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Synchrotron radiation characterization of magnetron sputtered WC-Co thin films on mild steel substrate

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Abstract

Mild steel offers versatile properties at lower costs. This has given the alloy a large application base in the industry. However, the increasing complexity and severity of service environments have shifted the focus of many industries to structure modification techniques, like physical vapor deposition to improve material properties and performance. Synthesis of WC-Co thin films by physical vapor deposition technology has attracted great research interest owing to the outstanding mechanical properties of the material and its potential to be utilized extreme engineering applications such as in wear-resistance, heavy cutting and excavation industries. The growth in the use of WC-Co thin films in the general mechanical industry is however slow due to lack of data on the tribological characteristics of WC-Co coated materials. Control and manipulation of synthesis parameters are of significant concern in order to tailor such material properties and performance. The focus of this paper is to, therefore, investigate the effect of Rf magnetron power and deposition temperature on the structure and sliding wear behavior of WC-Co thin film. The surface morphology and nature were acquired using x-ray photoelectron spectroscopy (XPS) and Grazing Incidence x-ray absorption spectroscopy (GI-XAS). To validate the synchrotron results, additional analysis was acquired from Scanning electron microscopy (SEM), Raman spectroscopy and surface profilometry to predict and point out optimum synthesis parameters for best properties of the film. Finally, the wear performance of the film-substrate system was determined and reported.

1. Introduction

Tungsten carbide is the leading material of interest for extreme industrial applications such as cutting, drilling and wear resistant coatings. This is because of the material’s excellent creep resistance, extreme hardness, good corrosion and wear performance [1–4]. WC also has higher elastic modulus and smaller thermal expansion coefficient as compared to other hard metal carbides. It is this property combinations and thermal stability which underlie WC the forefront material for wear resistant hard alloys especially for tool materials. Ever since the first synthesis of WC was reported by Moissan in 1892, intense studies on the W-C phase diagrams, atomic structure and properties were carried out and are still in progress. The mechanical properties of the tungsten carbide is strongly influenced by the microstructure [5].

Existing studies on the W-C systems has shown the presence of WC and W2C compounds thereby introducing complexities in the material structure due to compounds wide range of polymorphic modifications, temperature and composition differences. Most data on the W-C system is inconsistent as one phase can be designated in many ways adding more confusion to the phase-diagram data [6]. This motivated the study of WC
structure with the aim of accurately assessing the phases in RF magnetron sputtered WC thin films and its tribological applicability.

Due to the nature of these phases, synchrotron characterization techniques have to be employed in order to determine the positions of carbon and tungsten atoms, vacancies and the changes in structures under parameter variations. Synchrotron utilizes high intensity allowing for clear interaction signals and higher x-ray yields. The turnability of x-ray energy in synchrotron allows for a wide range of investigations on the samples since different techniques can be installed from the energy source. Extra sample preparation is unnecessary in synchrotron tests hence the sample microstructure is not affected as compared to using other characterization techniques such as XRD. The progressive development of synchrotron radiation since the 1940s have paved way to microstructural and phase change investigations of materials [7].

In addition, since the science and engineering of materials involves four interrelated components: processing, structure, properties, and performance, it is crucial to determine the tribological behavior of WC-Co thin film and correlate it with the thin film microstructure. In general, the tribological or wear deterioration eventually leads to material failure or loss of functionality thus, wear has large economic relevance as most maintenance and energy costs of machine related operations can be traced to losses induced during wear of mobile components [8].

2. Experimental

2.1. Sample preparation
RF Magnetron sputtering was used to deposit WC-Co thin films onto eight mild steel substrates, four sample for temperature variations (44 °C, 70 °C, 90 °C and 110 °C) at constant power and the other four samples for power variation (150 W, 200 W, 250 W and 300 W) investigation at constant temperature [9]. Pure WC-Co targets of diameter 75 mm and 3 mm thickness were sputtered onto 50 mm by 50 mm low carbon steel plates using the TF500 thin film deposition system from HHV Ltd, UK. The different substrates were sputtered simultaneously at an argon flow rate of 12 sccm, base pressure of 1.2 × 10⁻⁶ mbars and working pressure of 9 × 10⁻⁷ torr per session while varying the deposition parameters of choice as shown in table 1. The target to substrate distance within the sputtering chamber was set to 130 mm and the substrate holder rotation was set to a constant speed of 5 rpm to enhance uniform distribution of the film.

Prior to each deposition, 5 min sputter etching of the sample was performed by argon ion gas to remove any surface oxide layer and to clean any remaining contamination on the substrate and target surfaces.

