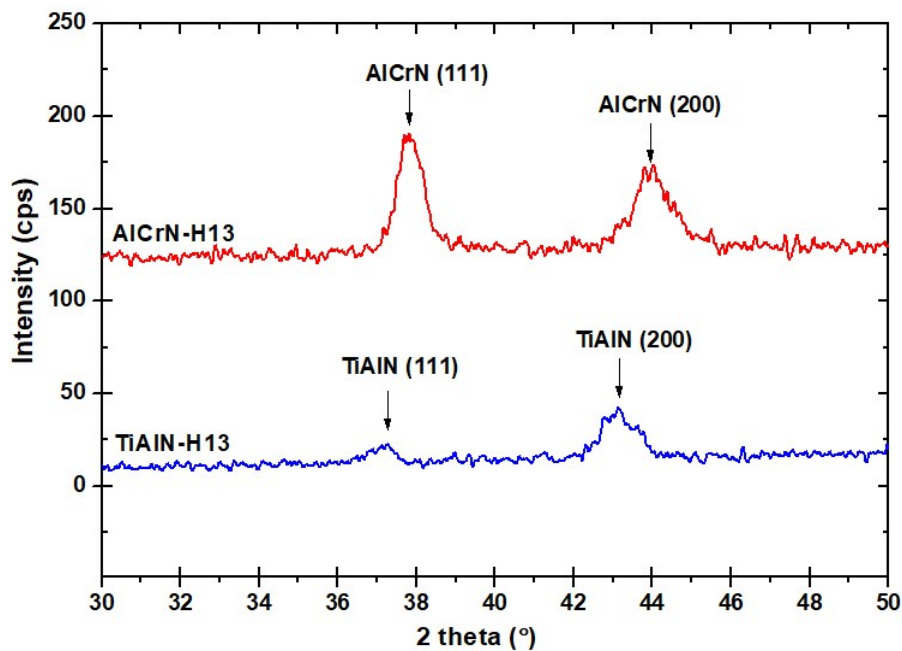


Figure 8-4: XRD spectra of the coatings.

8.2 Tribological and mechanical properties of coated tools

Average hardness and elastic modulus of the coatings from ten measurements are presented in Table 8-2. The hardness was obtained at an average maximum penetration depth of 0.4 μm which is below one-tenth of the coating thickness thus the substrate effect was eliminated. Both coatings possessed similar and typical hardness and modulus of elasticity values of 32 – 36 GPa and 400 – 450 GPa respectively, as reported elsewhere [98,109,117]. The high hardness of the coating can be associated with solid solution strengthening due to densification of grain boundaries resulting in the nano-crystalline structure of the coating [221].

Table 8-2: Mechanical and scratch properties of the coatings.

	H (GPa)	E (GPa)	L_{c1} (N)	L_{c2} (N)	CPR_s (N ²)
AlCrN-H13	34.2 ± 1.8	408 ± 54	12.3 ± 1.6	19.9 ± 1.2	93.2
TiAlN-H13	36.7 ± 2.9	414 ± 59	21.0 ± 0.5	24.7 ± 0.5	78.1

Scratch properties of the coatings are depicted in Figure 8-5 in which AE and COF signals are expressed as function of the normal load from where the critical loads were measured. The higher the L_{c1} (which defines the cohesive strength) the more difficult it is to initiate a crack within the coating. Also, the higher the L_{c2} (which defines the adhesive strength) the more difficult it is to delaminate the coating from the substrate. The evolution of the signal in Figure 8-5 clearly illustrate the cohesive failure load by the sudden peak in AE signal, while the adhesive failure load was detected by the closely repetitive dramatic peaks in the AE signal with corresponding raise and fluctuations in the COF signifying the indenter contact with the substrate. The average values of L_{c1} , L_{c2} and CPR_s from three scratch tests are presented in Table 8-2 for each of the coatings. In general, the coatings possessed

improved cohesive and adhesive strengths due to the nano-crystallite size. This results in better impediment to crack propagation and is consistent with values available elsewhere [49,153,222]. The L_{c1} and L_{c2} of AlCrN-H13 are correspondingly lower as compared to TiAlN-H13, however, the CPR_S of AlCrN-H13 is higher than for TiAlN-H13 as shown in Table 8-2. This behavior is attributable to the multiplication of cracks which hinder adhesion failure and thus yielded higher CPR_S toughness for AlCrN-H13. Figure 8-6 shows the scratch track taken at scratch distance around 7.5 mm and illustrates the adhesive failure characteristics of the coatings. AlCrN coating exhibited a micro tensile cracking while TiAlN possessed brittle failure characteristics.

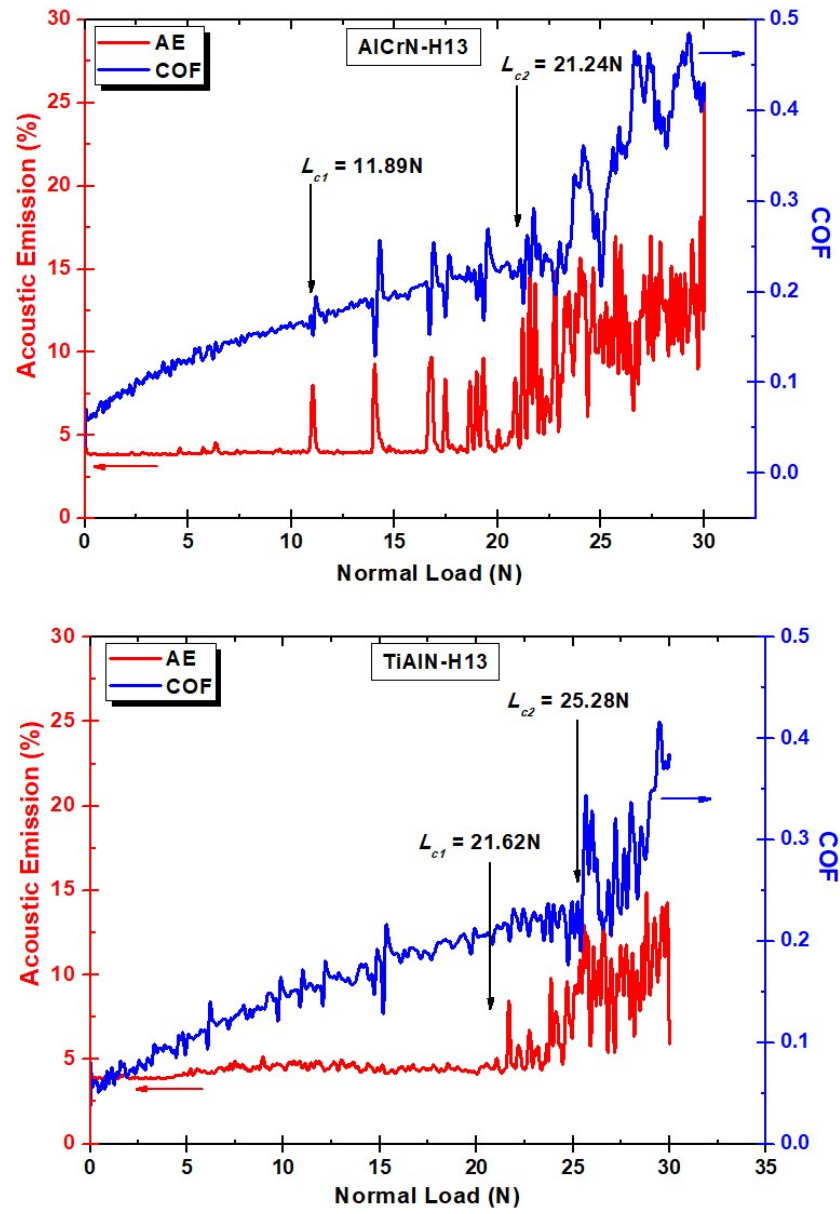


Figure 8-5: Typical scratch acoustic emission and COF as a function of the applied load for AlCrN and TiAlN coatings.

