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THE DIFFERENT PRACTICAL APPLICATION OF NIOBIUM CARBIDE COATINGS ELABORATED BY CVD PROCESS

Stela CONSTANTINESCU
"Dunarea de Jos" University of Galati, Romania
e-mail: stela.constantinescu@email.ro

ABSTRACT

In this paper, the different application of niobium carbide coatings onto hard carbide substrate was investigated using scanning electron microscope (SEM), X-ray diffractometer (XRD) and micro-hardness. The paper conducted a study on the friction coefficient and wear resistance as a function of load friction couple, for a series of NbC type thin layers; micro-hardness value measured in the coating layer was 29.800 MPa.

Scanning Electron Microscope was used to investigate the coating morphology and interface structure. X-ray mapping was also performed to characterise the elements in a semi-quantitative analysis. A Dron X-ray diffractometer with Mo Kα radiation operating was used for phase(s) identification. Adherence was assessed using a layer fingerprinting method using Rockwell hardness testers. CVD NbC coatings usually show only moderate or even poor corrosion protection for hard carbide substrates.

KEYWORDS: decorative, thin layer, wear resistance, adherence, corrosion

1. Introduction

Niobium carbide coatings find extensive applications in tribological, mechanical and even decorative applications. CVD, NbC coatings usually show only moderate or even poor corrosion protection for hard carbide substrates. The poor corrosion performance is not due to the intrinsic corrosion behaviour of the carbide coating itself. It results from small structural defects, pores and crack formed during or after deposition, which act as channels for the corrosion of substrate. We investigated the corrosion tests in water of niobium carbide coatings elaborated by CVD process.

If the vapour chemical deposition takes place within a tubular continuous reactor, a gas carrying the reacting species is passed over the sub-layer. At the sub-layer surface, the reacting elements undergo a number of chemical reactions leading to product formation. Part of the products are deposited on the sub-layer and part of it goes back to the gas stream [1, 2].

The thin layers developed inside of the NbC, were frequently used, when we talk about multi functionality. This aspect is correlated with the special properties of the films, which gives to the products, in the superficial area, performant properties and the possibility for tuning properties by variation of compositional ratio NbC.

From tribological point of view, the NbC layers are characterized by performant properties, including high hardness, good wear, high temperature stability and nice decorative appearance etc. Thus, from this point of view, these compounds are widely studied in the present, becoming important for applications such as the tribological ones.

Thin layers NbC can be deposited in an efficient mode, by using different procedures deposition of the Chemical Vapour Deposition (CVD) method. For preparing of these compounds as thin films, it is necessary a very attentive control of reactive gas flow, taking into account that this flow influences the final properties of the layers through the participations of the atomic elements present in the composition. As a conclusion, based on an intelligent approach of the fabrication of these materials, there is a possibility to tune their properties in the required direction, for certain industrial applications [4, 5].

Regarding the different practical application possibilities of these layers, one which can be considered are the niobium carbides (NbC) films which are used on a large scale for improving the tribological properties of different cutting tools manufactured from high speed carbured, WC with 6%

Co type. The tribological investigation of these superficial treated tools led to the conclusion that using CVD process for obtaining the layers, concurred to increase the durability. The NbC layers offer to the tools surface finishing, in addition to a high wear resistance and low friction coefficient (roughness low) [2, 3].

On the other hand, during the cutting process, temperatures developed at tool-piece interface (due to the friction) are around 450-500 °C. There is no risk of tool-steel substrate deformation in the steel, and also there is no risk of modifying the specific mechanical properties of the deposited layer.

Measurements of surface defects, friction characteristics and wear coefficient made on NbC, layers, revealed that using Chemical Vapour Deposition (CVD) method for obtaining these layers, can contribute effectively to reduce wear process and to minimize components loss.

Regarding the abovementioned purposes, the different deposition processes of thin films, belonging to CVD and PVD deposition methods have played an important role in Surface Engineering sector.

