A REVIEW ON TITANIUM NITRIDE (TiN) HARD COATING ON SOME STAINLESS-STEEL SUBSTRATES.

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ABSTRACT
Titanium nitride (TiN) is a good coating material that gives a strong/hard coat over a material substrate. This study reviewed the surface modification of some stainless steel (SS 304, SS 316L and SUS 430) coated with titanium nitride (TiN) using physical vapour deposition method (Cathodic arc deposition). The characterization conducted with the aid of optical microscope (OM) from literatures and some mechanical properties (hardness and wear rate) were highlighted. The study indicated that titanium nitride (TiN) coating is more preferable on SS 304 due to the higher hardness (average) value of 2657 obtained compared to 1850 for SS 316L and 2276 for SUS430 using same coating process. However, the study showed that, SS 304 Stainless steel coated with TiN has low wear rate compared to the other two Stainless steel, and there is a reduction in the adhesion of the ball on the coated steel sample signifying a low wear mass. The coated material can be beneficial in the production of parts in door locking mechanisms, ball bearings surgical scissors, etc.

Keywords: Surface Modification, Characterization, Stainless Steel, Cathodic Arc Deposition, Coating.

Introduction

Stainless steel is made for high corrosion and wear resistance applications, it was reported in (Vettivel *et al.*, 2017) that only fewer number of studies in austenitic steels are available but a lot of researches on the synthesis and characterization of aluminium and titanium coated based materials are available in martensitic steels. However, due to stainless steel resistance against wear, they are not suitable for high machinability applications. Austenitic steels are better than the ferrous steel for corrosion/wear resistance (Vettivel *et al.*, 2017).

Titanium nitride (TiN) coatings are used to give better wear properties on the material substrates. Example, cast iron foundry tools are mostly exposed to sand abrasion and there is the need that it resist the wear due to the sand abrasion, the application of Titanium Nitride (TiN) coatings could provide such wear resistance (Nieh *et al.*, 1996).

In various materials of stainless steel, austenitic is identified for the tendency of better work and improved machinability (Veprek et al., 2005). However, physical vapour deposition (PVD) means of coating is a very good production method for the surface treatment (coating) of material, some advantages of the physical vapour deposition (PVD) when analysed with some coating methods include possession of increased density, provision of stronger bond between the coating and the film properties (Chenglong et al., 2006).

In this study, the surface modification and characterisation of TiN coating on SS 304, SS 316L and SUS 430 Stainless Steels substrate together with their mechanical properties (hardness and wear tests) were studied using the Cathodic arc deposition method. SEM morphology of titanium-nitride that was coated on the surface of steel shows macro droplets also known as globules of molten titanium (Ali et al., 2010).

Composition of the Stainless-Steel Materials

The commercialized Stainless steel (SS 304) is composed of 18-20% Cr, 8-12% Ni, 0.08% C, 0.75% Si, 2.0% Mn, 0.045% P, 0.03% S, 0.1% N, and Fe completing the balance (Meng-Tsun et al., 2014).

The Chemical composition of austenitic SS 316 L is 18% Cr, 14% Ni, 2% Mn, 2% Mo, 0.03% C, 0.045% P, 63.16% Fe, 0.75% Si and 0.03% S (Saravanan et al., 2015).

2.0 Physical Vapour Deposition Method (PVD)

Physical vapour deposition (PVD) describes different vacuum deposition methods that can be used to provide thin films and coatings. It is characterized by a process whereby coating material move from a condensed phase to a vapour phase and then return to a thin film condensed phase. This method is used in the coating of items that require thin films for mechanical, electronic, chemical or optical performance. Some examples include coated cutting tools for metal working and in a semiconductor material like thin film solar panels (Selvakumar and Barshilia, 2012).

Titanium nitride, Zirconium nitride, Chromium nitride and titanium aluminium nitride are the common industrial coatings applied by physical deposition method.

Examples of PVD Methods

PVD methods include; Cathodic arc deposition, Evaporative deposition, Electron beam deposition, Sputter deposition, Pulsed laser deposition, Pulsed electron deposition, Sublimation sandwich method etc.

Cathodic arc deposition: Electric arc is employed here to vaporize coating material from a cathode target. The vaporized coating material then condensed on the substrate forming a thin film. Metallic, composite and ceramic films can be deposited using this technique.