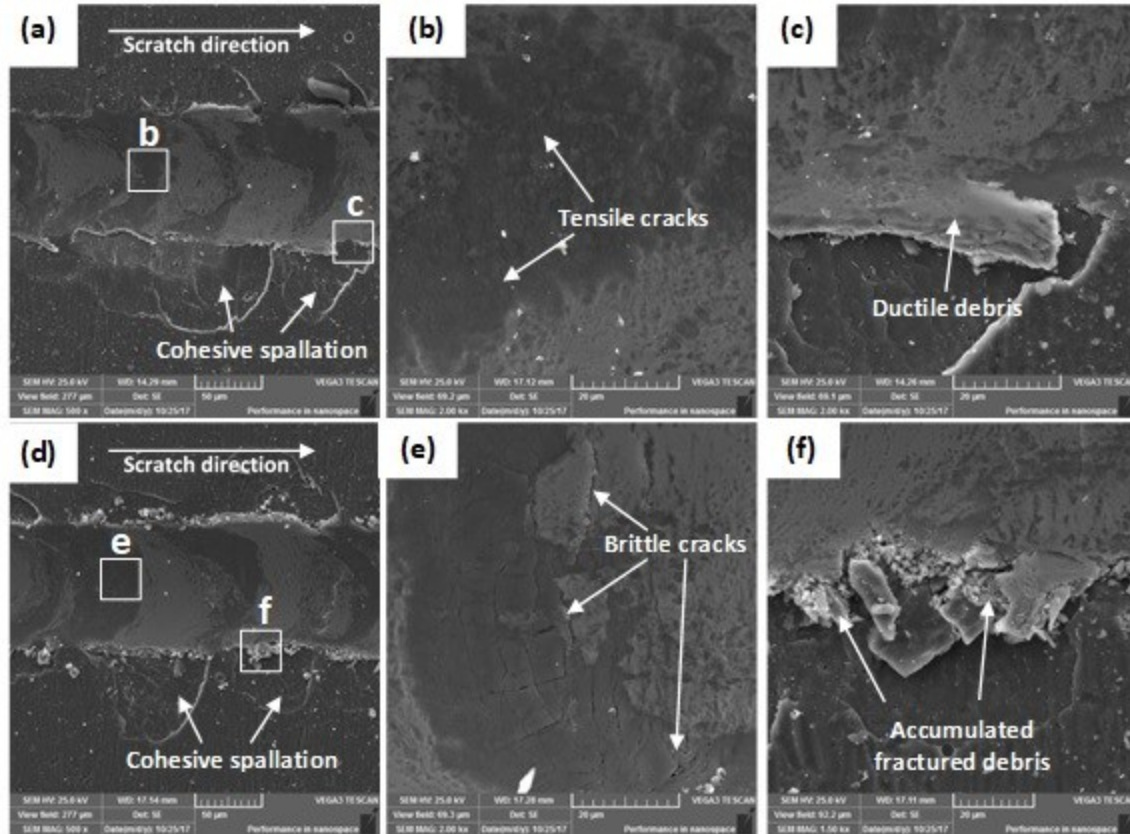


Figure 8-6: Scratch tracks showing the failure mechanism for AlCrN Hardness and critical loads of coated H13 tools.

8.3 Weld joint characterization

Top and bottom views of the joint produced after FSW process by the tools are shown in Figure 8-7. Flashes can be seen on the retreating side of the welds especially for the weld produced with the bare H13 tool. These flashes can be due to over plunging which can result from accompanying thickness variation often associated with HIP manufacturing process. Other factor includes extrusion effect of highly deformed molten materials [147]. Close observation reveals a tunnel like defect in the welds closer to the advancing side and it is pronounced with the weld produced by AlCrN-H13 tool. This can be caused by the large lateral forces which tend to separate the workpieces. Sequel to the high rotational

speed at low traverse speed, lateral forces would be exerted to adjacent molten material for longer duration which can result in the tunnel defect. However, full penetration weld was achieved as obvious from the bottom view in Figure 8-7.

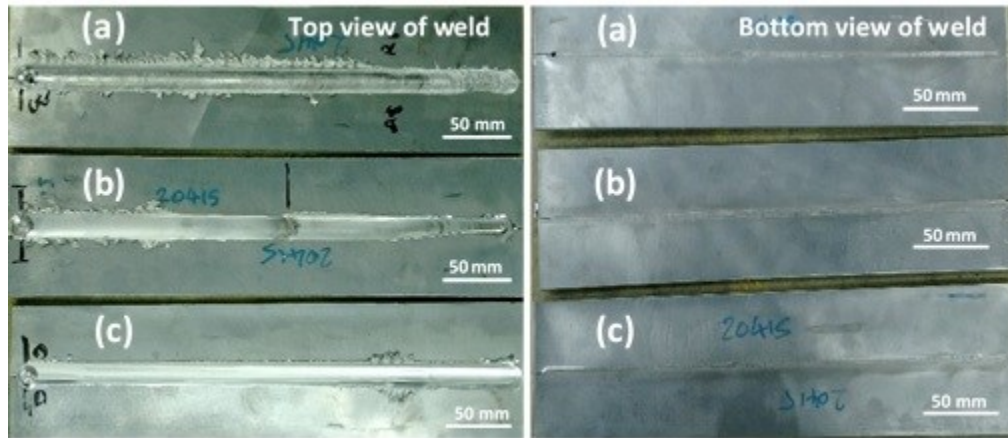


Figure 8-7: Top and bottom views of the FSW A2124/SiC/17p MMC welded by (a) bare H13 (b) TiAlN-H13 and (c) AlCrN-H13 tools.

The SEM microstructural image of the stir zone is presented in Figure 8-8. The effect can be observed from the fragmentation of SiC reinforcement after FSW process using the tools. SiC particles were severely fragmented in the welds produced by all the tools so much that the matrix alloy can barely be seen due to the fine fragmented SiC reinforcement homogenously distributed throughout the matrix. This is due to the high impact collision of coarse SiC particles with high hardness coated surfaces coupled with the dynamic stirring in the nugget zone. As for the bare H13 tool, with low hardness as compared to the coatings, the impact results in the observed extensive ploughing and subsequent wear. Figure 8-9 shows the EDS analysis of the nugget zone processed by the respective tools and it can be seen that no element from the tool was found in the nugget. This suggests that the observed tool wear occurred during the initial plunging stage of the process when the workpiece was relatively cold and hard. The hardness of the nugget zone is shown in Figure

8-10 as compared to as-received Al-MMC. It is obvious that the nugget zones exhibited higher hardness than as-received Al-MMC due to size refinement of the SiC particles and better distribution. The hardness of the nugget zones processed by the bare tool are similar to that processed by the coated tools. This is consistent with the fact that there was no significant difference in the particle size of nugget zones after FSW.

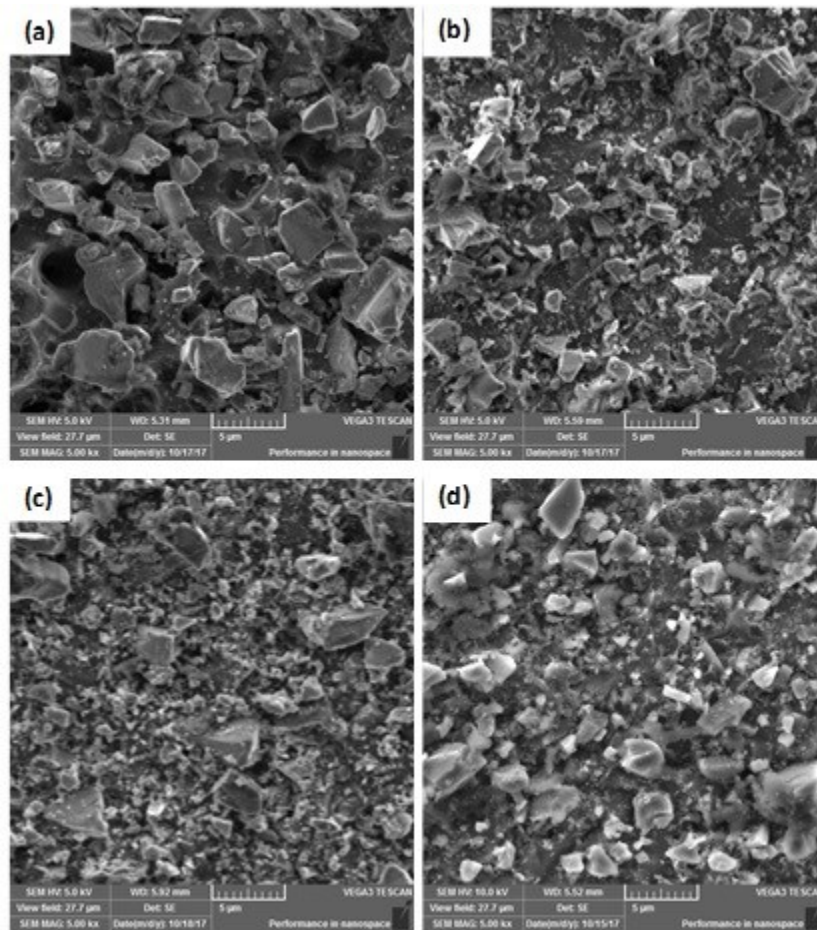


Figure 8-8: Morphology of the SiC reinforcement (a) before, and after FSW process by (b) Bare H13 (c) AlCrN-H13 and (d) TiAlN-H13 tools.