2. Experimental

Experimental were made of NbC thin films by CVD method, using as raw material pure niobium and ferroniobium. While heat treatment was used concentrated HCl vapour and CH_4 to obtain $NbCl_4$ and NBC as reactions below:

$$Nbs + 4HCl = NbCl_4 + 2H_2$$
$$NbCl_4 + CH_4 + H_2 = NbC + 4HCl + H_2$$

Characterisation of coating deposed by CVD method was done using scanning electron microscope (SEM), X-ray diffractometer (XRD) and Micro-hardness.

Was conducted a study on the friction coefficient and wear resistance as a function of load friction couple, for a series of NbC type thin layers. The thickness of these layers was 6, 8, 10 µm and these ones were obtained through the Chemical Vapour Deposition – CVD process.

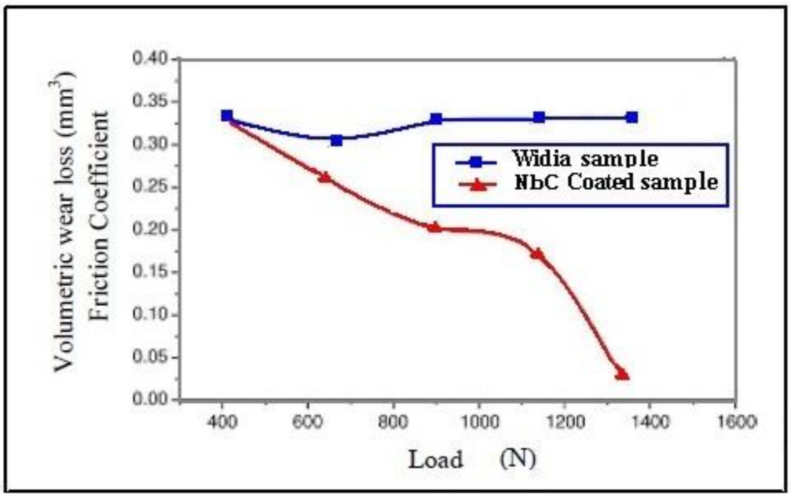

Fig. 1. *The friction coefficient of both surfaces, layers of NbC and widia sample against loads applied to the contact*

This study was done in friction conditions, in a comparative mode, based on samples coated and uncoated samples with NbC.

The friction couple was designed from the coated sample (fixed) and another mobile half-couple made from bearing steel, under conditions of linear motion "come and go", with the linear speed of 0.5 m/s. Thus, regarding the coated samples with NbC, according with Figure 1, with increasing friction couple load, the friction coefficient decreased significantly [6].

For higher loads (more than 900 N), it has been registered a slight positioning at a constant level of friction coefficient value; after this, it was registered an important decrease of this parameter till values of approximately 0.025 when the load reached 1350 N.

Friction coefficient values of widia sample, uncoated samples remained broadly constant, at values of approximately 0.33, for the entire load interval 400 - 1350 N.

Therefore, the friction behaviour of the coated samples is superior to the same one, specific of uncoated samples in a load dry friction conditions.

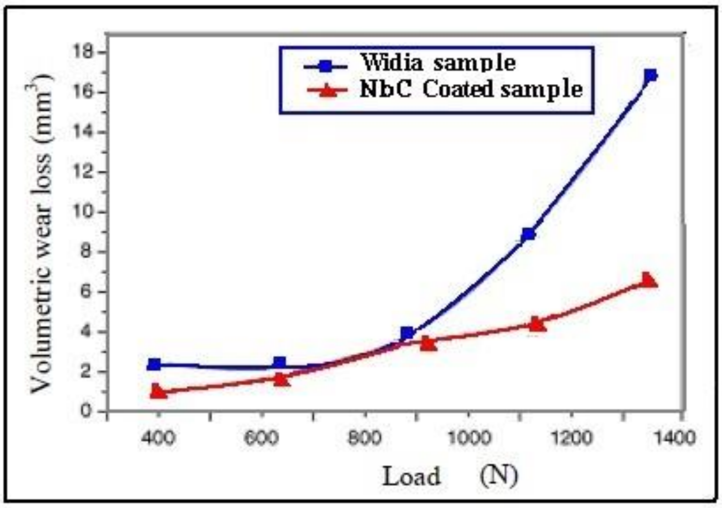

Fig. 2. *Volumetric wear loss of samples against loads applied to the contact*

Figure 2 shows the dependence between the mass material loss and the applied contact load.