Evaporative deposition: This technique requires the material to be deposited to be heated to a high vapour pressure by electrical resistance heating in high vacuum (He and Kretzschmar, 2012).

Electron beam deposition: In this technique, the material to be deposited is heated to high vapour pressure by electron bombardment in high vacuum and is moved by diffusion to be deposited by condensation on the (cooler) substrate.

Sputter Deposition: This technique involves removing coating material from target that is a source and deposited on to a substrate such as silicon wafer.

Pulsed laser deposition: In this PVD method, a high-power pulsed laser beam is focused inside a vacuum chamber to strike a target of the material that is to be deposited. This coating material is vaporized from the target and deposited on to a substrate as a thin film.

Pulsed electron deposition: This is a technique, in which a highly energetic pulsed electron beam removes a melted material from the target generating a plasma stream.

Materials and Methods in the Review

Surface Preparation

One of the most paramount processing activities in the investigation of the processes and characterization methods for any surface coating of a metal substrates is Surface Preparation. This is done in essence in order to clean or remove unwanted material that can have an adverse effect on the coating and performance of the substrate material in future.

Moreover, the substrate material specimens of diameter 40 mm and 7 mm thickness were cut with the aid of an oil-lubricated carborundum slitting wheel. When the cutting of the specimens was completed, the specimens were ground using silicon carbide paper of grade(s) 220, 400, 800 and 1200 respectively with subsequent polishing of those specimens with the aid of a rotating wheel of 0.1microns diamond paste using Jean Wirtz PHOENIX 4000 polishing machine.

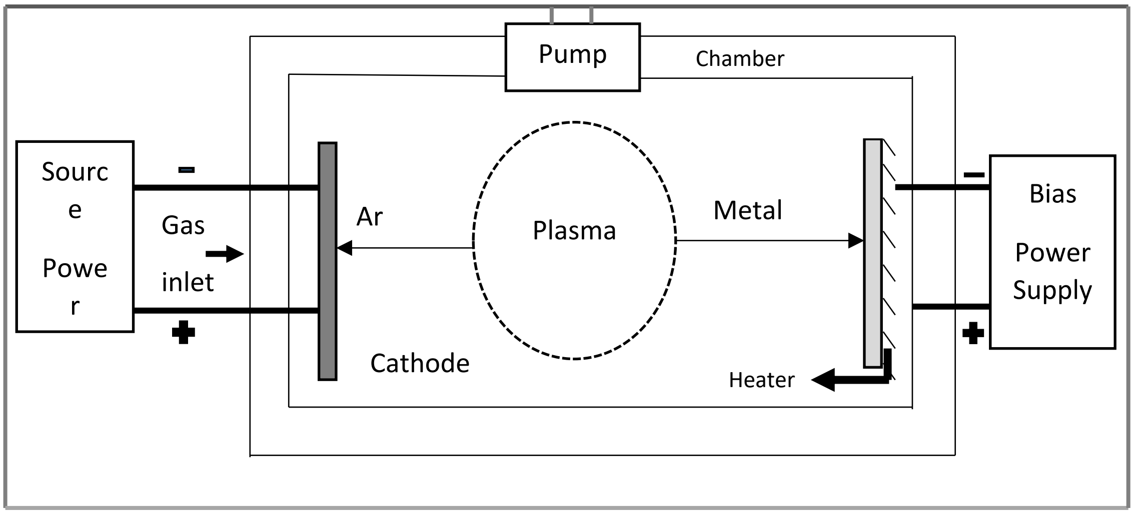
Consequently, when the cutting, cleaning and polishing were completed on the specimens, Titanium Nitride coatings were applied for the desired goal (Dogan *et al.*, 2002).

Although, in some preparatory process for Titanium-Nitride coating deposition, prior to the deposition, the substrate is bombarded using an argon-ion plasma. The Ar-ion bombardment accomplishes the task of sputter-cleaning the substrate surface. This physical sputtering clears away any foreign atoms, atom species like oxides including surface hydrocarbons that may be present. The sputtering also removes a small amount of the material substrate's itself (Nieh *et al.*, 1996).