2.2. Crystallographic and microstructural determination

2.2.1. X-ray photoelectron spectroscopy (XPS)
The electronic structure and elemental composition of the thin film was carried out at the Siam Photon Laboratory, beamline 3.2a (photo emission spectroscopy, PES) of the synchrotron light research institute of Thailand. The BL3.2a utilizes a grating monochromator for the undulator radiation. The samples were loaded into the chamber together with a 99.9% pure gold thin film. Clean coated samples were loaded into the chamber and secured using a double sticky carbon tape. A vacuum was created in the chamber, with a desired voltage for better image contrast selected. Elemental composition was detected by the Energy Dispersive Spectroscopy (EDS).

2.2.2. Scanning electron microscopy (SEM)
The quanta 450 SEM was used to study WC-Co the film microstructure. Clean coated samples were loaded into the sample holder and secured using a double sticky carbon tape. A vacuum was created in the chamber, with a desired voltage for better image contrast selected. Elemental composition was detected by the Energy Dispersive Spectroscopy (EDS).
x-ray Spectroscopy (EDS) for different phases of the images and reported in terms of weight percentages. For detailed SEM operations, refer to [10].

2.2.3. Surface roughness
The Bruker contour GT profilometer was used to determine the roughness of the samples. This equipment uses coherence scanning interferometry to distinguish differences in surface profiles. Cleaned samples were loaded into the machine, surface profiles and respective images of the surface were captured. In-depth information of the equipment and method refer to [11]. The profilometer used reports roughness properties in terms of the S parameter rather than the conventional R parameter. The S parameter gives better surface profile predictions due to its 2D analysis of the surface as compared to the 1D line analysis used in the R parameters.

2.3. Wear test
Wear analyses were conducted using a multifunctional tribometer (Rtec-instruments, San Jose, CA, USA). The equipment can perform tribology, indentation, scratch and mechanical tests. It has inbuilt imaging modules such as interferometer, microscopes, AFM and Raman spectrometer which can be used to produce micrographs and surface profiles of the wear scar. The experiment was conducted on a ball-on-flat mode at room temperature under dry (unlubricated) wear conditions. The wear test parameters used in this study are shown in table 3.
3. Results and analysis

3.1. Crystallographic and microstructural analysis

3.1.1. SEM

The SEM microstructures and respective EDS analysis are shown in figures 2 and 3. As the deposition temperature and the RF power is increased, it is observed from the micrographs that the number of tungsten carbide phases are increased. This is validated by the respective EDS analysis, there is increased elemental tungsten and carbon detection as temperature is increased. This suggest that more crystallization and formation of the WC thin film is achieved at elevated temperatures and higher deposition power.

3.1.2. Surface roughness

Table 4 shows the vales of the roughness properties of the sample surfaces. The reported roughness parameters include the arithmetic mean of absolute height (Sa), kurtosis of the topography height distribution (Sku), skewness of topography height distribution (Ssk), maximum peak height (Sp) and maximum peak height (Sv). Three dimensional (3D) visuals of surface roughness on different sample surfaces is presented in figures 4 and 5. From the surface images, the increase in temperature decreases the surface roughness. This trend has been observed for several thin films and is attributed to the evolution of the microstructure in the structure zone model from zone 1 to zone T [12] due to the growth of grains with preferred orientation dictated by increased adatom mobility and grain boundary diffusivity. Changes in the surface roughness for the power variation is not very significant which might be due to the temperature employed which was not optimized due to the capacity of our equipment.

Figure 2. Surface SEM images surface for deposition temperature (a) 44 °C (b) 70 °C (c) 90 °C (d) 110 °C and their respective EDS spectra (e)–(h).

Figure 3. Surface SEM images surface for deposition at RF powers (a) 150 W (b) 200 W (c) 250 W (d) 300 W and their respective EDS spectra (e)–(h).
3.1.3. XPS
XPS studies were conducted on the tungsten carbide thin film to determine the electronic structure of the nanoparticles during variation of synthesis parameters. The data-set of these XPS results for power and temperature variations are shown in figures 6 and 7 respectively. Prominent peaks were observed for oxygen, carbon and tungsten as well as small traces of cobalt. Tungsten peak is observed at aa of cobalt metal as a binder for the WC. Although the spectra are very similar for all varying, the oxygen and carbon peaks differs in intensity. High intensities are observed for films deposited at Rf power 250 W and again in the spectra of substrate temperature 90 °C. The different intensity values for the oxygen and carbon as well as the unidentified peak observed at 240 eV (90 °C spectrum) does not follow trend hence can be attributed to surface contaminations which could have taken place anytime from sample preparation prior to deposition to the handling of samples during the tests.