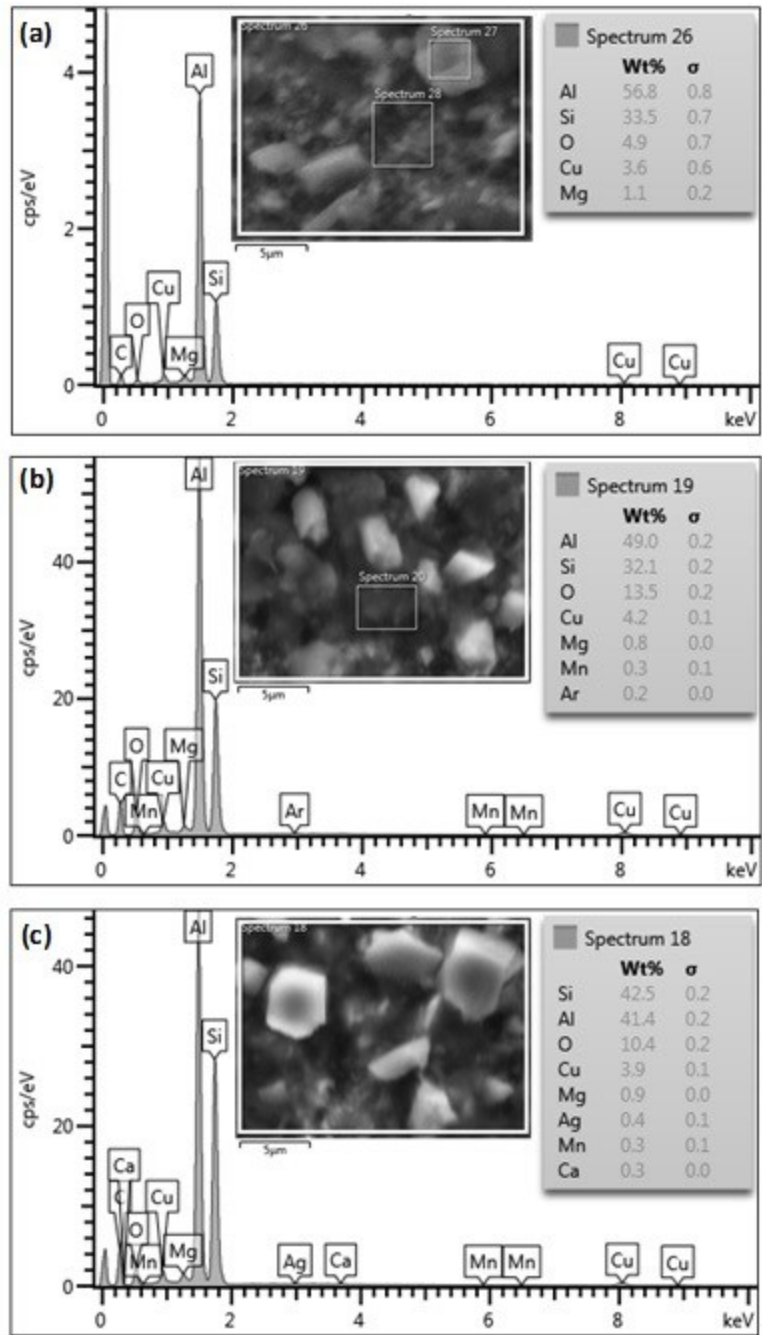


Figure 8-9: EDS analysis of the nugget zone produced by (a) Bare-H13 (b) AlCrN-H13 (c) TiAlN-H13.

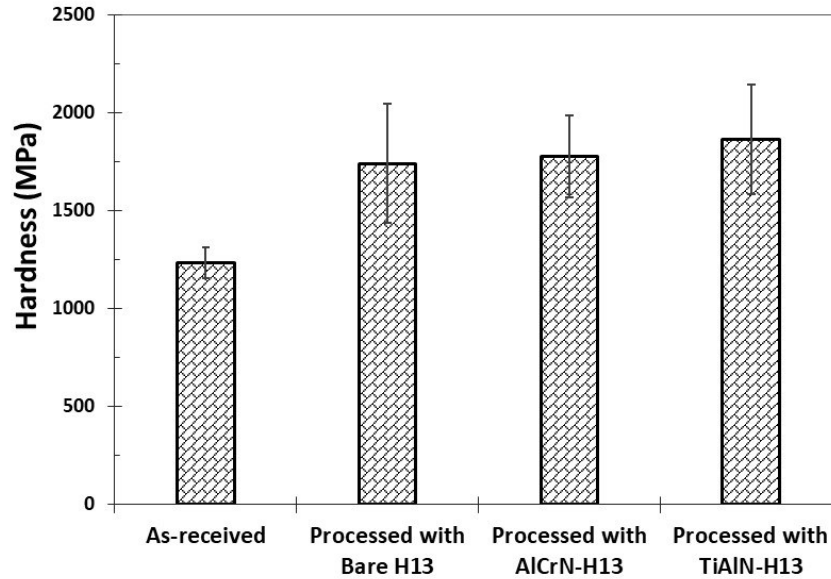


Figure 8-10: The hardness of the nugget zone after FSW process of A2124/SiC/17p MMC as compared to as-received Al-MMC.

8.4 Tool Wear and Characterization after FSW

Figure 8-11 (a-b), (c-d) and (e-f) show wide field SEM images of the bare H13, AlCrN-H13 and TiAlN-H13 tools, respectively, before and after the FSW process. It is interesting that the AlCrN and TiAlN coatings on the H13 tool were still present except for some amount of wear and localize damage of the coating. This also illustrates that the coatings possessed better adhesion to the tool. Tool wear was evaluated quantitatively by the net weight of the tool before and after FSW process for weld distance of 380 mm. After FSW process and before measuring the weight, all the tools were soaked in NaOH solution for 5 – 10 minutes to remove any buildup and accumulation of aluminum on the tools, then rinsed and air-dried. Figure 8-12 shows the weight loss and the wear rate expressed in grams per welding distance in meters.