Surface Modification Process (Cathodic Arc Deposition Process)

Cathodic arc deposition was initiated with the striking of high current, low voltage arc on the surface of the cathode (Ti) which generates a small highly energetic emitting area known as cathode spot. Localized temperatures of about 600 ^{0}C to 700 ^{0}C gives a high velocity of 104 m/s jet of vaporized cathode material, leaving a crater behind the cathode surface. The cathode spot is active time and self-extinguishes and re-ignites in a new area close to the last crater. This process causes the apparent motion of the arc. Nitrogen was then taken as a reactive gas into the chamber during the evaporation process. Ionization and excitation can take place during interaction with the ion flux and the compound Titanium-Nitride (TiN) was deposited to the steel (Vettivel *et al.*, 2017).

However, Vettivel *et al.*, 2017 reported from Dearnley and Aldrich-Smith, 2004 that physical vapour deposition (PVD) is the most accurate coating technique but cathodic arc deposition (CAD) performs well in the formation of strong bonding of coating over the base metal, indicating the importance of the coating on the mechanical properties and microstructure. Figure 1 below shows a schematic of the Cathodic arc deposition process (Saravanan *et al.*, 2015).



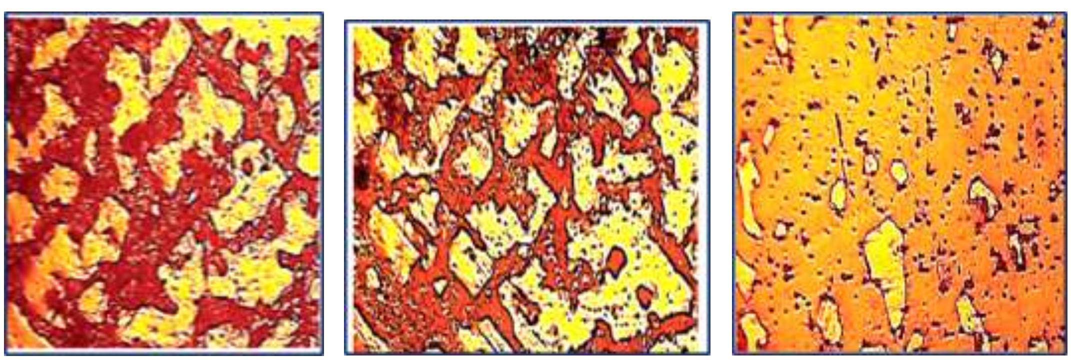
Source: (Saravanan *et al.*, 2015)

Figure 1: ***Schematic representation of the cathodic arc deposition***

Characterization of Titanium-Nitride coating

Optical Microscope (OM)

In the Microscopic analysis, the specimen's image coated with Titanium-Nitride (TiN) using Optical microscope (OM) is shown in figure 2 below. The study observed from the image that particles of nitrates along the surface of SS 304 stainless steel are distributed uniformly.



Source: (Vettivel *et al.*, 2017).

(a) *(b)* *(c)*

Figure 2: ***Optical microscope image: (a)TiAlN coated, (b) AlCrN coated, (c) TiN coated.***

Review of Performance Test

Hardness Test

A Wilson Halbert hardness tester (0.005-1kg) in conformity with standard ASTM: E09 on TiN coated surfaces at room temperature. The reading as shown in table 1 below gives the hardness effect on SS 304, SS 316L and SUS 430 coated with TiN.

