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Tungsten carbide thin films Review: Effect of deposition parameters on film microstructure and properties

R.R. Phiri[a,] O.P.Oladijo[a,b*] , E.T.Akinlabi[b]

[a] *Department of Chemical, Materials and Metallurgical Engineering, Botswana International University of Science and Technology, Palapye Private Bag 0016, Botswana*
[b] *Department of Mechanical Engineering Science, University of Johannesburg, Auckland Park,Kingsway Campus, Johannesburg, South Africa*

Abstract

In this work, the property of physically deposited thin WC films with respect to deposition parameters and conditions reported by previous researchers is being reviewed. The study provides deeper insight to the effect of deposition parameters as well as preliminary selection of parameters for optimization of the WC film preparation for improved tribological properties for industrial applications. Not much studies of WC thin films deposited though PVD methods have been reviewed hence the significance of this review. This brief review references a broad range of published work on WC thin films. The work focuses on the structural properties of the thin film and application emphasis is on wear, corrosion and hardness properties. The film microstructure, wear behavior and temperature effects are typically explained by the Thornton zone model.

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Keywords: Tungsten carbide; Deposition parameters; Wear; Thornton zone model

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1. Introduction

Cemented carbides such as tungsten carbides (WC) are the leading materials of interest in extreme engineering and technological applications such as in wear-resistant coatings, serious cutting and drilling industries, aerospace and marine [1-3]. This is due to their excellent mechanical and specific physical properties such as high melting point , near-impeccable hardness, chemical resistance, high thermal stability , low coefficient of friction and good electrical conductivity[4]. Other notable feature of WC is the extremely high modulus of elasticity (just above

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*Corresponding author.
E-mail address: seyiphilip@gmail.com

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700GNm^{-2}) , value which is only exceeded by diamond[5]. These unusual properties are achieved through a combination of a hard and brittle phase in a ductile and deformable binder. As a result synthesis of nanocrystalline tungsten carbide coatings offers a great opportunity to develop such properties especially for tribological applications.

Table 1.Typical Properties of WC

Density	**Young's modulus**	**Poisson's ratio**	**Melting point**	**Boiling point**	**Thermal conductivity**
15.63 g/cm	700 Gpa	0.2	2830 °C	6000 °C	110 W(m,K)

Tungsten carbide exist as a simple hexagonal structure with lattice parameters a=0.291nm and c=0.284nm[6]. The tungsten atoms occupies the 0, 0,0 position while the carbon atoms encloses the tungsten and occupies positions 1/3, 2/3, ½ or 2/3, 1/3, ½ resulting in non-centrosymmetric crystal structure shown[7] in figure 1.

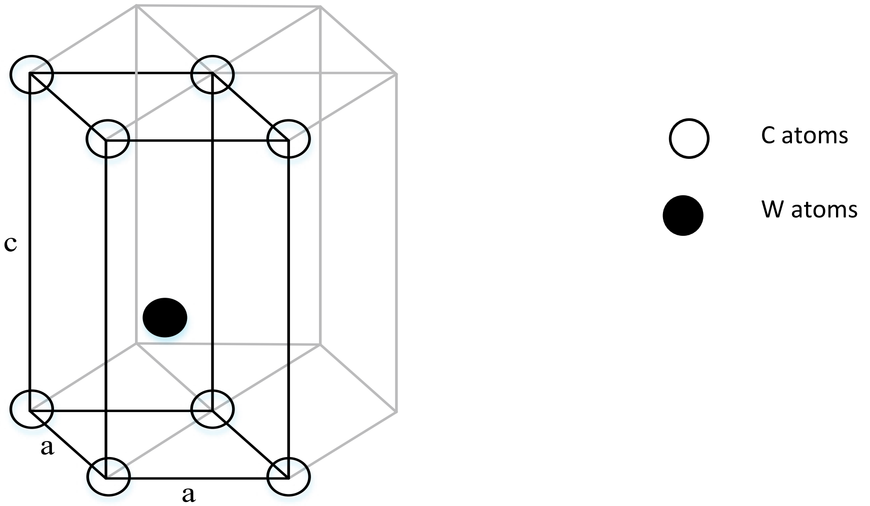

Figure 1. Tungsten carbide crystal structure.

Cobalt is highly preferred over other materials as a binder for WC due to its excellent adhesive effect and wetting of WC in the solid state[8]. Tungsten carbide-cobalt coatings continue to receive popularity in research due to successful deposition have been achieved using a broad scope of substrates materials such as stainless steel , mild steel, silicon , and aluminum alloys[2,8]. Aviation industries are considering tungsten carbide coatings as the best alternatives of replacing hard chromium coatings for wear protection of landings gears and other aircraft air frame components.

The deposition of this carbide can be achieved through physical vapor deposition (PVD) and chemical vapor deposition (CVD) methods depending on the specific application of interest. CVD deposits thin films onto materials though various chemical reactions while PVD deposit thin films through physical techniques mainly sputtering and evaporation. PVD method is highly preferable to CVD due to a much higher adhesion, lower temperatures and since it is environmentally friendly. As such, there exist a considerable studies on physical deposition of thin WC films. A diagram illustrating the factors contributing to the thin film structure is shown in figure 2.

