PROPERTIES AND APPLICATION OF B₄C COATS WITHIN THE CHEMICAL VAPOUR DEPOSITION

Assoc. Prof. Dr.Eng. Stela Constantinescu, Drd.eng. Lucica Orac

University “Dunarea de Jos “ of Galati
Faculty Metallurgy and Science Material
Street Domneasca. No.111, Galati, 800008, Romania
E-Mail : stela.constantinescu@email.ro

Abstract

Chemical vapour deposition (CVD), is a process where by the surface properties of a metal or non-metal are altered by the generation of a layer with special chemical and physical properties. This alteration in surface properties is produced by subjecting the substrate materials to a single gas or a combination of gases at elevated temperatures. One type of C.V.D. process is carried out in a heated retort and the chemical reactions that occur are initiated in the space around or on the surface of the substrate.

The ultimate properties of the coatings are further dependent on the nature and composition on the substrate. Therefore, in theory a vast number of substrate coating combinations is possible, each ultimately with its own set of physical and chemical characteristics. Due to overheating and granulation growth by recrystallization an acute decrease in the bending ultimate strength occurs. Under or decarburated materials also containing fragile phases feature poor ultimate strength. Hardness is affected by microporosity, granulation of WC phase, purity and composition, extent of homogenization of the liquid and carbons. The excessively high sintering temperature results in a lower density which further negatively affects the mechanical strength. The magnetic saturation increases with higher Co contents; it is worth mentioning that bigger grain alloys have a force considerably lower than that of fine grain ones.

1. INTRODUCTION

The experiments conducted to obtain thin layer of carbure by the vapor chemical deposition method have followed an original path to make B₄C directly in the working room thus avoiding the import of these hazardous substances. The BCl₄ is obtained in the heat treatment chamber by adding chloride acid vapors passed over the incandescent pure boron. The B₄C coated plates feature higher endurance capabilities than those uncoated for the same cutting speed both for steel and white cast iron. The experiments on the widia thin layer plates during cutting show that endurance increases by 3 to 5 times as compared with the uncoated plates endurance [1].

The widia plates coating with thin B₄C layers entirely suppresses the inconveniences of a relatively rough topography of the common sinterized carbides while preserving the adequate material mechanical strength.

The layer begins loosing its tenacity if its thickness increases considerably exceeding the thickness 10 μm mainly due to the lower strength characteristics. This together with the increase in the inner tensions results in cracks and breakings in the layers [2].

The thickness of the deposit layer increases with the time of exposure to the working temperature. The final structure of the deposited layer is given by various effects such as, the adsorption of impurities, the incorporation of gaseous, the co-deposition of another elements, the crystallization, etc. The ultimate properties of the coatings are further dependent on the nature and composition on the substrate.
2. EXPERIMENTAL RESEARCHES

To obtain thin $\text{B}_4\text{C}$ layers, plates of type S.N.U.N.15.04.08, K20 and T.P.U.N. 22.04.08, P30 were made. The thickness of the boron carbide layer was determined by the microscope and the Kalotest device. The operation of the latter is based on a housing which cuts the deposited $\text{B}_4\text{C}$ layer [3].

The phases coming from the vapor which contain the diffusion element and the carrying gas pass through three main stages; vapor formation, transportation and deposition. These stages differ in terms of chronology and make up a whole process. According to its essence, such a process is a chemical transport reaction expressed by the solid substance interaction (A) with the gas or vapors (B). In this case only gas products are obtained [4].

![Figure 1. The chart of CVD method: 1. gas source; 2. flow gauges; 3. evaporator; 4. cyclone; 5. pump; 6. reactor; 7. oven; 8. gas gauge; 9. thermocouples; 10. fan.](image)

Upon conveying the gas, two processes are possible: isotherm, without forced flow; anisotherm, with forced flow. With the latter process, saturation with gas diffusion by contact-free procedure is reported.

Formation of $\text{B}_4\text{C}$ is the result of some heterogenous reactions where $\text{BCl}_4$ fed as vapors into the reaction room reacts with $\text{N}_2$ and $\text{H}_2$ according to the following equations:

\[
\text{BCl}_2 + 2 \text{HCl} \rightarrow \text{BCl}_4 + \text{H}_2 \quad (1)
\]

\[
\text{BCl}_4 + \text{H}_2 + \text{CH}_4 \rightarrow \text{B}_4\text{C} + 4\text{HCl} + \text{H}_2 \quad (2)
\]

Reactions can be regarded as starting reaction and is crucial for the process velocity as a whole. Boron tetrachloride, a shortage and imported material with an innovative production solution for it, directly in the working area. The reactor used may be either vertical in layout (see Figure 1).

In case of chemical deposition from vapour taking place into a tubular continuous reactor, a conveying gas containing the reactive species is carried over the under layer [5].

At the surface of the under layer, the reactive elements suffer a series of chemical reactions leading to formation of products. A part of these reactions products form the deposit layer and the other goes back to the gas flow.
3. RESULTS AND DISCUSSIONS
The thickness of the layer deposited increases with the time of exposure at the working temperature. The depth of the layers in three cutting plates was determined. Micro-hardness was determined by Neophot microscope. Cutting plates of thin B4C layers of 6.0, 8.0 and 10.0 μm depths were also tested [6]. The Vickers micro-hardness test is carried out in compliance with loads of 0.0098 to 9.8 N. Micro-hardness is calculated by the relation:

$$HV = \frac{2F \cdot \sin \frac{136}{2}}{d^2} = 1,854.4 \cdot \frac{F}{d^2} \quad (3)$$

where: F-expressed in kgf/mm²; d- average trace diagonal ;

The results obtained are given in the table no. 1.

