THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^0. 2 – 2010, ISSN 1453 – 083X

CHARACTERISATION OF NIOBIUM CARBIDE COATING OBTAINED BY CHEMICAL VAPOUR DEPOSITION

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ABSTRACT

The experiments conducted to obtain thin layer of carbide by the vapour chemical deposition method have followed an original path to make NbC directly in the working room thus avoiding the import of these hazardous substances. The $NbCl_4$ vapoursare obtained in a heat treatment chamber by adding chloride acid vapours passed over the incandescent ferro-niobium.

Characterisation of coating deposed by CVD method was done using scanning electron microscopy (SEM), X-ray diffraction (XRD) and microhardness measurements. The thickness of the NbC layer was determined using an optical microscope and the Kalotest device. The thickness of the CVD deposit layer increases with the time of exposure to the working temperature. The values of the NbC thin layers measured by the Kalotest device are in good agreement with the values measured by microscopic analysis but slightly lower. SEM measurements were used to investigate the coating morphology and interface structure. X-ray mapping was also performed to identify the chemical elements in a semi-quantitative analysis. Dron X-ray diffractometer with Mo K_α radiation operating was used for phase(s) identification.

KEYWORDS: thickness, NPCVD, widia, layers, interface, microhardness, pressure.

1. Introduction

The vapour chemical deposition is a widely spread method of making thin layers. It has been gaining ground lately as opposed to the conventional vapour, chemical and special deposition procedures.

Compared with the other methods, the vapour chemical deposition features the following advantages: highly pure thin layers obtained by a suitable choice of the initial materials and reactions; perfectly crystalline layers due to growth under appropriate equilibrium conditions, relatively high temperatures possibility to cover the samples with thin layers of complex shape, the process is and can be automated and adapted to full scale processing of a large number of sub-layers. [1]

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.

Before examining the vapour chemical deposition reactions it must be determined if the reaction is thermodynamically possible. The reaction will be thermodynamically possible if the calculated concentrations (partial pressures) of the reactants, under equilibrium conditions, are less than their original concentrations. The calculation of the equilibrium concentrations from the equilibrium constant involves a good choice of the number of gas spaces which can be higher than two and the number of independent relations. A relation implies the equilibrium expression depending on the free standard reaction energy and temperature. The other relation consists in that the system pressure is the sum of the partial pressures. If some reactants possess more than one valence state, the reaction should contain the reactant under its most stable valence state. [2]. Hard alloys made out of metallic carbides manufactured to an industrial scale for cutting processing can be divided in two categories, according to their use. The second category of industrial products comprises the alloys out of many carbides used in cutting process of materials with long and continuous chips (all sorts of steel).

2. Methods

2.1. Materials

S.N.U.N. 15.04.08 type NbC coated and uncoated samples have been investigated. Active and constructive dimensions of samples S.N.U.N. 15.04.08. used were: α= 8, γ=4, χ =40, λ= 0.

For this purpose for samples preparation the maximum limit of the cutting speed was taken higher than the usual speeds to obtain plate durability under the most difficult operation condition which should not excessively increase the time of the experiments and the material consumption. [3].

2.2. Deposition Method

The experiments conducted to obtain a thin layer of carbide by the vapor chemical deposition method have followed an original path to make $NbCl_4$ directly in the working room thus avoiding the import of these hazardous substances. The $NbCl_4$ is obtained in the heat treatment chamber by adding chloride acid vapors passed over the incandescent pure titanium. Lab-scale systems have been designed with the possibility of use at industry scale for small production. The support temperature was established at about 1130^{o}C so that the NbC can provide a suitable deposition of the thin NbC layer. The thickness of the deposit layer increases with the time of exposure to the working temperature. The NbC coated plates feature higher endurance capabilities than those uncoated for the same cutting speed both for steel and white cast iron.

2.3. Characterization

The characterisation of the coating deposed by CVD method was done using scanning electron microscope (SEM), X-ray diffractometer (XRD) and microhardness measurements. The thickness of the NbC layer was determined by the microscope and the Kalotest device. [4].

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

The advance(s), is 0,096 mm/rot and deep cut (t) is 0,5 mm, respectively for all the samples.