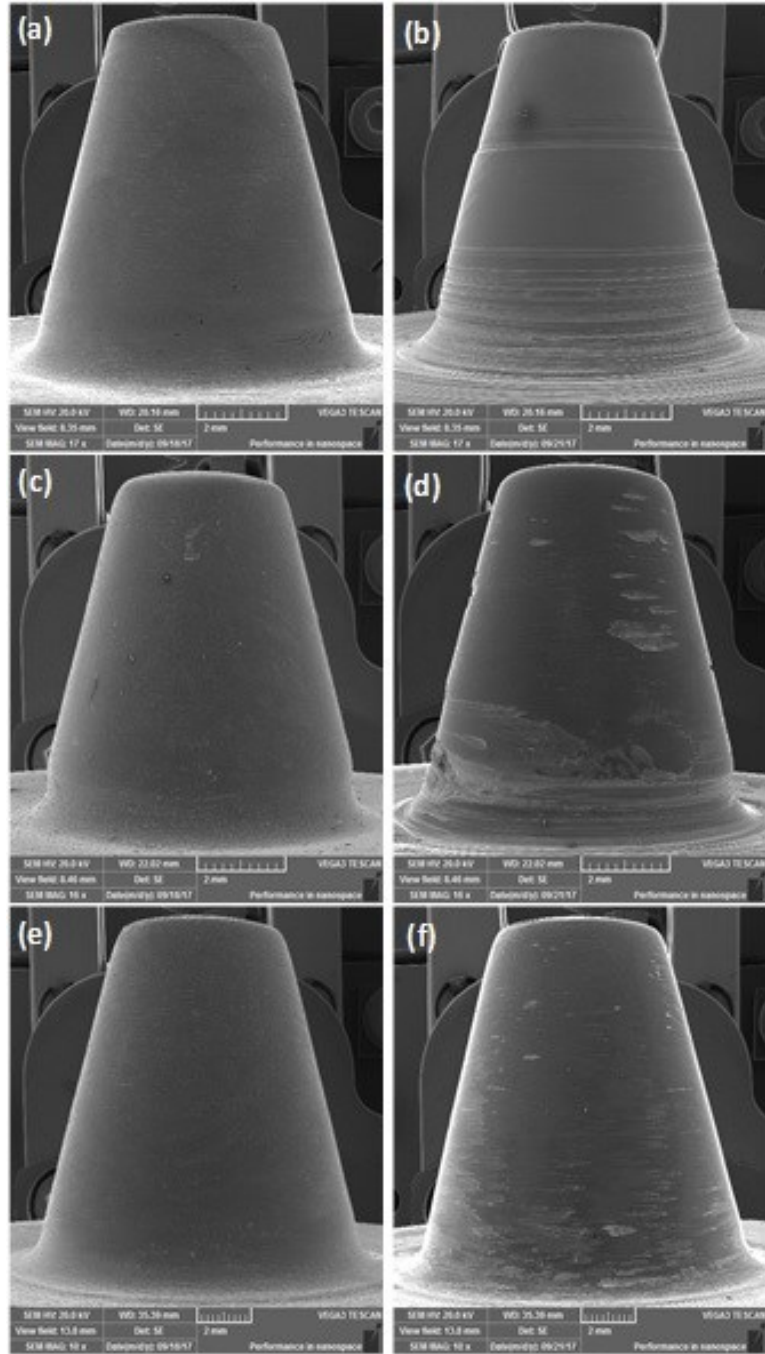


Figure 8-11: SEM image of bare H13 tool (a) before and (b) after FSW process, TiAlN-H13 tool (c) before and (d) after FSW process, and AlCrN-H13 (e) before and (f) after FSW process.

It is found that AlCrN-H13 tool exhibited the lowest wear while the bare H13 tool experienced the highest wear with about 91% and 81% higher than AlCrN-H13 and TiAlN-

H13 tools, respectively. In other words, the coatings have improved the wear resistance of the FSW H13 tool by a minimum of 80%. This can be attributed to the excellent mechanical properties of the coatings and their high thermal stability and better oxidation resistance.

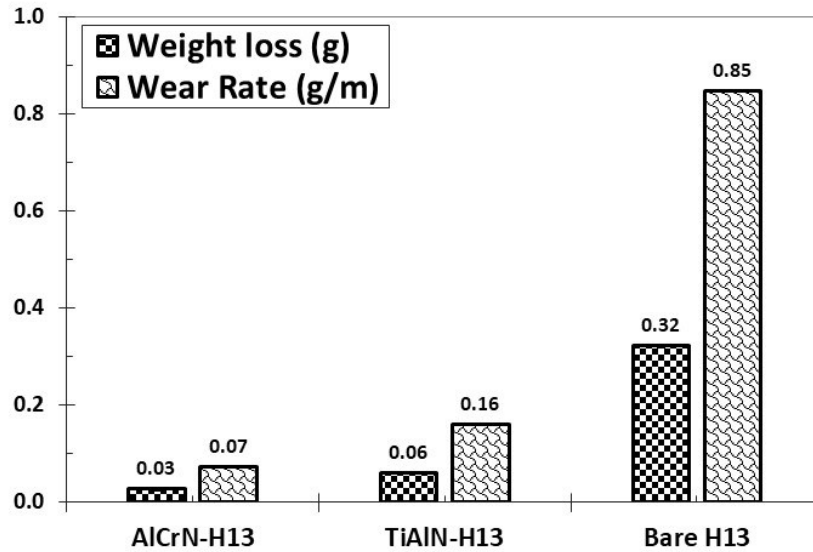


Figure 8-12: Weight loss and wear rate of the tools.

Figure 8-13 shows the tool shank maximum temperature, which reflects the amount of heat dissipated from the tool, while the tool shank average temperature is the mean of the transient maximum temperature of the dissipated heat from the tool as it progresses. It shows that the tool shank of the bare H13 was quickly heated up to the maximum temperature just after the plunging stage unlike the shank of the coated tools whose temperature gradually increased over the welding distance. The raise in the temperature of the tools' shank signifies that more heat is dissipated from the tool pin and shoulder and conducted out from the weld. This is associated to the high thermal conductivity of the H13 tool steel ($\sim 24.5 \text{ Wm/K}$ up to 600°C), which caused rapid conduction of the frictional heat generated, as compared to that of the coatings which have lower conductivity (typically between $4 - 11 \text{ Wm/K}$ for a wide temperature range [223]). Consequently, the average

maximum temperature on the shank of the bare H13 tool was 350 °C for about 80% of the welding distance. This suggests that considerable amount of heat is rapidly being conducted out of the weld and thus less softening of the workpiece exposed the tool to more severe wear condition.

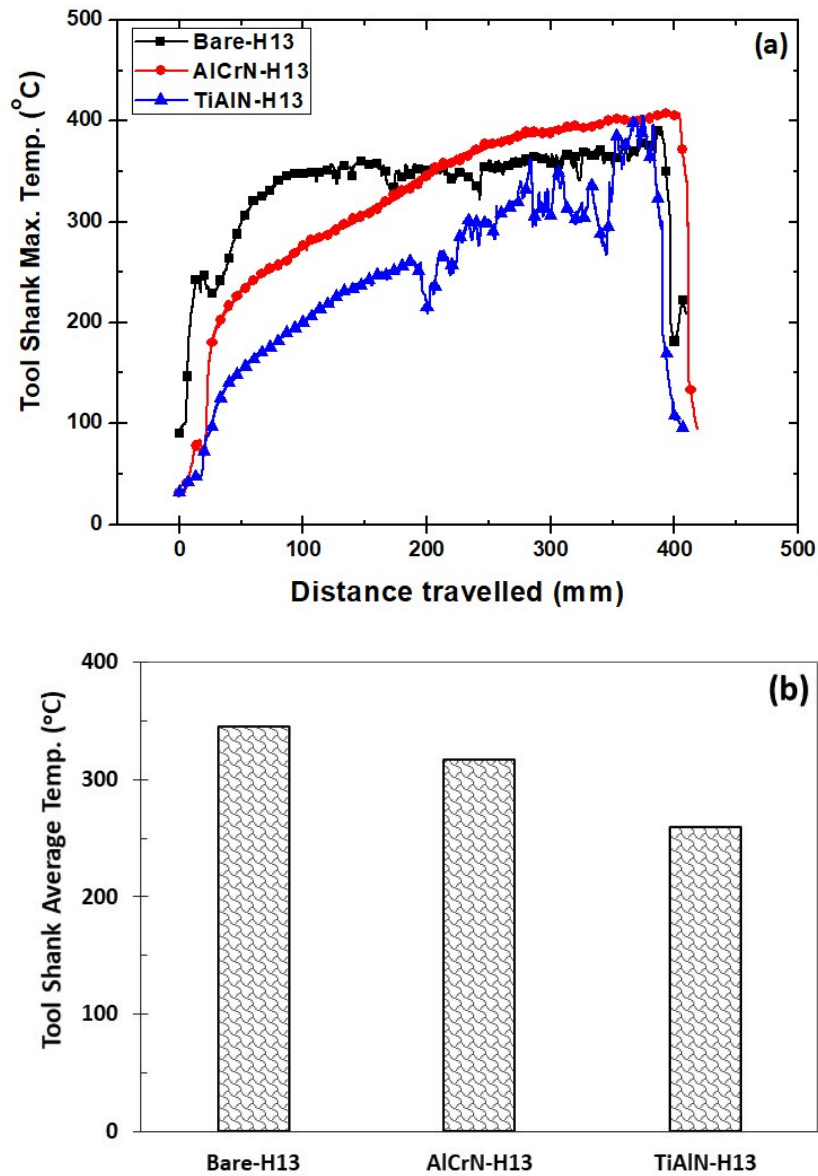


Figure 8-13: (a) Maximum tool temperature variation with distance and (b) average maximum tool temperature.