Table 4. WC thin film surface roughness properties.

| Sample | Sa (nm)   | Ska | Sp (nm) | Ska | Sq (nm) | Ssk | Sv (nm) |
|--------|-----------|-----|---------|-----|---------|-----|---------|
| 150 W  | 433.7 ± 29| 8 ± 2| 4479.5 ± 171| 583.6 ± 32| −1.2 ± 0.4| −6012.67 ± 791 |
| 200 W  | 204.1 ± 54| 62.5 ± 25| 4349.8 ± 109| 313.6 ± 75| −2.23 ± 0.5| −7053.9 ± 1902 |
| 250 W  | 484.2 ± 27| 9.2 ± 2| 4873.4 ± 345| 658.5 ± 41| −1.4 ± 0.3| −6397 ± 899 |
| 300 W  | 379.6 ± 15| 5.4 ± 0.1| 4630.8 ± 294| 497.6 ± 18| −0.52 ± 0.1| −4848.9 ± 496 |
| 44 °C  | 136.6 ± 24| 89.5 ± 40| 3808.2 ± 549| 201.1 ± 23| 1.2 ± 1.9| −8583.5 ± 796 |
| 70 °C  | 263.2 ± 31| 22.6 ± 4| 4456.8 ± 174| 429.4 ± 66| −2.5 ± 0.9| −7487.6 ± 1317 |
| 90 °C  | 252.2 ± 21| 5.8 ± 0.1| 4128 ± 369| 337.8 ± 26| −0.26 ± 0.1| −4402.9 ± 138 |
| 110 °C | 310.4 ± 2 | 5.49 ± 0.3| 4351.5 ± 133| 402.23 ± 2| −0.124 ± 0.09| −5518.66 ± 1232 |

3.1.4. GI XAS
Grazing incidence XAS was used to probe the local electronic structure of WC thin films on mild steel substrates. Although phases of the film were obtained, the thickness and the near surface layer could not be acquired due to the high surface roughness of the sample. The high surface roughness resulted in reduced signals brought about by variations of x-ray amplitude due to random changes of incident light. The changes in local incident angles produced large integrated volume of scattering and thus higher elastic and inelastic contribution to the noise.

Figure 4. Three-dimensional surface roughness images for samples deposited at substrate temperatures (a) 44 °C, (b) 70 °C, (c) 90 °C and (d) 110 °C.
Background correction, levelling and energy calibration was performed to normalize the spectrum such that the baseline of the amplitude function of the edge are near zero before interpreting the data. Figure 8(a) depicts the L3 edge WC spectra for thin films deposited at 110 °C and 250 W, W foil was used as a standard material. Additionally, the edge shifts were determined from the maximum of the first derivative of the spectra as shown in figure 8(b). The WC films have the same oxidation states but are not metallic/solid in nature as depicted in figure 8(b) by the shift to the right from the W foil peak. To investigate the local coordination environment and atom positions within the carbides, the tail of the spectra was Fourier transformed giving plot of FT magnitude versus radial distance. From the plot’s contributions of W-C and W-W coordination are observed at relative distance of 1.4 Å and 2.3 Å.

3.2. Tribological performance

3.2.1. Coefficient of friction (CoF)

The friction behavior of the WC film was determined by measuring the coefficient of friction for all samples at varying deposition parameters, temperature and power. The frictional behavior was reported in figures 9 and 10.
Figure 7. XPS spectra of WC/Co thin film deposited at varying temperature.

Figure 8. WC L edge GI-XAS spectra for W foil and WC thin films. (a) Normalized GI-XAS spectra, (b) 1st derivative of normalized spectra showing absorption edge and (c) Fourier transform magnitudes [9].

Figure 9. Influence of deposition temperature on the coefficient of friction.
Figure 10. Influence of deposition power on the coefficient of friction.

Figure 11. Cross section of wear scar for deposition temperature variation; (a) 44 °C, (b) 70 °C, (c) 90 °C and (d) 110 °C under constant 10N load.

Figure 12. 3D images of wear scar for deposition temperature variation; (a) 44 °C, (b) 70 °C, (c) 90 °C and (d) 110 °C under constant 10N load.
respectively. As the deposition temperature is increased, the coefficient of friction increases. Similarly, coefficient of friction increases as the rf power increases (see figure 10). This behavior is expected, since the roughness and increasing crystallinity of the film with temperature would exert higher resistance to the sliding motion. The fluctuation of the CoF observed is due to the following:

(i) The continuous breakage and detachment of the hard tungsten carbide layer
(ii) The formation and breakage of the oxide layer on the fresh peeled surface producing debris which in turn affect the friction behavior of sliding surfaces.

As observed, the deposition temperature of 110 °C and rf power of 300 W displaced the highest values of CoF, and therefore higher wear resistance followed by 90 °C and 250 W. the least friction resistance was recorded for the 150 W sample.