Table 1. *Domains of the parameters values of the cutting conditions*

Rot. speed, n, [rot/min]	450	500	530	570	610	630
Speed cutting, v, [mm/min]	110	123	130	140	150	154

In Table 1 the values of the parameters of the cutting conditions for S.N.U.N. 15.04.08.are shown.

The operation of the latter is based on a housing which cuts the deposited NbC layer. The values of the thin NbC layers as measured by the Kalotest device are in good agreement with the values measured by microscopic analysis but slightly lower. 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 K_α radiation operating was used for phase(s) identification. Microhardness was determined by Neophot Micromet micro-hardness tester at a load of 100 gf. [5].

3. Results and discussion

Mention must be made that the optimum layers in the cutting process are the NbC layers having thickness within 4 - 10μm above these values, the layers lose tenacity and become fragile. As result of the thermal treatment which means heating up to 1130^{0}C degrees for various exposure times, layer thickness within 2,5 - 15μm was achieved .[6,7]. The plates were covered with an adherent coat of NbC of yellow color.

The thickness of the thin layers increases with the time of exposure to the working temperature as illustrated in Fig.1.

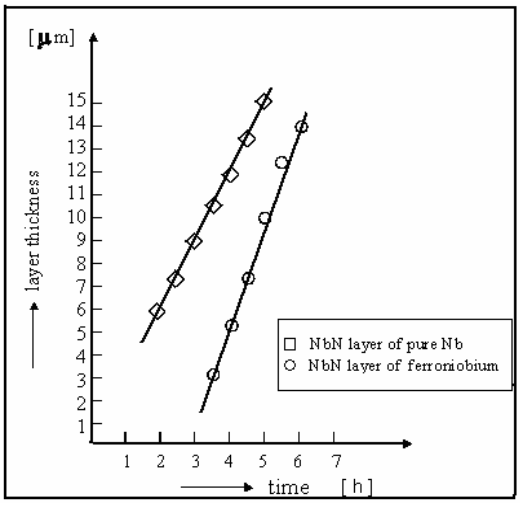


Fig.1. *The thickness of the thin NbC layers increases with time.*

Micro-hardness of WC-NbC-Co alloys is affected by a large number of elements connected to the raw material, purity and component dispersion in the alloy and the solid solution quality and grain size of components. In the factory process, these elements are

playing an ultimate role in the effective micro-hardness measurement of the material with a given chemical composition (Fig.2).

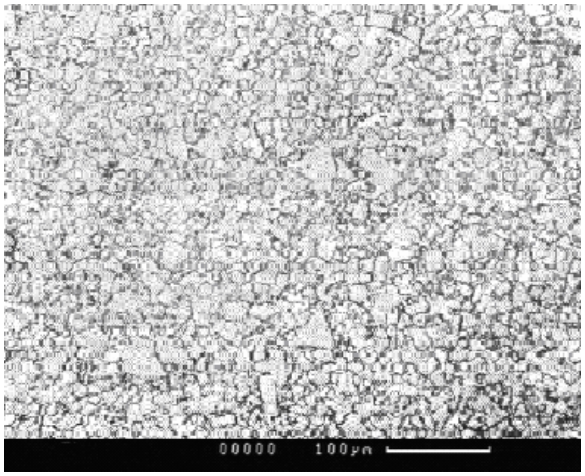


Fig.2. *Metallographic appearance of alloy with 80%WC, 18%NbC, 6%Co.*

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 $HV_{0,05}$ = 29500 MPa is in good agreement with the data from the literature.

Measurements were made on NbC covered thin plates which thickness range between 6, 8 and 10µm. [8]. Micrography, Fig. 3, 4, 5, shows an adherent layer which is uniform and homogenous over the entire depth.