Table 1: ***Hardness value of TiN coated on SS 304, SS 316L and SUS 430.***

S/No.	Sample Location	SS 304	SS 316L	SUS 430
1	TiN	2812	1850	2276

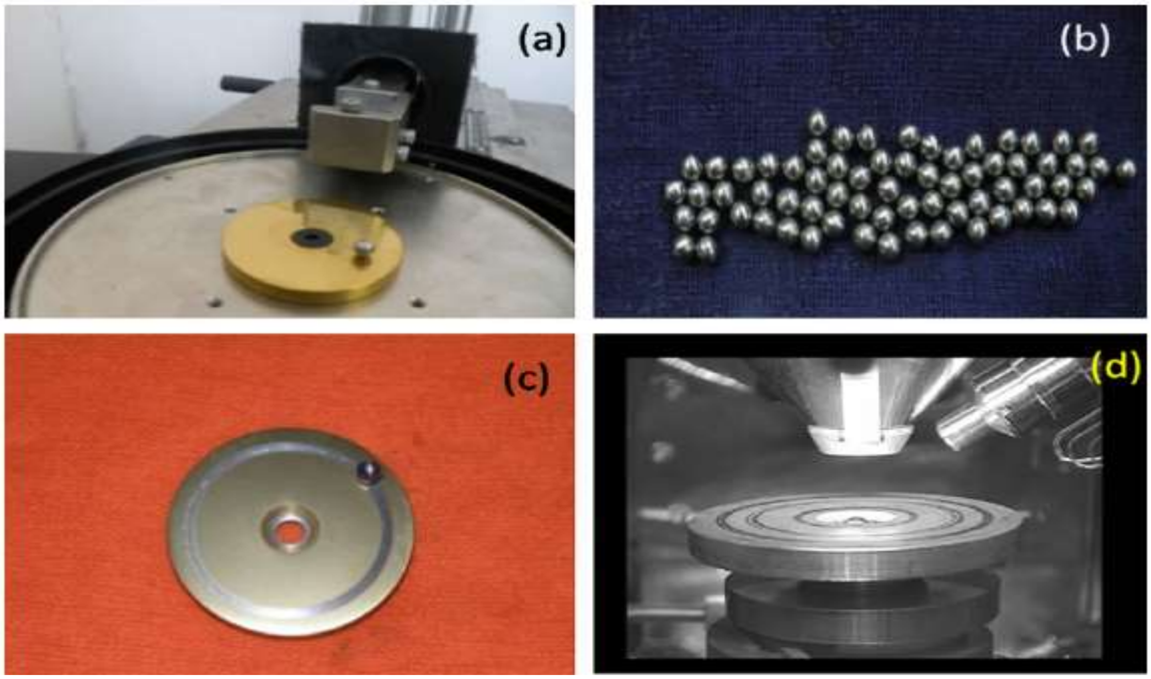
Source: (Vettivel et al., 2017; Saravanan et al., 2015 and Hsu et al., 2012).

However, the study shows that TiN have higher hardness value than the other two mentioned coated materials, although the value of AlCrN coated specimens is closer to that of the TiN coated specimen with TiAlN having the least hardness value compare to TiN and AlCrN coated specimens. The aluminium in TiAlN coating lowers its hardness value but in the coating with AlCrN, the chromium provided a higher bonding and thereby increasing the value of its hardness with particles of nitrate.

5.2 Wear Test conducted from literatures

In the study, a ball-on-disc wear tester (DUCOM, Model: Tr20LE, India) was used to conduct the wear test in conformity with ASTM: G99, DIN 50324 standards. A 6mm diameter Ti-6Al-4V alloy balls were used in the wear test experiment, and this ball which is fixed contacts the rotating disc of the TiN coated stainless steels (SS 304, SS 316L and SUS 430).

Prior to the commencement of the test, the whole specimens were thoroughly cleaned with acetone and dried, a temperature of around 27^0C was maintained and a dry sliding conditions ensured. During the test, the rotating disc of the TiN, TiAlN and AlCrN coated stainless steel (SS304) slides against the 6 mm diameter Ti-6Al-4V alloy ball (whose axis was at 90^0 to surface of the disc) with a constant rotation (rpm) for a time interval of 15min but with a varying applied load between 10-30 N. To ensure repeatability, the test was conducted three times on each sample, the images of the experimental setup and the coated samples are as shown in figures 3 and 4 respectively.



Source: (Saravanan *et al.*, 2015)

Figure 3: (a) Ball-on-disc wear setup, (b) Ti-6Al-4V alloy balls, (c) wear track of ball-on-disc and (d) wear track visualization

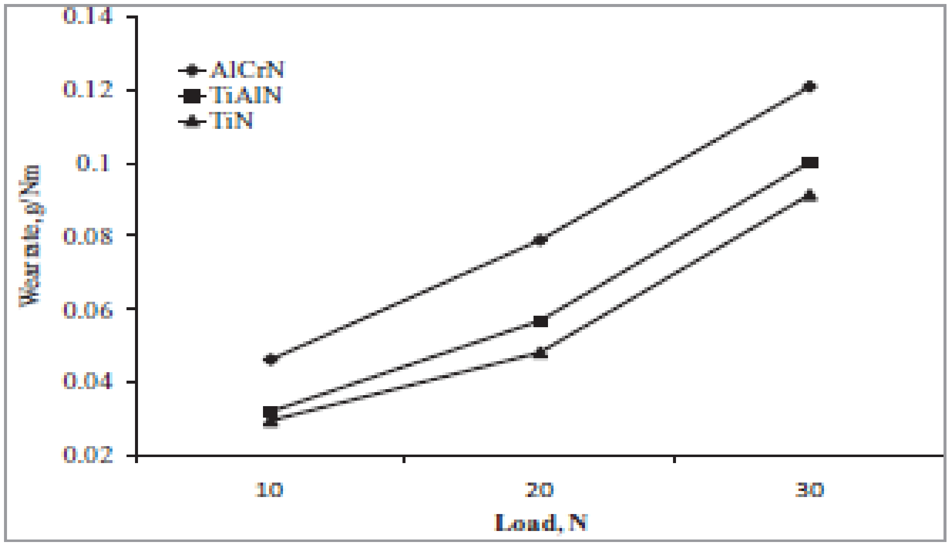
Source: (Vettivel *et al.*, 2017).

