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CHARACTERISATION OF CVD NIOBIUM CARBIDE COATINGS ON HARD CARBIDE SUBSTRATE

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ABSTRACT

Hard coatings are often used for mechanical properties such as wear and friction resistance. The corrosion behaviour may also be an important criterion for industrial applications of these coatings. In this paper, the protective behaviour of niobium carbide coatings onto hard carbide substrate was investigated in 3% NaCl and 1M H_2SO_4 solutions. The corrosion behaviour of the carbide coatings depends not only on the intrinsic electrochemical properties of the coatings, but depends also by the surface defects such as roughness, deposited droplets during CVD process and mainly by pinholes, cracks and scratches. The experiments conducted to obtain thin layer of carbide through the vapour chemical deposition method have followed an original path to obtain NbC directly in the working room thus avoiding the import of these hazardous substances.

Characterisation of coating deposed by CVD method was done using scanning electron microscope (SEM), X-ray diffractometer (XRD) and Knoop hardness. Scanning Electron Microscope 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 value (Knoop hardness) measured in the coating layer was 30.000 MPa.

KEYWORDS: niobium carbide, hard coatings, saline and acidic solutions, 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 intrinsec 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 [1].

We investigated the corrosion behaviour in saline and acid solution 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 numbers of chemical reactions leading to product formation. Parts 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 possible thermodynamically. The reaction will be possible thermodynamically 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. 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 types of carbide used in cutting process of materials with long and continuous chips (all sorts of steel).

2. Methods

2.1. Experiments

The electrochemical techniques used to characterize the corrosion behaviour of coated samples are linear voltammetry [2]. Linear sweep voltammograms were recorded in the potential range from - 1000mV to 1000mV at the scan rate of 50mV/min using PGP 201 potentiostat.

A three electrode system with an electrochemical cell volume of 100mL was used to perform the experiments [3].

The auxiliary electrode was a platinum sheet and the reference electrode was saturated calomel electrode. The working electrode was the experimental samples which has an electroactive area of 1cm^2.

The sample geometry is shown in Table 1.

Table 1. *The constructive and active geometry of the plates*

Plates type	Utilisation group	The worked material	The plate geometry							
			Constructive				Active			
			α	γ	χ	λ	α	γ	χ	λ
SNUN 15.04.08	K20	White Cast iron	0	12	60	0	8	4	40	0

The corrosion behaviour of the layers has been determined by introducing in two corrosive environments: 3%NaCl and 1M H_2SO_4 solutions, at room temperature.

2.2. Characterisation

Characterisation of coating deposed by CVD method was done using scanning electron microscope (SEM) and X-ray diffractometer (XRD). 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 [4].

Table 2. *Domains of the parameters values of the cutting conditions*

Plate type	Processed material	n	v	s	t
		[rot/min]		[mm/rot]	[mm]
SNUN 15.04.08 K20	white castion	450	110	0.096	0.5
		500	123	0.096	0.5
		530	130	0.096	0.5
		570	140	0.096	0.5
		610	150	0.096	0.5
		630	154	0.096	0.5

In Table 2 the values of the parameters of the cutting conditions are: n - rotation speed [rot/min]; v - speed cutting [mm/min]; s - advance [mm/rot]; t - deep cut [mm].

The operation of the latter is based on a housing which cuts the deposited NbC layer. Samples for metallographic analyzes 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.

The micro hardness tests show that we have NbC, value $HV_{0,05}$ = 30000MPa is in good agreement with the data from the literature [5].

3. Results and discussion

The optimum layers in the cutting process are the NbC layers having thickness within 4 - 10µm above these values, the layers loose 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 with 2.5-10µm were achieved [6]. The thickness of the thin layers increases with the time of exposure to the working temperature as illustrated in fig.1.

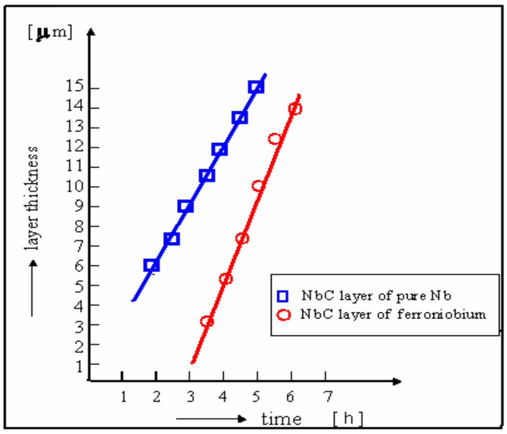

Fig. 1. *The thickness of the thin NbC layers increases with time*

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 effective micro-hardness measurement of the material with a given chemical composition (fig. 2).

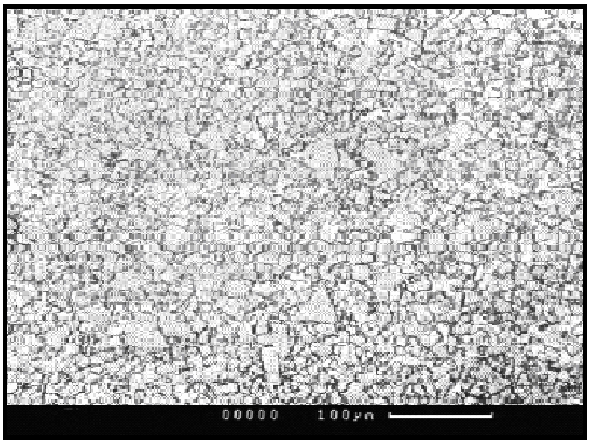

Fig. 2. *Metallographic appearance of alloy with 80%WC, 12%NbC, 8%Co, x1500*

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.