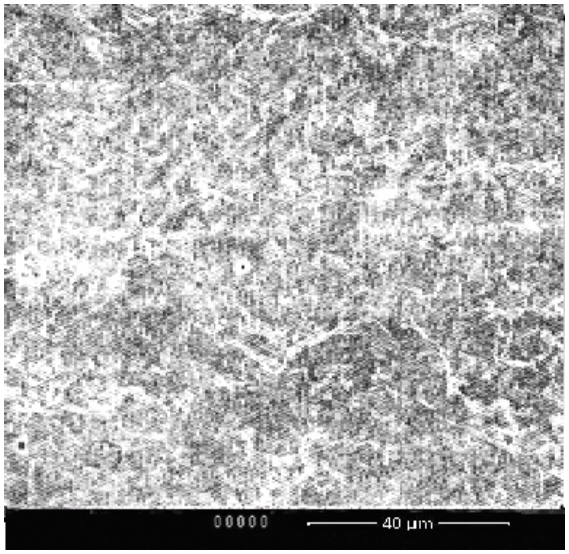


Fig.3. *SEM image (micrograph) of an uncoated plate surface.*

Figures 3 and 4 show superficial aspects of the layers deposited by CVD compared to the 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 [9].

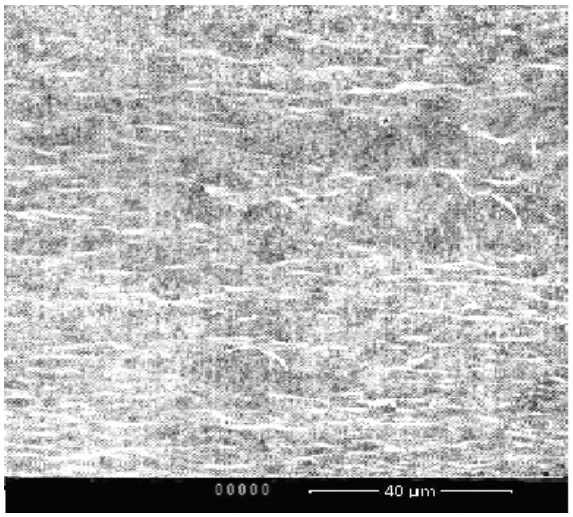


Fig. 4. *SEM image of the monolayer covered surface of NbC.*

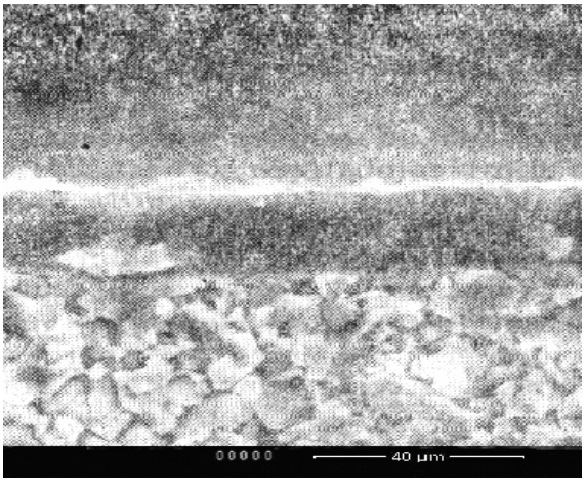


Fig.5. *SEM cross section of NbC sample covered with a 6µm NbC.*

In Figure 5, the metallographic appearance is set for good quality coated plates. NbC coating is composed of uniform thickness and the grain, have crystal columnar layer. Almost uniform grain isomorphic layer and its purity ensure proper behavior at cutting premises [10].

As regards the requirements imposed on the substrate, they have the maximum compressive strength combined with good impact resistance, good tensile strength at bending, and a high temperature and good resistance to thermal shocks.

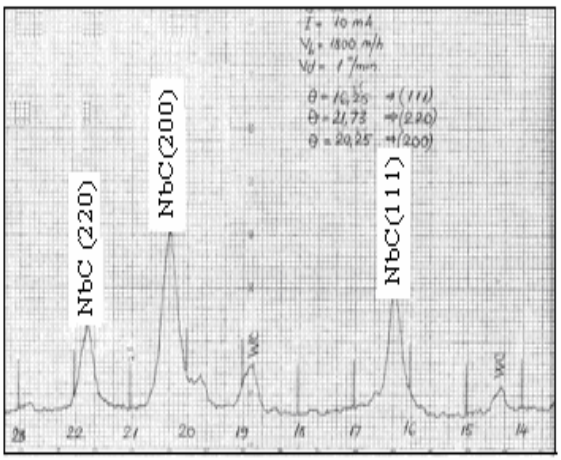


Fig.6. *X- ray diffraction spectrum of NbC coating.*

The best results are obtained for layer depth of 8 μm, with homogeneous and even structure, a feature that can be emphasized by means of diffraction pattern analysis, Fig. 6. The values of the thin NbC layers as measured by the Kalotest (Fig.7) device are in good agreement with the values measured by microscopic analysis but slightly lower.