(a) (b) (c)

Figure 4: coating on stainless steel(SS304) (a) TiAlN, (b) TiN and (c) AlCrN

An electronic weighing machine with an accuracy of ±0.0001g was used to measure the mass of the wear loss of the coated discs before and after the tests. The specific wear rate was obtained from the mass loss using the relation:

Specific wear rate = weight loss / (Load applied X distance of sliding) in g/Nm. (Saravanan *et* al., 2015).

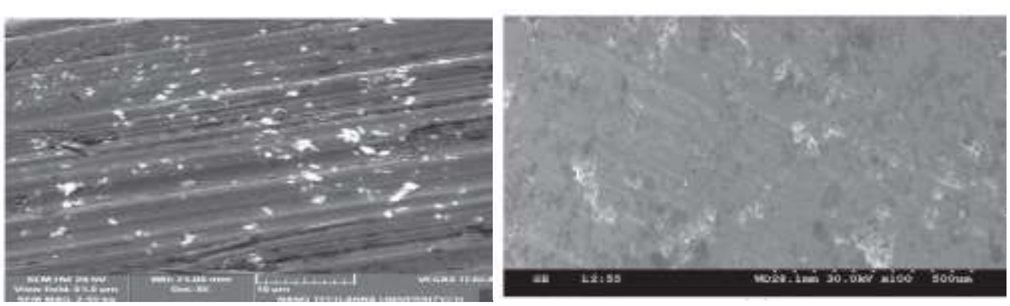


Source: (Vettivel *et al.*, 2017).

Figure 5: ***Wear rate of AlCrN, TiAlN and TiN coated on SS304***

Analysis of the worn surface from review

Figure 6 (a) and (b) below shows the SEM image of TiN coating on SS304 under a force of 20 N and 5 N respectively. This indicates the existence of mechanism micro-pits, debris and delamination due to the existence of temperature caused by the ball and disc contact due to the sliding movement of the ball. However, from results obtained it shows that TiN coating on SS304 steel gives fine grain structure and high surface hardness and remove adhesion against the ball indicating a low wear mass on TiN coatings on SS304. (Vettivel *et al.*, 2017).



(a) (b)

Figure 6: SEM image of TiN coating on SS304 under applied load (a) 20 N and (b) 5 N

6.0 Advantages and Disadvantages of Cathodic Arc Deposition (CAD) Process.

Some of the **advantages** of the cathodic arc deposition method include:

i. High level of atom ionization in the plasma.
ii. The technique can be used to deposit metallic, ceramic, and composite films.
iii. Low-processing temperatures allow for the coating of heat-sensitive substrates.
iv. Better adhesion can be achieved as a result of the intermixed reaction zone.
v. Multi-layered coatings and functionally graded compositions can easily be produced.
vi. It has the ability to enhance coating uniformity.

Some **disadvantages** of the Cathodic arc deposition method are:

i. Coating complex geometries can be difficult due to line-of-site process.
ii. Macro particles of metals and liquid droplets (1-15 µm) during flash evaporation occur

Conclusion

From the study and review conducted, cathodic arc deposition was chosen among all other PVD modification processes due to some of the advantages stated above, among which are its ability to enhance coating uniformity and its low-processing temperatures which allow for the coating of heat-sensitive substrates. The SEM image was employed to determine the existence of bonding over the specimen and the coating material. However, when TiN was coated on stainless steels SS 304, SS 316L and SUS 430; it clearly indicated that TiN is best suited for coating SS 304 Stainless Steel in order to improve its mechanical properties than applying it on SS 316L and SUS 430. It has improved hardness and a reduced wear rate, with this enhanced capability, the coated specimens can be used in the production of parts in door locking mechanisms, ball bearings, surgical scissors, etc.

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