3.2.2. Wear track and profile
The wear morphology for the coated substrates shows evidence of abrasive wear mechanism due to the profound ploughed groove observed (figure 12). This is expected owing to the soft mild steel substrate surface being squeezed out of contact region due to interaction with the hard E52100 alloy steel ball used. However, as the deposition temperature is increased the size of the groove is decreased (figure 11). This implies that an increase in deposition temperature increases the wear resistance of the material, this is might be due either the hardening of the substrate by the heat induced or the increased formation of the hard WC layer onto the relatively softer mild steel surface. The corresponding 3D images of the wear scar depicted in figure 12 shows decrease in wear degradation as the temperature in increased. This is attributed to the increase in crystallization and thickness of the hard WC-Co thin film on the soft mild steel surface making it less susceptible to wear.

On the basis of the measured wear scar geometries, the wear volume is calculated and presented in table 5 and figure 13. As expected, the wear volume decreases with increasing temperature and power. The calculated wear volume is governed by the following equation [14]:

![Figure 13. Influence of deposition parameters on wear volume.](image)

Table 5. Wear scar geometries for the determination of wear volume.

| Sample (Parameter) | Wear depth (μm) | Wear width (μm) | Wear volume (μm³) |
|-------------------|-----------------|-----------------|-------------------|
| WC 1 (44 °C)      | 0.585           | 244.1           | 13694             |
| WC 2 (70 °C)      | 0.392           | 281.7           | 12221             |
| WC 3 (90 °C)      | 0.357           | 262.9           | 9694              |
| WC 4 (110 °C)     | 0.199           | 317.4           | 7876              |
| WC 5 (150 W)      | 0.41            | 225.4           | 8183              |
| WC 6 (200 W)      | 0.345           | 276.1           | 10332             |
| WC 7 (250 W)      | 0.235           | 281.7           | 7326              |
| WC 8 (300 W)      | 0.105           | 289.2           | 3450              |
Where $V$ is the wear volume, $D$ is the ball diameter, $d$ is the wear scar width and $h$ is the scar depth.

4. Conclusion

XPS was successfully used to investigate the electronic structure and phase compositions of the WC-Co thin film for different deposition parameters used. Crystallographic and microstructural analysis confirmed the presence of W, C and O phases in the film as well as their variation with respect to different sputtering parameters. Surface roughness of the film increases with increasing temperature and rf power to 250 W then declines. The film structure is generally the same for all deposition rf powers used, however increasing temperatures leads to higher levels of crystallinity of the WC phases and hence improved wear performance. Wear volume of the samples is lower at both higher deposition temperatures and higher rf power settings.

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References

[1] Stadler S, Winarski R P, Ederer D L, Maclaren J, Van Ek J and Moews A 2001 *The Electronic Structure of Tungsten Carbide* (Calif: Long Beach)
[2] Kurlov A S and Gusev A I 2006 Tungsten carbides and W–C phase diagram *Inorg. Mater* **42** 121–7
[3] Fang S, Llanes L and Bähre D 2017 Wear characterization of cemented carbides (WC–CoNi) processed by laser surface texturing under abrasive machining conditions *Lubricants* **5** 20
[4] Tavsanoglu T, Begum C, Alkan M and Yucel O 2013 Deposition and characterization of tungsten carbide thin films by DC magnetron sputtering for wear-resistant applications *JOM* **65** 562–6
[5] Yousfi A 2016 Microstructure Development of WC–Co Based Cemented Carbides During Creep Testing PhD Thesis Physics, 2019
[6] Kurlov A S and Gusev A I 2006 Phase equilibria in the W–C system and tungsten carbides *Russ. Chem. Rev.* (https://doi.org/10.1070/RC2006v075n07ABEH003606)
[7] Suwanpinij P 2016 The synchrotron radiation for steel research *Adv. Mater. Sci. Eng.* **2016** 2479345
[8] Paulo Davim J 2013 *Tribology in Manufacturing Technology* (Paris: Springer) I
[9] Phiri E T, Oladijo R R, Nakajima O P, Rattanachata H and Akinlabi A 2019 Structural and morphological dataset for rf-sputtered WC-Co thin Films using synchrotron radiation methods *Data in Brief.* **25** 1–18
[10] Dufek M and Haynes M 2003 The Quanta FEG 200, 400, 600 User’s Operation Manual chapter 1 Safety and Handling
[11] Larkin P 2011 IR and Raman spectroscopy. *Principles and spectral interpretation* ISBN: 978-0-12-386984-5
[12] Hochstrasser-Kurz S et al 2008 ICP-MS, SKPFM, XPS, and Microcapillary Investigation of the Local Corrosion Mechanisms of WC–Co Hardmetal *J. Electrochem. Soc.* **155** C415
[13] Waychunas G A 2002 Grazing-incidence x-ray absorption and emission spectroscopy *Rev. Mineral. Geochemistry* **49** 267–315
[14] Hsu S M and Shen M C 2005 *Wear Mapping of Materials, Wear—Materials, Mechanisms and Practice* (New York: Wiley)