However, the average maximum temperature on the shank of AlCrN-H13 tool was about 320 °C, with less than 47% of the welding distance reaching 350 °C and above, and about 60% of the welding distance is below 300 °C as shown in Figure 8-13. Also, the shank of TiAlN-H13 tool experienced lower temperature with an average maximum temperature of 275 °C with less than 10% of the welding distance reaching 350 °C. This signified that more heat is retained in the weld which aided in better softening of the workpiece and thereby reducing severity of the condition on the coated tools. The difference in the measured tool shank temperature of AlCrN and TiAlN coatings might be due to the possible difference in their thermal conductivities. AlCrN and TiAlN coatings have a wide range of thermal conductivity depending on factors such as grain size, Al/Cr or Al/Ti ratio, surface roughness and temperature [223–225]. It is important to note that the tool shank temperature does not represent the actual temperature of the tool during the welding process, which was not measured in this study due to technical limitation. In general, the temperature of the tool during the FSW depends on the amount of friction heat generated and this is influenced by the surface condition and properties of the workpiece material (rubbing counterface) as well as the process parameters. Sequel to the high thermal stability and oxidation resistance of these coatings, especially AlCrN coating, they are expected to offer higher oxidation resistance at the actual working temperature of these tools [98,160,226].

8.5 Tool wear mechanism

The tool wear, as earlier shown in Figure 8-11 (b), (d) and (f), respectively, is more severe close to the root of the pin and on the tool shoulder. This is because the temperature is maximum at this location where the combination of the rubbing and stirring action of the

tool results in the frictional heat generated for the process. This heat is thereafter conducted down the thickness of the workpiece for softening the surrounding bulk materials. It is also observed that the wear mechanism differs among the tools. Besides oxidation, bare H13 tool showed continuous deep striation wear by hard SiC particles moving in a horizontal direction along with the matrix due to the stirring action of the tool pin. The striation as observed in high magnification images is uniform and of different width. This shows that the material flow around the tool is uniform and that the striation is caused by the hard particles. This agrees with fact that frustum-like thread-less FSW tool enhances uniform material flow and lowers the turbulent material flow which causes abrasive wear of threaded tools [124,227]. This is a typical wear mechanism of bare thread-less tools during FSW of SiC reinforced Al-MMCs as shown in other studies [32,132]. However, coated AlCrN-H13 and TiAlN-H13 tools showed abrasion and chipping wear mechanisms of various severity. The abrasion occurred due to the hard particle erosion of the tool coatings. Higher magnification images as shown in Figure 8-14 and Figure 8-15 revealed the wear mechanism of the coated tools. Chipping dominate the wear mechanism observed on TiAlN-H13 tool, which may result from large and sharp SiC particles striking the tool at an acute angle as can be observed (as in Figure 8-14 and Figure 8-15) from the shape of the chipped areas having an entry and exist like features. The chipping is more severe as the affected areas were large and deep and possibly exposing the substrate. Figure 8-14 shows severe wear and damage on TiAlN-H13 tool close to the shoulder resulting from significant and repeated chipping of the coating. The considerable chipping experienced by TiAlN-H13 tool result in the high wear as compared to AlCrN-H13 tool where the dominant wear mechanism is surface abrasion from fragmented SiC particles.

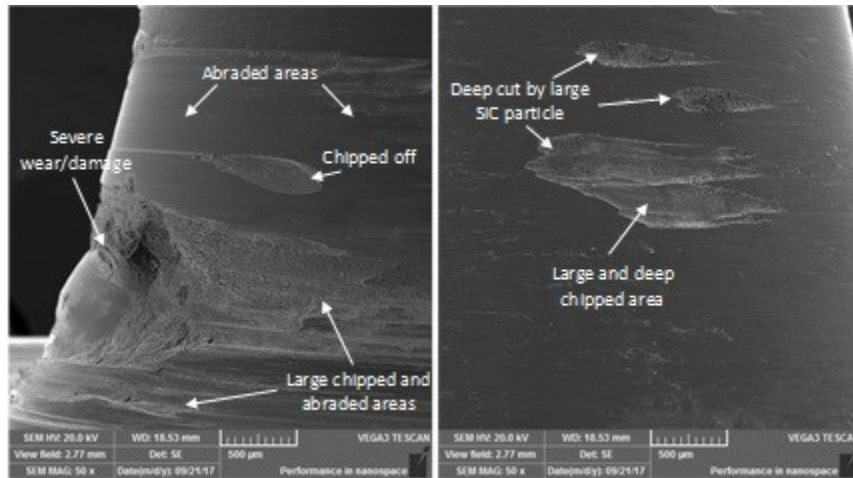


Figure 8-14: Wear characteristics on TiAlN-H13 tool.

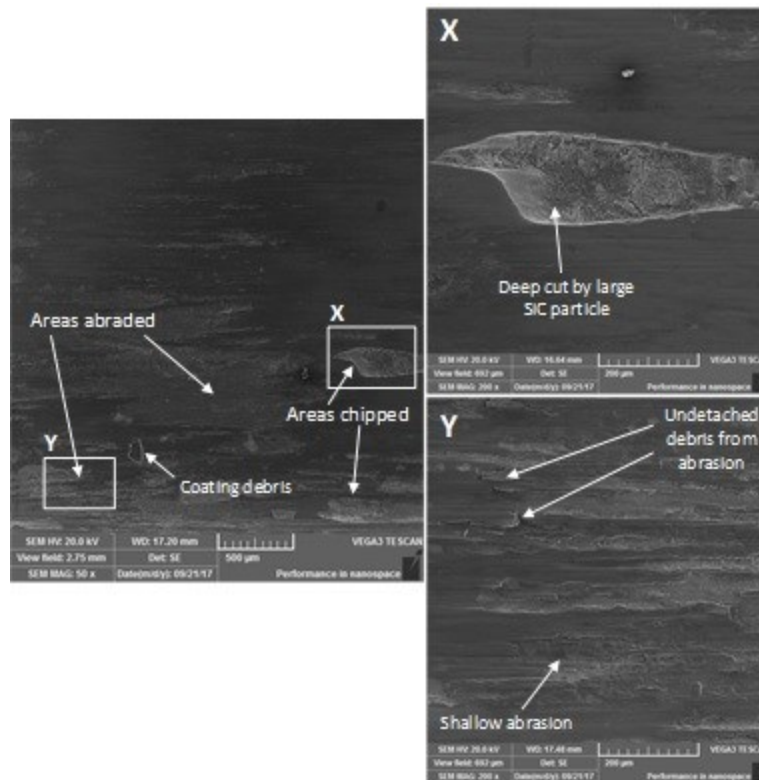


Figure 8-15: Wear characteristics on AlCrN-H13 tool.

AlCrN-H13 also suffered from chipping as obvious in Figure 8-15, but they were less severe and fewer affected areas, hence the observed difference in the wear rate. This can

be associated to the superior scratch toughness of AlCrN coating (refer to Table 8-2), which enables it to offer better resistance to crack propagation thus provide better chipping resistance as compared to TiAlN coating. Figure 8-16 and Figure 8-17 show the EDS mapping analysis of the worn coated tools. It is obvious from the analysis that the wear on TiAlN-H13 tool is more severe than on AlCrN-H13 tool. Also, the chipping wear mechanism is more damaging to the coating as compared to the abrasive mechanism. Large amount of the substrate material (Fe) were detected in the chipped areas which means the coatings have been completely removed, thereby exposing the tool to harder SiC particle and elevated temperature.

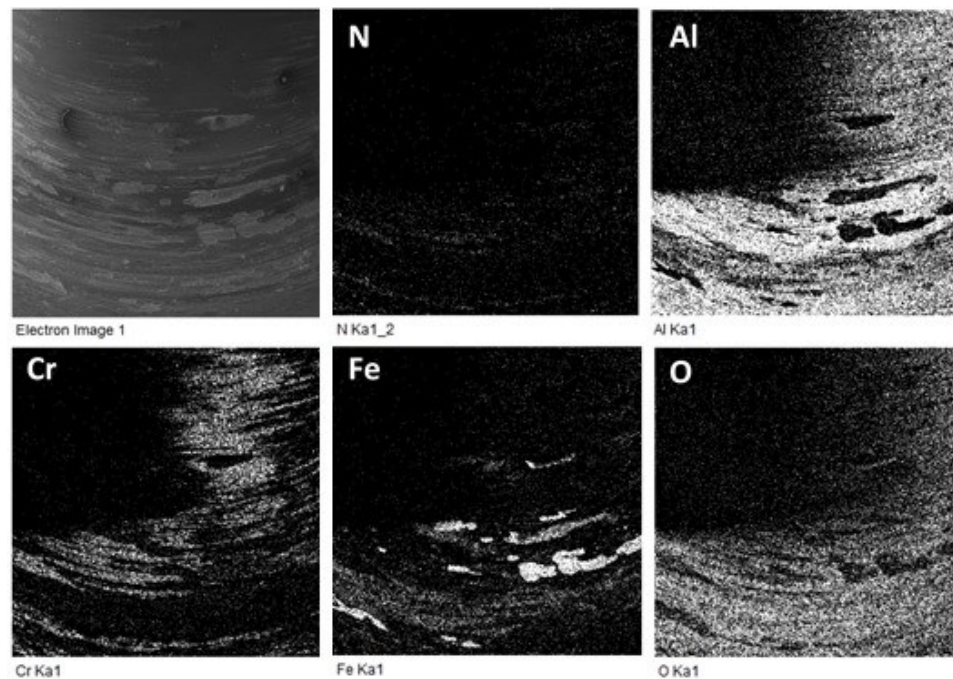


Figure 8-16: EDS mapping analysis of AlCrN-H13 tool after FSW process.