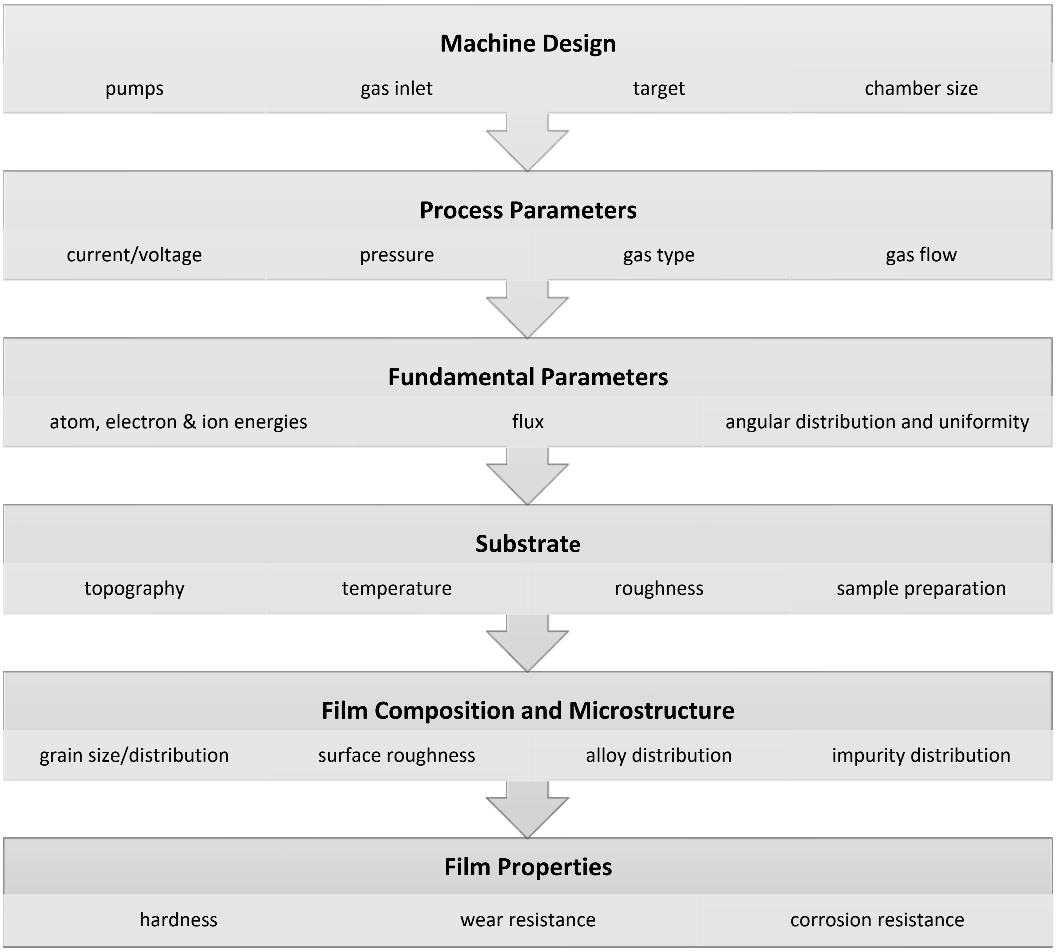

Figure 2. Factors contributing to the thin film structure.

2. Properties of WC thin film coatings

It is crucial to understand the structural features of WC thin film in order to fully understand and assess their effectiveness for different applications. There are several studies on the structural properties of tungsten carbide coatings [4, 5, 9-12]. The results show that there is a link between PVD WC film microstructure, tribological properties and mechanical properties as depicted in Figure 3.

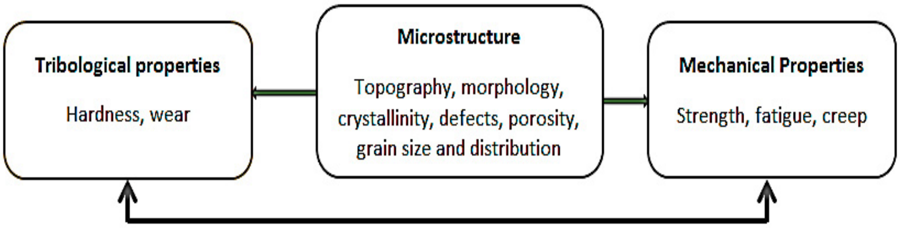

Figure 3. Flow diagram of the correlation of WC thin film microstructure and tribo-mechanical properties.

The mechanical and tribological properties of WC are significantly attributed to their microstructure [13, 14]. For instance, the impact of grain size on hardness and material strength can be derived from the hall petch effect. The grain distribution contiguity and the volume fraction of the binder also play their roles to impact film properties. In WC-Co composites, the factor with the most profound influence on the hardness is the volume fraction of the carbide phase since it is very hard whist the binder is soft and ductile[14].