For smaller loads (400-900 N), the mass loss was not significant, but for values over than 900 N (900 N to 1350 N), the mass loss increased. It can be underline that this increasing of wear is more significant for the uncoated samples (17 mm^3) in comparison with those coated with NbC which reached a maximum of 6.8 mm^3 mass loss [7, 8].

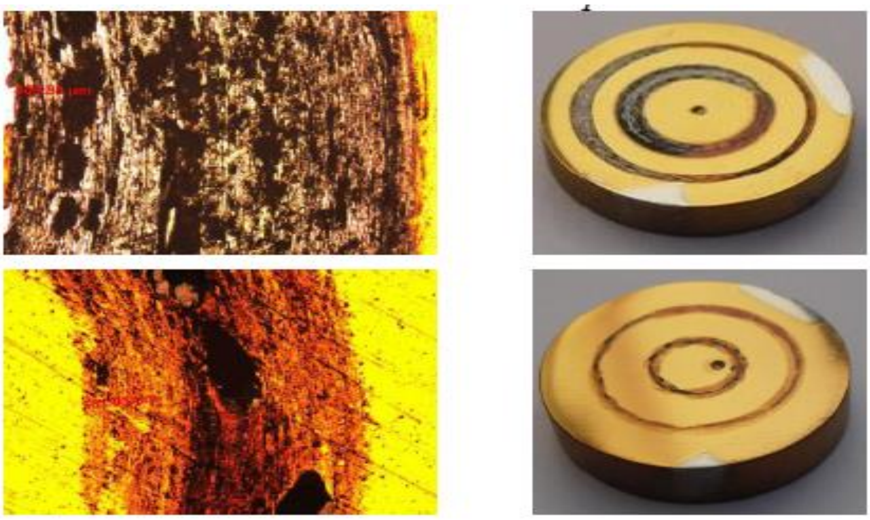

Fig. 4. *Optical images (a) and photo (b) of traces of wear on the samples*

The NbC coated plates feature higher endurance capabilities than those uncoated for the same cutting speed both for steel and white cast iron.

The parameters of the cutting conditions were chosen in the range of the values used on the working machines at the Arcelor Mittal Steel Galati.

In Figure 3 is represented wear to plates coated with NbC thickness of 6, 8, 10 μm in the process of cutting. The graph wear over time (VB = f (τ)) was traced at intervals of time corresponding to a part of the processing passage, the second and third passes. First passage time is 7.1 min to 14.2 min for second and 21.3 min for third passage

The operation of the latter is based on a housing which cuts the deposited NbC layer. Samples for metallography were prepared by polishing, this prevented damage to the dissimilar interface (strate – substrate) during polishing SEM was used to investigate the coating morphology and interface structure. X-ray mapping were also performed to characterise the elements in a semi-quantitative analysis. Dron X-ray diffractometer with Mo Kα radiation operating was used for phase(s) identification.

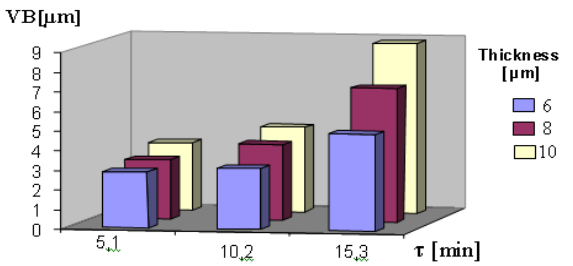

Fig. 3. *Variation wear VB = f (τ) to plates coated with NbC thickness of 6, 8, 10 µm in the process of cutting*

Analysing graph wear over time (Figure 3) it is noted that the character of these curves, in all cases, is normal, especially in working with smaller cutting speeds for using plates coated with NbC [9].

Using a "ball-on-disc" type tribometer, it was evaluated and compared the tribological performance of NbC films. These layers were deposited on widia plate, WC 94% and 6% Co type, by Chemical Vapour Deposition Process – CVD.