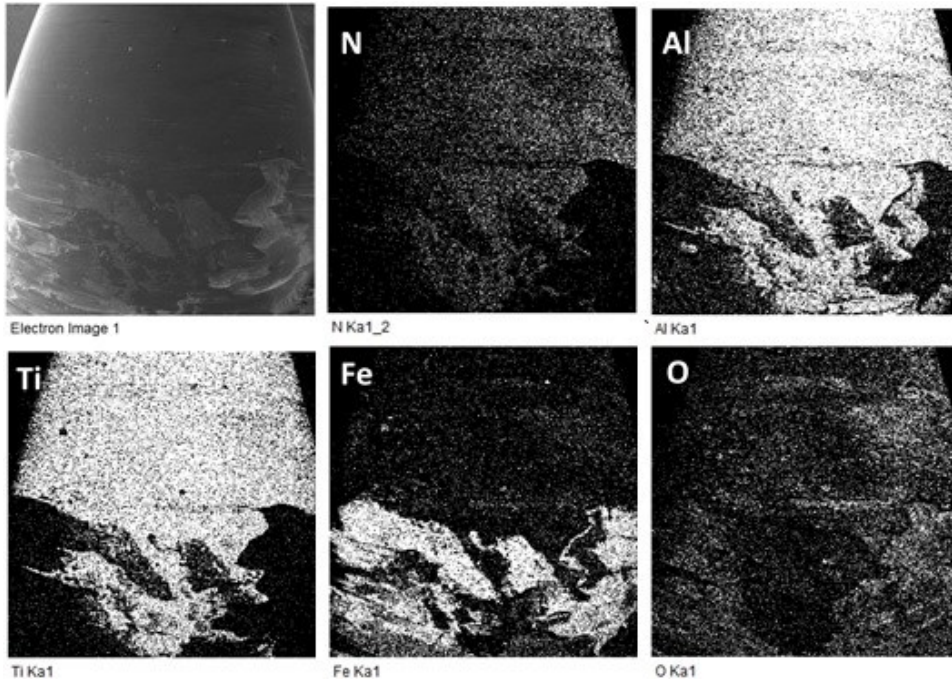


Figure 8-17: EDS mapping analysis of TiAlN-H13 tool after FSW process.

The plunging stage which consists of plunging and the dwelling time is often misconstrued the most severe stage for FSW tool wear due to the fact that the workpiece is still cold, and the huge wedge force required to push the tool into the workpiece. In order to evaluate the tool wear during this stage, force-controlled bead-on-plate plunge and dwell test with a plunging force of 10 kN and 10 s dwelling time, respectively, were applied. The plunging force and dwell time were selected from the FSW process and are the average plunging force and the dwell time measured and used during the welding process. Also, the rotation speed was kept constant at 1000 rpm as in the welding process. The weight loss was measured after every two plunges (i.e. two plunges and two dwells). Figure 8-18 shows the weight loss for the coated FSW tools as compared to the bare H13 tool. It is seen that the tool wear increased with increasing the number of plunges for the bare tool, however, no significant wear was observed on the coated tools. The wear of the bare H13 tool was about 50 mg after 6 plunges while the wear on the coated tools was still below 1 mg. Table 8-3

shows the tool wear in terms of both weight loss and wear rate during the traversing and plunging stages of the FSW process. Tool wear during the plunging stage if expressed as a percentage of the total tool wear during the FSW process is 0.8, 0.2 and 2 % for AlCrN-H13, TiAlN-H13 and Bare-H13 tool, respectively. This suggests that very little fraction of the tool wear occurred during the plunging stage as compared to the entire welding distance.

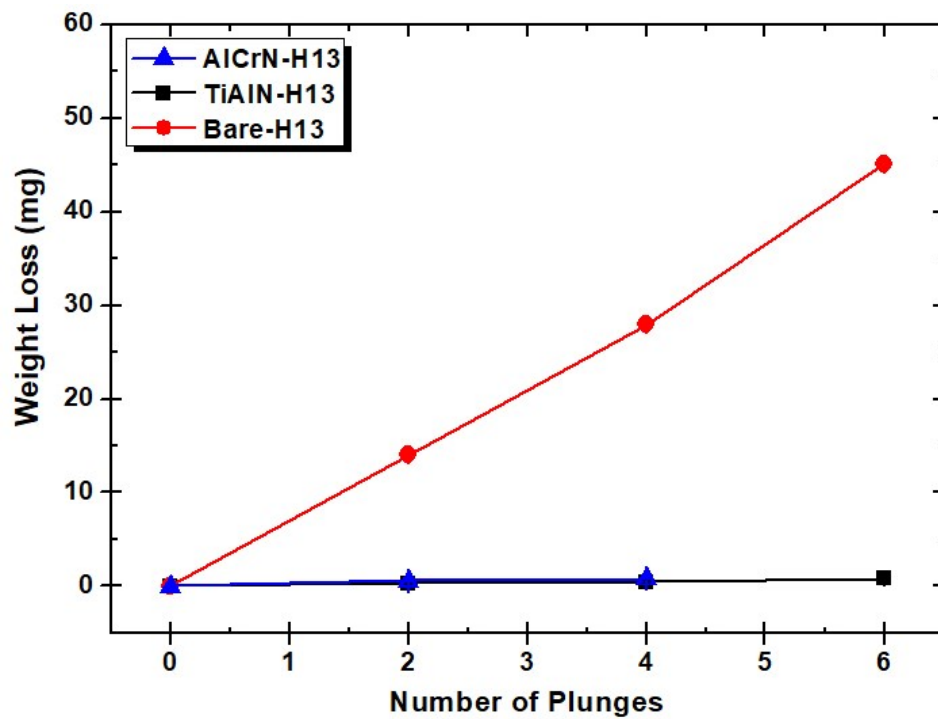


Figure 8-18: Weight loss as function of number of plunges.

Table 8-3: Comparison of the wear during traversing and plunging stages in FSW.

	Weight Loss (mg) after FSW (for 380mm distance)	Weight Loss (mg) after 6 plunges in Plunging test	Wear rate during plunging stage (mg/plunge)	Wear rate during traversing (mg/mm)
Bare H13	321.62	45.11	7.52	0.83
TiAlN-H13	60.70	0.82	0.14	0.16
AlCrN-H13	27.29	0.86 (4 plunges)	0.21	0.07

In other words, majority of the tool wear occurred during traversing stage. In fact, since the frictional heating continues with traversing, the tool wear will depend on the weld distance. This also agrees well with several findings [32,228] which showed that during FSW of Al-MMCs both the effective tool wear and wear rate increased with increasing weld traverse distance. The wear during traverse stage is associated with the translation and vortex flow of material [229,230]. Considering that the tools used in this study are thread-less, the plastic flow in the direction of the workpiece thickness (perpendicular to the tool rotation plane) due to threading is absent, thus, plastic flow in the direction of the rotation of the tool (parallel to tool rotation direction) is obviously the resultant cause for wear [124,231]. The direction of the abraded and chipped areas of the coated tools as observable in Figure 8-14 and Figure 8-15 is an evidence to this flow. Hence, FSW tool is continuously being exposed to new hard SiC particles of various shapes and at different contact angles with the tool during traversing. Sharp-edged particles colliding with the tool at an acute angle results in the deep cut through the coating while abrasive erosion wear is caused by the blunt particles. From Table 8-3, it is observed that the wear rate at the plunging stage is higher for the bare tool while no significant difference is observed in the wear rate at both stages for the coated tools. Interestingly, the coatings contribution in each of the FSW stages shows a minimum of 97 % reduction in the wear rate during the plunging stage. Similarly, during the traverse stage about 80 and 92 % decrease in the wear rate was recorded respectively when TiAlN-H13 and AlCrN-H13 coated tools were used. It is important to note that TiAlN-H13 seems to offer better wear resistance at plunging when the workpiece is still cold. This may be associated to its high hardness as compared to AlCrN-H13. However, during traverse stage, when the frictional heat has build-up, AlCrN-

H13 is more thermally stable and thus the observed reduced wear rate of 56 % lower as compared to the wear rate of TiAlN-H13 during traversing.