The thickness of the layer deposited increases with the time of exposure at the working temperature.

The steel ball diameter is 12 mm. Since the shell diameter is much less than the one of the ball, the layer thickness can be calculated by the values x and y from the relation below:

$$S = \frac{x \cdot y}{R}$$

Where: R= the steel ball rase.

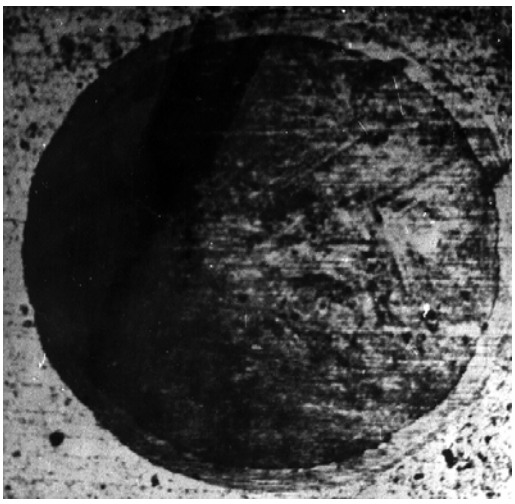
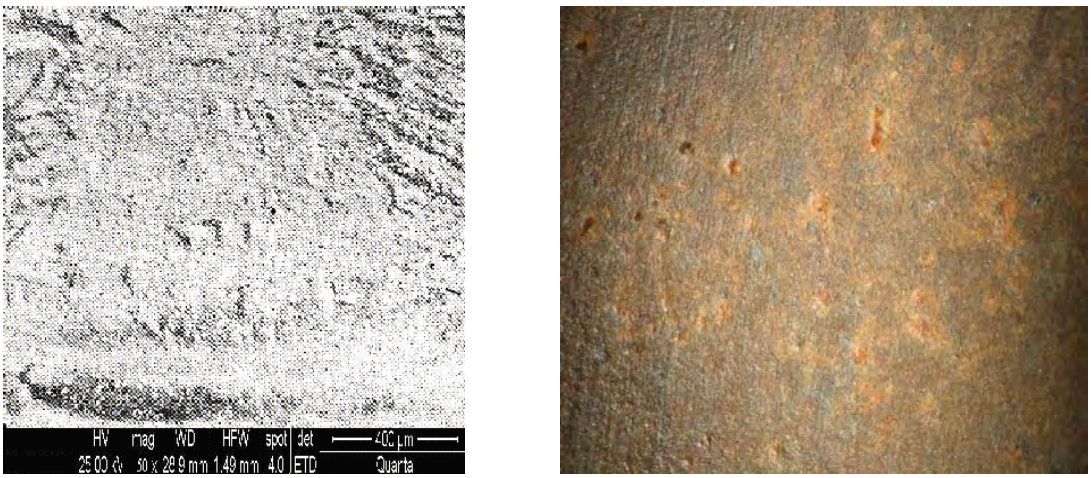