In Figure 4 are represented optical images (a) and photo (b) of traces of wear on the samples.

3. Results and discussion

The optimum layers in the cutting process are the NbC layers having thickness within 4 – 10 µm above these values, the layer's loose tenacity and become fragile. As result of the thermal treatment which means heating up to 1068 ^{o}C degrees for various exposure times, layer thickness within 3 – 10 µm was achieved [10]. The thickness of the thin layers increases with the time of exposure to the working temperature as illustrated in Figure 5.

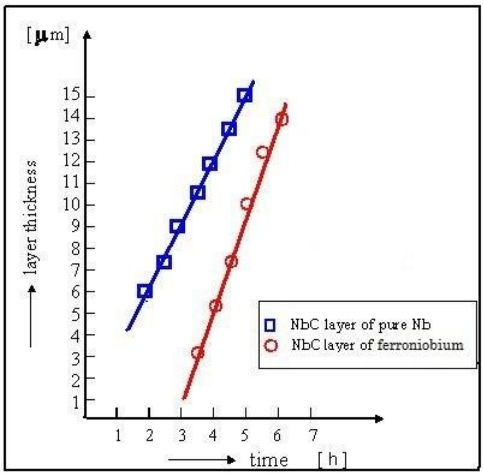

Fig. 5. *The thickness of the thin NbC layers increases with the time*

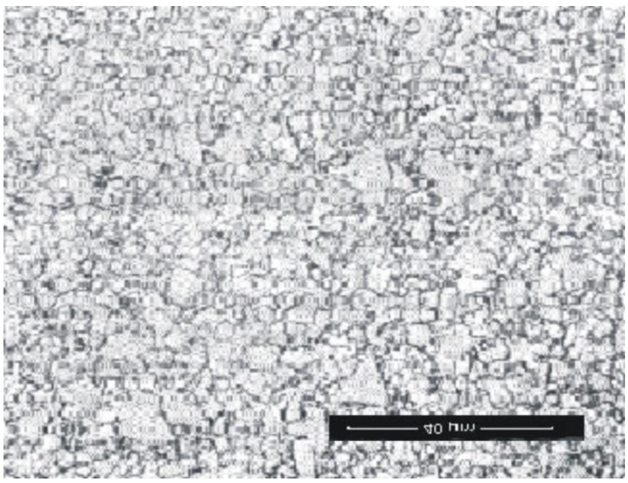

Fig. 6. *Metallographic appearance of alloy with 94 %WC, 6%Co, x1500*

Figure 6 shows the alloy structure metallographic with 6% Co and 94% WC, fine grained. In this figure the basic constituent - tungsten carbide - the form recrystallized called α2. Cobalt is presented in Figure 6 more crowded between WC crystals, showing the structure and some porosity.

WC crystals have a stable structure appearing in the form of equilateral triangular prism or parallelepiped with rectangular base.

Figures 7 and 8, superficial aspects of the layers are deposited CVD compared to monolayer NbC uncovered a plate appearance, classic, studied by electron microscopy. It is clear difference in size of crystals of layer size and size uniformity and surface roughness [13, 14].