8.6 Tool Life Estimation

The life of the coated tools was estimated with Equation 8-1 [232] which is used for determining the thickness w that will be worn out after a duration t .

$$w = f_1 f_2 k P V t \quad 8-1$$

w is the wear in terms of the thickness of coating remove for a duration t representing the tool life, P is the pressure and V is the maximum velocity which is the summation of the maximum rotation speed and the traverse speed. k is the proportionality factor determined from laboratory wear test. f_1 and f_2 are constants to account for temperature and surface condition and are assumed to be 0.5. k was determined using Equation 8-2 [233].

$$k = \frac{v}{WNT} \quad 8-2$$

Where W is the applied load, N is the sliding velocity, T is the sliding time and v is the wear volume determined from the wear laboratory test.

In estimating the life for the coated tools, the following assumptions were made; (i) tool wear is uniform throughout the weld distance, (ii) the coating thickness is uniform and (iii) the coating friction coefficient is low. Table 8-4 shows the estimated tool life in minutes and meters of weld distance for a life criterion of 6 μ m loss in the coating thickness. It should be noted that the estimated tool life will be additional to the tool life of bare H13

tool. This means that TiAlN and AlCrN coatings will extend the bare H13 tool life by 2.6m (44min) and 3.2m (53min), respectively, under this process condition.

Table 8-4: Tool life estimation showing the coated tools' life in time and weld distance.

	k (m³s/N.m.s)	w (μm)	P (MPa)	V (m/s)	PVx10⁶ (N/m.s)	Tool life (min)	Tool life in distance (m)
TiAlN-H13							
Coated Tool	1.55x10 ⁻⁹	6	39	0.15	5.85	44.0	2.6
AlCrN-H13							
Coated Tool	1.28x10 ⁻⁹	6	39	0.15	5.85	53.0	3.2

The life of the coated tools was projected for different PV as shown in Figure 8-19 according to Equation 8-1. The PV entails three main FSW process parameters; the forging force, rotational speed and traverse speed, making it an important parameter which influence the tool life. It can be observed that as the PV increases the tool life decreases sharply at low PV and then gradually at higher PV. At a PV of 2×10^6 N/m.s (i.e. one-third of the PV used in the current study), the tool life is 7.5 and 10.5 m, which is almost 3 and 3.3 times higher, for TiAlN and AlCrN coated tools, respectively. The tool life reduces to 5.5 and 6.6 m, respectively, at a PV of about 3×10^6 N/m.s, and further reduced to 1.6 and 1.9 m at very high PV of 10×10^6 N/m.s for TiAlN and AlCrN coated tools, respectively. It is interesting that even at very high PV which depict very high production rate, the coating can provide substantial increase in the tool life of between 1.5 – 2 m in addition to the tool life of the bare tool.

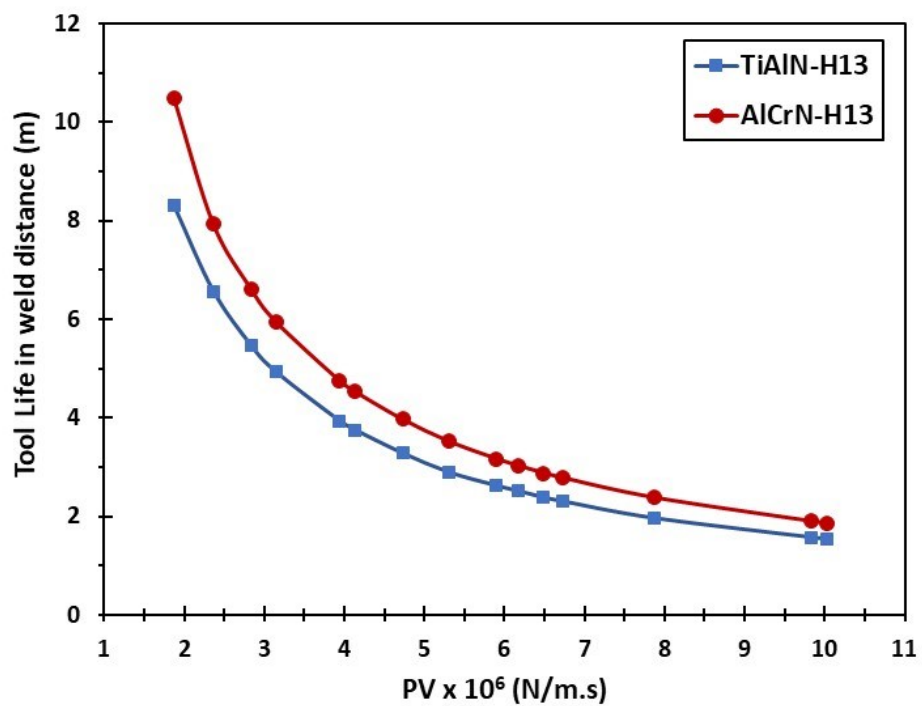


Figure 8-19: Tool life in terms of weld distance (m) verses PV for the coated tools.

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

In this dissertation, cathodic arc PVD binary (TiN, CrN) and ternary (AlCrN, AlTiN) nitride-based coatings were characterized, evaluated and tested. Appropriate coatings were then selected and investigated for wear protecting of friction stir welding tools during welding of Al alloy and Al composite. Basic characterization techniques were used to investigate the mechanical, structural and microstructural properties of the coatings. Screening tests involving scratch test, tribological analysis (wear and friction), corrosion resistance behavior and oxidation resistance tests of the coatings were conducted to compare the performance of these coating under various conditions. Based on the understanding from the comparative tests conducted, ternary coatings were deposited on FSW tools and their contribution to wear resistance of FSW tools during welding of Al alloy and composite were investigated.

9.1 Conclusions Pertaining to Properties of the Coatings

The findings from the evaluation and characterization of the PVD coatings conducted in this dissertation can be summarized below according to the respective analysis:

9.1.1 Corrosion resistance behavior of the coatings

The corrosion resistance of CA-PVD TiN, CrN, CrAlN and TiAlN coatings were evaluated in both 1M HCl and 3.5% NaCl solutions. The coatings were thin, dense and fortified with a bond-coat to increase coating adhesion.

1. The charge transfer resistance can be ranked in this order; $\text{TiAlN} > \text{CrN} > \text{TiN} > \text{CrAlN}$ in both media while the pore resistance followed $\text{CrAlN} > \text{CrN} > \text{TiAlN} > \text{TiN}$ in HCl solution and $\text{TiAlN} > \text{CrN} > \text{CrAlN} > \text{TiN}$ in NaCl solution.
2. To compare the various coatings performance in both media, TiAlN exhibited the highest protective efficiency and the lowest porosity while CrN coating exhibited the least corrosion resistance. The corrosion resistance efficiency increased in the order CrN, TiN, CrAlN and TiAlN in HCl and CrN, CrAlN or TiN and TiAlN in NaCl solution.

9.1.2 Tribological properties of the coatings

Scratch and wear resistance behavior of cathodic arc PVD deposited TiN, CrN, $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$ and $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ coatings were analyzed. The main findings of this part of the study are:

1. The scratch test showed that the binary coatings possessed superior adhesion strength over the ternary coatings. CrN coating exhibited the highest adhesive strength and scratch crack propagation resistance of 6.26 N and 31.86 N², respectively. Based on the adhesive strength, the coatings can be ranked as: $\text{CrN} > \text{TiN} > \text{Al}_{0.68}\text{Cr}_{0.32}\text{N} > \text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$. The failure mode of the binary coatings during the scratch test was predominantly ductile tensile cracking while the ternary coatings failed more severely by through-thickness cracking with spallation damage within the track while chipping failures were observed on both sides of the track.
2. Wear test results showed that the COF of the coatings exhibited similar trend. $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$ coating has the highest COF while CrN showed the lowest COF. It

was also found that for coatings with similar hardness properties, the wear behavior was mainly influenced by roughness and the coating ability to form well adherent and dense oxides. The ternary coatings exhibited better wear resistance than the binary coatings with an average of 68, 67 and 55 % improvement in the wear resistance at 15, 20 and 25 N normal loads, respectively.