Table 1
The Vickers micro-hardness

<table>
<thead>
<tr>
<th>No of tests</th>
<th>Time of exposure, [s]</th>
<th>No divisions</th>
<th>Diagonal d, [μm]</th>
<th>$d^2$ [μm²]</th>
<th>Load [N]</th>
<th>Micro-hardness HV0.05 [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>15</td>
<td>2.15</td>
<td>0.78</td>
<td>0.62</td>
<td>0.001</td>
<td>30189</td>
</tr>
<tr>
<td>2.</td>
<td>15</td>
<td>3.02</td>
<td>1.10</td>
<td>1.23</td>
<td>0.002</td>
<td>30145</td>
</tr>
<tr>
<td>3.</td>
<td>15</td>
<td>4.83</td>
<td>1.75</td>
<td>3.08</td>
<td>0.005</td>
<td>30100</td>
</tr>
<tr>
<td>4.</td>
<td>15</td>
<td>6.89</td>
<td>2.48</td>
<td>6.16</td>
<td>0.010</td>
<td>30075</td>
</tr>
<tr>
<td>5.</td>
<td>15</td>
<td>1.78</td>
<td>3.92</td>
<td>15.42</td>
<td>0.025</td>
<td>30038</td>
</tr>
<tr>
<td>6.</td>
<td>15</td>
<td>1.52</td>
<td>5.55</td>
<td>30.90</td>
<td>0.050</td>
<td>30000</td>
</tr>
</tbody>
</table>

Micro-hardness is not a constant, as Vickers hardness, in spite of the prints geometry similarity , but it decreases with higher test load depending on the print size. The micro-hardness samples show that we have B4C, the value HV0.05 =30000 MPa (about 30000 N/mm² ) in good agreement with the literature data [7].

**Figure 2.** Variation of hardness, breaking bending resistance and compression resistance of the alloys WC-Co

**Figure 3.** The metallographic aspect and of the alloy of 80% WC ,12% B₄C, 8%Co x 1500
As to hardness, there is a tight correlation between the Co content and the WC-Co alloys produced under identical conditions. As shown in figure 2, hardness decreases with the increase in the cobalt content [8].

Hardness reaches max values with the optimum sintering temperature and then it decreases as a result of carbon recrystallization and alloy super-sintering. An excessive sintering time, even if the temperature is optimum, has the same effect, i.e., lower hardness.

With the microstructure of the alloys of type WC – B₄C – Co, as compared with those studied, new phases occur in WC and Co. These are solid solutions in B₄C - WC where the amount of WC dissolved into B₄C is higher or lower. In these cases, the metallographic attack combined with the heating of the sample subject to the attack clearly and distinctly underlines the alloys phases. Figure 3 shows the metallographic aspect of the alloy of 80% WC, 12% B₄C, 8% Co. Under this structure, the brilliant angular crystals are of phase WC, the gray spherical element is the solid solution while the element in the dark carbon grains is the sintering bondage - the cobalt [9].

The structure becomes even more complex with the pseudo-alloys of type WC – B₄C – Co.

Depending on the temperature and reciprocal solubility conditions, a number of solid solutions of B₄C - WC can form; they depend on the WC and B₄C solubility and reciprocal solubility. Under structural equilibrium conditions, both the WC phase and the homogenous solid solutions along with the cobalt can form in the structure. Under practical sintering conditions, the equilibrium is not always achieved and the structure frequently reveals solid non-homogenous solutions of B₄C-WC, some richer in B₄C.

Measurements were carried out on B₄C coated plates of various thickness of 6.0, 8.0, 10.0 μm. The thickness of the thin layer increases with the exposure time at the working temperature as illustrated in figure 4.

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The experiments conducted to obtain thin layer of carbide by the vapor chemical deposition method have followed an original path to make B₄C directly in the working room thus
avoiding the import of these hazardous substances. The B\textsubscript{4}C is obtained in the heat treatment chamber by adding chloride acid vapors passed over the incandescent pure borum Figure 6 shows the XRD pattern of carbide thin layer deposed on widia substrate. The thin layer is not B\textsubscript{4}C pure phase, diffraction peaks of WC are also present, indicating the chemical interaction between the substrate and the atmosphere during chemical vapor deposition process. High intensity of the diffraction peaks of WC crystalline phase from widia substrate indicates that the B\textsubscript{4}C coating consists of very thin layer.

Lab-scale systems have been designed with the possibility of use at industry scale for small production. The support temperature was established at about 1170\textdegree C so that the B\textsubscript{4}C can provide a suitable deposition of the thin B\textsubscript{4}C layer [12].

Very good results were obtained for three hours exposure times leading to optimum layer thickness of 6.0 \textmu m.

![Figure 6. XRD pattern of B\textsubscript{4}C thin layer deposed on widia substrate](image)

The B\textsubscript{4}C coated plates feature higher endurance capabilities than those uncoated for the same cutting speed both for steel and white cast iron. The experiments on the widia thin layer plates during cutting show that endurance increases by 2 to 4 times as compared with the uncoated plates endurance.

The layer begins losing its tenacity if its thickness increases considerably exceeding the thickness 10.0 \textmu m mainly due to the lower strength characteristics. This together with the increase in the inner tensions results in cracks and breakings in the layers.
REFERENCES