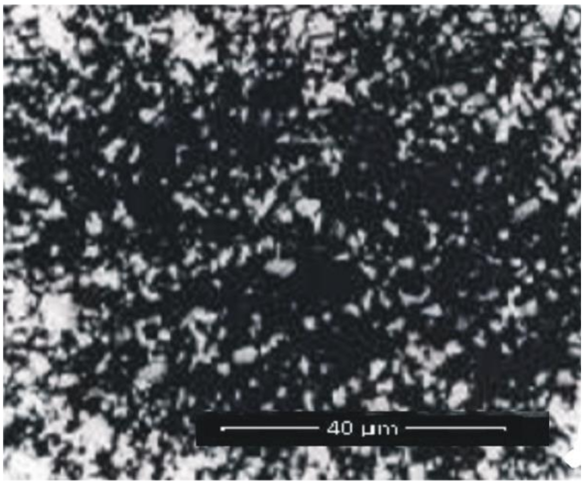

Fig. 7. *Uncoated plate surface appearance - SEM electron microscopy*

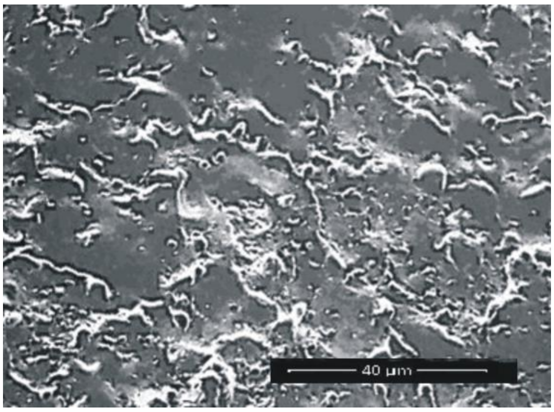

Fig. 8. *Monolayer covered surface plate appearance NbC-electron microscopy SEM*

The uncoated plate surface is rough, because carbide crystals are visible. NbC coated plates germination is observed through nodular much smoother surface thus, the surface is smooth, not slippery and practically with no apparent crystallization. For this reason, coatings provide scope for a much better behaviour from cutting and greater resistance to wear.

Grades are pursued to achieve coatings are out good surface roughness and a good layer purity combined with high uniformity of grain layer.

In Figure 9 metallographic appearance is set for a good quality coated plate. NbC coating is composed of uniform thickness and the grain, having crystal columnar layer. Niobium carbide coating is uniform and adherent throughout its thickness as shown by the metallographic analysis.

Almost isomorphic layer uniform particle size and purity to ensure good behaviour on cutting premises.

The micro-hardness was measured by the Vickers method. The micro-hardness measurements were carried out on plates coated with thin layers of niobium carbide with a thickness of 6 µm different, 8 µm and 10 µm. Micro-hardness is not a constant like Vickers hardness, in spite of the geometrical similarity, but decreases with higher testing charges depending on the size of the print. The micro-hardness tests show that we have NbC, value HV 0.05 = 29 800 MPa is in good agreement with the data from the literature.

Adherence was assessed by thin layer fingerprinting method using Rockwell hardness testers (diamond cone), the press load 1491 N (150 kgf). This method is used for rapid evaluation of thin film adhesion. Good adhesion on NbC layer by bonding HF4 index shows that interfacial region remains as in normal [15, 16]. In Figure 10 are shown optical fingerprint images after Rockwell indentation for determining adherence NbC films.