3. The main wear mechanisms of the binary coating were abrasive and oxidation wear while the ternary coatings showed combined adhesive and abrasive wear mechanisms. $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$ coating showed slight improvement in wear resistance over $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ coating. This can be due to the huge tribo-oxide layers observed on the counterface which positively influenced the wear resistance behavior of $\text{Al}_{0.50}\text{Ti}_{0.50}\text{N}$ coating. Numerous surface defects and thus high surface roughness coupled with relatively low plastic deformation resistance (H^3/E^2) could be responsible for the relatively lower wear resistance behavior of $\text{Al}_{0.68}\text{Cr}_{0.32}\text{N}$ coating.

9.1.3 Oxidation behavior of the coatings

The oxidation resistance behavior of CA-PVD TiN, CrN, TiAlN and AlCrN coated steel samples were examined isothermally at 800°C, 900°C and 1000°C for 5hrs in air. The main findings of this part of the study are:

1. Oxidation of TiN was severe at temperature ≥ 700 . Surface morphology after oxidation at temperature ≥ 800 showed severe damages and delamination of oxides formed on TiN coatings at all tested temperatures. Cross-sectional examination revealed the formation of oxide phase at the substrate/coating interface of CrN coatings at tested temperature above 800°C.

2. AlCrN coating showed enhanced oxidation resistance properties due to the formation of both Al_2O_3 and Cr_2O_3 which are both effective barrier against oxidation. The specific weight gain in AlCrN coating was about 100% lower compared to that of TiAlN coating. The oxidation rates were in the order of $\text{TiN} > \text{CrN} > \text{TiAlN} > \text{AlCrN}$.
3. All coatings exhibited significant hardness drop after isothermal heating at high temperatures. The ternary coatings exhibited higher retained hardness after isothermal heating at high temperature than binary counterparts.

9.1.4 Effect of vacuum annealing on the coating

The influence of vacuum annealing at 700, 800, 900 and 1000 °C on the corrosion behavior of CA-PVD CrAlN and TiAlN coatings in 1M HCl solution was investigated. The as-deposited coatings were dense, uniform and of fine structure with stoichiometry formula of $\text{Cr}_{0.34}\text{Al}_{0.67}$ and $\text{Ti}_{0.50}\text{Al}_{0.49}\text{N}$, respectively. The following are the main conclusions that can be drawn from this part of the study:

1. After vacuum annealing, the mechanical properties of TiAlN increased with annealing temperature possibly due to age hardening. However, the hardness of CrAlN decreased due to recovery and stress relaxation.
2. EIS and PDP results indicated that the corrosion resistances of the as-deposited and annealed coatings have improved compared to bare 304 SS in 1 M HCl solution. Electrochemical methods showed that the corrosion resistance performance of CrAlN coating increased with increases in the annealing temperature up to 1000 °C. The corrosion resistance of TiAlN coating reached maximum at 800 °C and then dropped.

9.1.5 Evaluation of AlCrN-coated W-25%Re-HfC sintered sample

The mechanical and tribological properties of CA-PVD AlCrN coating on spark plasma sintered W-25%Re-HfC composite was examined to explore the feasibility of improving the life and performance of expensive FSW tools by applying CA-PVD AlCrN coating. The mechanical, scratch, and wear resistance properties were characterized. The followings are some important conclusions from this part of the study:

1. AlCrN coated W-25%Re-HfC sample showed improved mechanical properties with hardness and modulus of elasticity of about 27 and 264 GPa, respectively. The coating exhibited excellent adhesion to the substrate and high cohesive strength.
2. The specific wear rate of the coated sample was 90% lower than the wear rate of uncoated W-25%Re-HfC sample. SEM micrographs showed that the coating sustained the applied load without failure or delamination.
3. The coated sample showed oxidation wear mechanism with low cycle fatigue which led to fracture and formation of debris. The uncoated sample experienced abrasive wear. The oxidation of the coated sample led to the formation of Al_2O_3 and Cr_2O_3 oxides which resulted in improved wear resistance. The improved wear resistance of the coated sample was attributed to several factors including higher hardness, high adhesion to the substrate, relatively low COF, and the formation of oxides which provided well-bonded protective layer.

9.2 Conclusions from the Evaluation of Coated Tools during FSW of Al Alloy and Composite

The contribution of coated FSW tools in improving the wear resistance and/or deformation during FSW joining of Al alloy and composite were investigated and the followings are a summary of the major findings:

9.2.1 AlCrN coated FSW tool for welding aluminum alloy

Cathodic arc PVD AlCrN coating was successfully deposited on FSW tool made from chrome alloy 4140 steel. The structural, mechanical and tribological properties were characterized and the coated FSW tool was tested on a bead-on-plate weld joint. Uncoated tool was comparatively tested under same welding parameters to understand the contribution of the coating.

1. Scratch test results showed that the adhesive and cohesive strength of the coating were 11 and 19 N, respectively. The tribological test revealed that AlCrN coated FSW tool exhibited enhanced wear resistance. The specific wear rate of the uncoated flat sample was over tenfold the wear rate of the coated flat sample.
2. FSW test results revealed that the AlCrN coated FSW tool produced defect-free and full penetration weld without failure, delamination of coating or diffusion of coating material into the weld. The AlCrN coated FSW tool exhibited enhanced tool dimension stability. In specific, no appreciable variation in pin length was observed for the coated tool while up to 10% variation in pin length was estimated for the uncoated 4140 steel FSW tool.

9.2.2 AlCrN and TiAlN coated tools for FSW of Al-MMC

AlCrN and TiAlN CA-PVD coatings were deposited on hardened H13 tool steel FSW tool for butt welding of 8 mm thick AA2124/SiC/17p MMC. The contribution of the coating to the wear resistance after FSW of Al-MMC was evaluated in comparison with bare H13 tool. The following conclusions can be inferred from this part of the investigation:

1. AlCrN and TiAlN coatings deposited on hardened H13 tool exhibited improved mechanical properties and excellent adhesion strength. The scratch test revealed that AlCrN coating offered higher crack resistance properties due to its superior toughness as compared to TiAlN coating.
2. The nugget zone of the welded AA2124/SiC/17p showed improved mechanical properties compared to the as-received Al-MMC workpiece. The use of these coatings did not deteriorate the weld properties. The coated FSW tools appeared to improve the surface finish of Al-MMC.
3. Appreciable improvement in the wear resistance of FSW tool was recorded when the tool was coated with AlCrN and TiAlN. AlCrN and TiAlN coated H13 tools demonstrated wear rate reduction of about 92% and 80%, respectively, as compared to bare H13 tool. Dominant wear mechanisms of AlCrN and TiAlN coated tools were abrasive erosion and coating chipping off. Severe striation and oxidation characterized the wear mechanism of the bare tool.
4. A simplified analysis approach has shown that the life of tool used FSW of AA 2124/17%SiC can be improved with the use of thin layer AlCrN and TiAlN coatings.

9.3 Recommendations

Based on the study conducted in this dissertation the following are recommended for further investigation:

1. Long distance weld should be conducted to evaluate the life of coated FSW tools during Al-MMCs welding under various process parameters to establish failure curves which can serve as a guide for selecting appropriate welding parameters for coated tools.
2. Multilayer cathodic arc PVD coatings can also be explored since there is much flexibility in improving the adhesion, toughness, hardness as well as the oxidation resistance of the coating. Other advanced coatings can also be evaluated for this application.
3. These coatings should be investigated also for FSW of high-strength high-temperature materials such as steels and titanium alloys in which case the wear of FSW tools is of serious concerns and challenges to the process. Appropriate tool material should be selected with enhanced toughness at high temperatures as well as having similar thermal expansion coefficient with the coatings to avoid thermal mismatch.
4. The simulation and modeling of the coated FSW tool can help to improve the understanding of the coating behavior, wear mechanism and predict the actual temperature during the process, as well as reduce the time and cost for running long/several experiments especially for tool life estimation.

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Publications:

Patent (US Issued):

1. **Adesina, Akeem Yusuf**, Iyad T. Alzaharnah Bekir S. Yilbas, Process for determining weld quality using flexural characteristics (US: 9,851,332 B2)
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