Most microstructural studies are conducted using scanning optical microscopy, electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy and x-ray diffraction (XRD) to acquire the morphology of the film. The surface topography of the thin films involves techniques such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM). A typical cemented carbide microstructure acquired by SEM is shown in figure 4. The lighter regions are grains of hard tungsten carbide (WC) bound together by darker colored thin layers of cobalt.

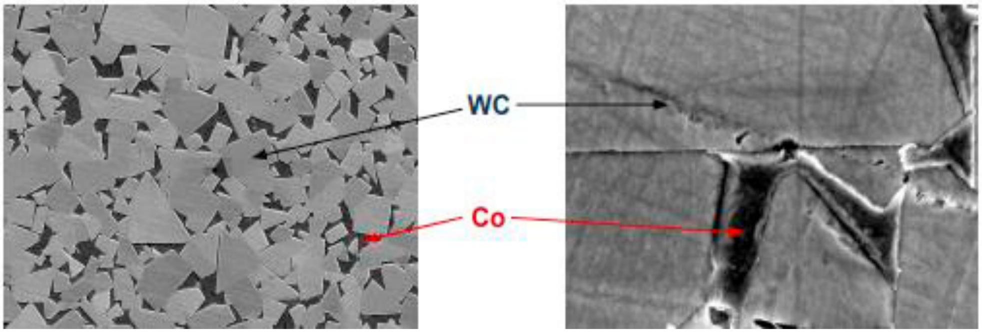

Figure 4. Typical WC-Co SEM micrograph[15].

3. Effect of deposition parameters

Due to the non-equilibrium nature of vapor deposition techniques used in thin films, the resulting properties and microstructure of the thin film are highly influenced by deposition parameters such as temperature, gas pressure, ion bombardment, and so on [16]. An overview of factors influencing the microstructure of WC thin films from previous studies is presented in Table 2. It is therefore very important to consider these factors carefully when tailoring WC film for wear and corrosion application.

Table 2. Factors influencing microstructure of physically deposited WC thin films

Reference	Film/substrate	Deposition method	Factors reported	findings
[4]	W/ Steel substrate	Rf magnetron sputtering	-Effect of deposition temperatures on the thin film -Influence of heat treatment on the evolution of the film microstructure	-For temperature range of 500-800°C no formation of tungsten carbide phases was observed -WC phases can be obtained from the coated samples by annealing at temperatures greater than 900°C
[5]	WC+Ni/ stainless steel & glass substrate	Non-reactive d.c magnetron sputtering	-Deposition temperature -Choice of substrate	-WC_x formation is a function of substrate temperature. -Hardness for different substrates is non-significant
[10]	Nano WC/ austenitic 316 stainless steel	DC magnetron sputtering	-The influence of coating thickness on the wear performance of the film	-An increased microhardness was achieved (10 times greater than that of the substrate alone. -Better coating performance attained using nano size WC particles than micro size WC particles. -Coated samples achieves better tribological properties than the untreated substrate.
[11]	WC-Co/ Aluminum alloy	EBPVD	-Effect of C_2H_2 on the microstructure of the WC thin film	-The film deposited in the presence of C_2H_2 indicated more nano-metric phases. -Hardness of coating containing WC and W_2C phases was twice of the one with only Co and C phases.
[17]	WC-NiCrBSi/ AISI steel	HVOF	-Effect of post treatment	-Evidence of phase transformation observed. -Attenuation of residual stress gradient indicated after heat treatment

4. Formation of structures

Structure zone models (SZM) has been used to classify structural morphologies of thin films deposited under low mobility conditions. SZM are based on normalized temperatures T/Tm which describes the thermally induced adatom mobility and consist of three main zones namely zone 1, transitional zone T and zone 2[18, 19]. Deposition/substrate temperature is denoted by T, Tm is the melting point of the material. Zone 1 is characterized by fine, porous and even amorphous microstructure due to low adatom mobility brought about by low substrate temperatures. The transitional zone T comprises of coarse structures in a preferred crystallographic orientation and zone 2 where substrate temperatures are very high, coarser/columnar structures are formed due to grain growth and recrystallization processes. The material properties such as hardness and strength can therefore be extrapolated from the type of microstructure obtained, for instance, high hardness is expected from zone T due to the hall petch effect of fine particles and moderate porosity as shown in Figure 5.

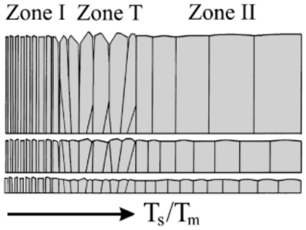

Figure 5.SZM schematically representation of microstructural evolution of a thin film as a function of normalized temperature [20]

5. Conclusion

It was established that the substrate conditions, process parameters and post-processing treatment have a significant influence on the thin film microstructure and the properties of the thin films of WC-Co. the Thornton zone model is used to describe the film microstructure evolution taking into account the deposition temperature and melting temperature of the material involved. WC-Co films possess a great potential application in high wear susceptible industries such as in turbine coatings and aerospace bearings, hence it is necessary to have a better understanding of the film microstructure and factors affecting it.

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