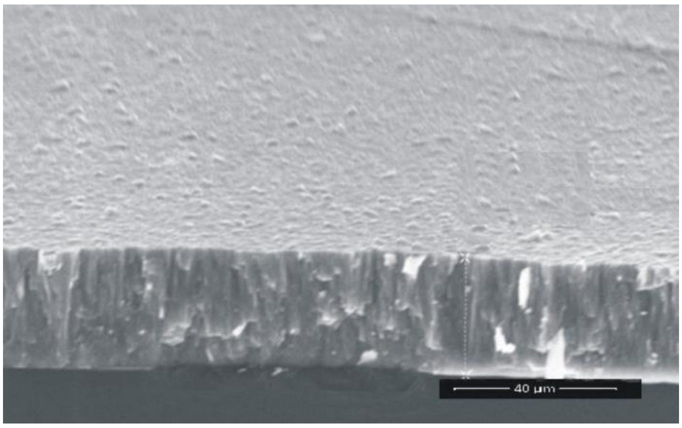

Fig. 9. *SEM images of NbC layer*

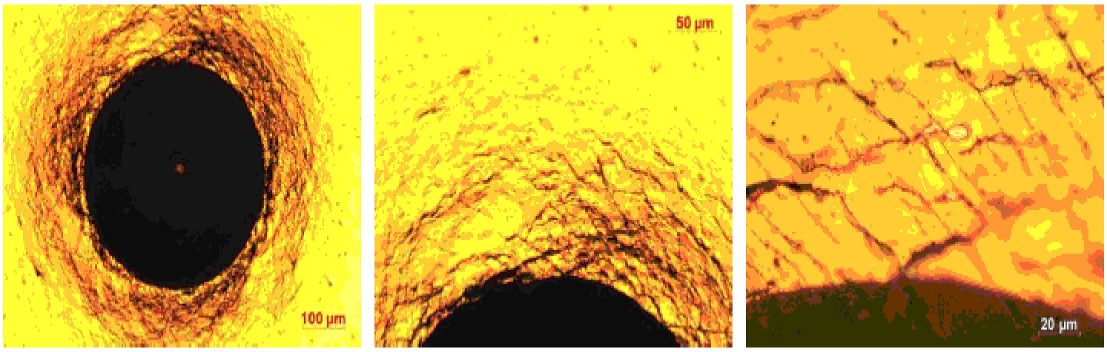

Fig. 10. *Damages formed on NbC coatings during Rockwell C testing*

XRD investigation revealed that it could be obtained a cubic crystallographic arrangement (Figure 11). The result is favourable and certify existing thin NbC layer (the maximum curves diffractometer) [17, 18]. The conclusion drawn from the analysis is that the diffractometer NbC layer which is not susceptible of cracking during tense operation.

CVD NbC coatings usually show only moderate or even poor corrosion protection for hard carbide substrates. The poor corrosion performance is not due to the intrinsic corrosion behaviour of the nitride coating itself. It results from small structural defects, pores and crack formed during or after deposition, which act as channels for the corrosion of substrate [19, 20]. We investigated the corrosion tests in water of titanium nitride coatings elaborated by CVD process.

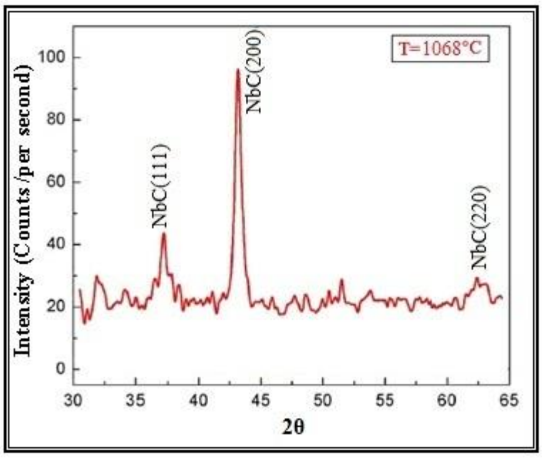

Fig. 11. *X- ray diffraction spectrum of NbC coating*

Fig. 12. *Surface appearance of uncoated NbC samples after corrosion*

a b

Fig. 13. *Surface appearance of covered NbC samples after corrosion a) 6 μm; b) 8 μm*

As seen in Figures 13a, 13b uncoated surface NbC samples have surface oxides by 40% if the samples coated with the thickness of 6μm NbC have slight traces of surface oxides on 5% non-stick surface and covered with NbC samples with thickness of 8μm surface shows no oxides.

Uncoated samples and coated with thin layers of NbC were exposed to corrosion in water for 600 h. In uncoated samples, the corrosion rate increases with time, and in the case of the samples coated with NbC corrosion rate decreases over time. It was noted that in corrosion test in water, samples covered with NbC channel are stronger compared with uncoated samples NbC.

4. Conclusions

These coatings have good wear resistance, abrasion resistance, corrosion resistance and a strong strate-substrate interface. This leads to formation of thick and rough coating. The coating is finely grained, adherent, dense and free from cracks. However, some porosity is observed in the coating layer.

The thin layers NbC with a thickness of approx. 10 μm, obtained by Chemical Vapour Deposition – CVD process on widia substrates, presented a better wear resistance and a lower friction. Graphs wear over time, VB = f (τ), are the normal character.

Diffractometer analyses certify the existence of a thin NbC layer, and it is not likely crack sticky in operation.

Good adhesion on NbC layer by bonding HF4 index shows that interfacial region remains as in normal situation.

Micro-hardness is not a constant like Vickers hardness, in spite of the geometrical similarity, but decreases with higher testing charges depending on the size of the print efficient value.

The layer begins losing 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. This has been attributed to poor wetting characteristics.

In corrosion test in water, samples covered with NbC channel are stronger compared with uncoated samples NbC.

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