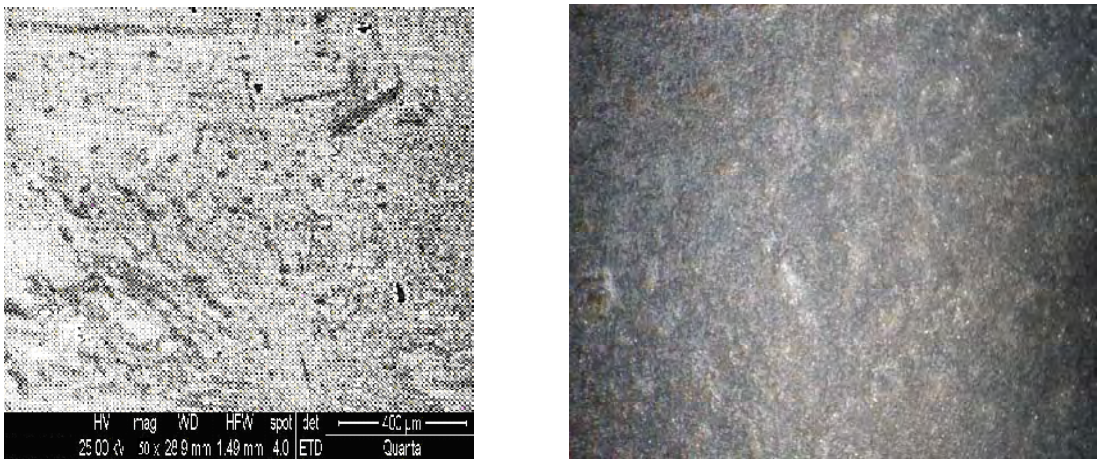
Fig.7. *The sphere shell of NbC by the Kalotest.*

As seen in Figures 8, 9, 10, uncoated surface NbC samples have surface oxides by 70% if the samples coated with the thickness of 6μm NbC have slight traces of surface oxides on 5% non-stick surface and covered with NBN samples with thickness of 8μm surface shows no oxides. It is noted that in corrosion test in water, samples covered with NbC channel are stronger compared to uncoated NbC samples.



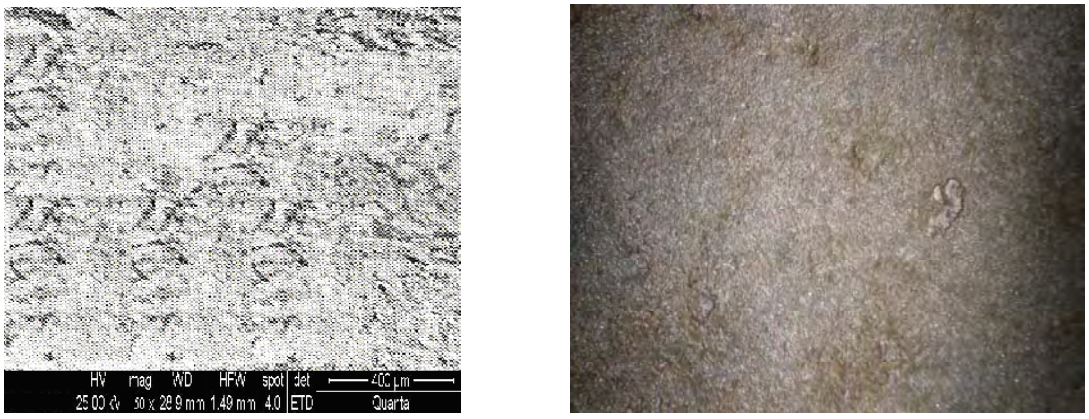
a) *b)*

Fig. 8. *Surface of uncoated NbC samples: a) before corrosion, b) after corrosion.*



a) *b)*

Fig. 9. *Surface of covered NbC samples 6 µm: a) before corrosion, b) after corrosion.*



a) *b)*

Fig. 10. *Surface of covered NbC samples 8µm: a) before corrosion, b) after corrosion.*

4. Conclusions

The obtained coatings have good wear resistance, abrasion resistance, corrosion resistance and a strong layer -sub layer interface. This leads to formation of thick and rough coating. The coating is finely grained, adherent, dense and fee from cracks. However, some porosity is observed in the coating layer. The widia plates coated with NbC thin layers entirely suppress the inconveniences of a relatively rough topography of the common sinterized carbides while preserving the adequate material mechanical strength. The thickness of the NbC thin layers increases with the time of coating. The layer begins loosing its tenacity if its thickness increases considerably exceeding the thickness of 10µm 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. Corrosion test in water of the samples covered with NbC show better corrosion behavior with respect to the uncovered ones.

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