Measurements were made on NbC covered thin plates which thickness range between 6, 8 and 10µm [7, 8].

Micrographies, figs. 3, 4 and 5 shows a layer which is uniform and homogenous over the entire depth.

Figure 3 clearly show a strong interface between NbC and the substratum.

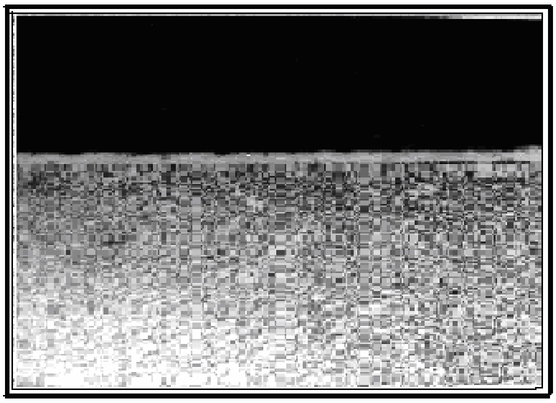

Fig. 3. *SEM micrograph of the cross section of NbC coating showing strong stratum - substratum interface, x2000*

There is a clear indication that metallurgical bond formed at the fusion zone. Figure 4 exhibits the coating morphology at a higher magnification. A fine grained structure of the coating is observed with some surface porosities. However, the coating is free from any cracks.

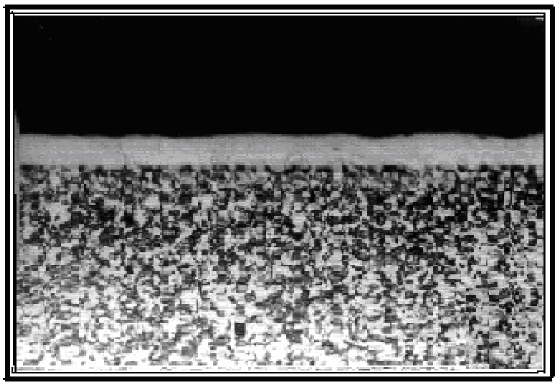

Fig. 4. *SEM micrograph of the NbC coating showing coating morphology, x2000*

Fig. 5. *SEM micrograph of the cross of NbC coating showing micro-hardness, x2000*

Microhardness value (Knoop hardness) measured in the coating layer was 30,000MPa while on substrate the hardness was 17,000MPa. Figure 5 is the SEM micrograph of the cross section of the coating and substrate with microhardness indentations. The small indentations in the coating layer are indication high hardness values as compared to the substrate which shows a large indentation.

The indentation at the interface is of intermediate size in accordance with micro- hardness values. No crack initiation or propagation is observed from any of these indentations.

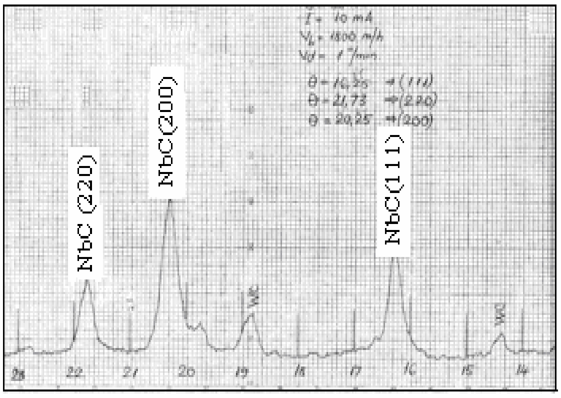

Fig. 6. *X- ray diffraction spectrum of NbC coating*

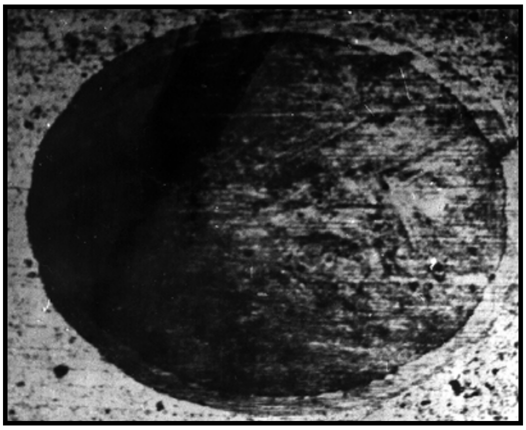

Fig. 7. *The sphere shell of NbC by the Kalotest*

From the experimental data obtained from electrochemical measurements we chose the Tafel method to study the corrosion behaviour (exemplified in figure 8 for polarization curves obtained in 3%NaCl). The figure 9 presented the Tafel curves

The niobium carbide coating diagram (Figure 6) presents diffraction lines which are characteristic the most intense peak of NbC compound corresponds to the (200) diffraction plane.

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 steel ball diameter is 12mm. Since the shell diameter is much less than that of the ball.

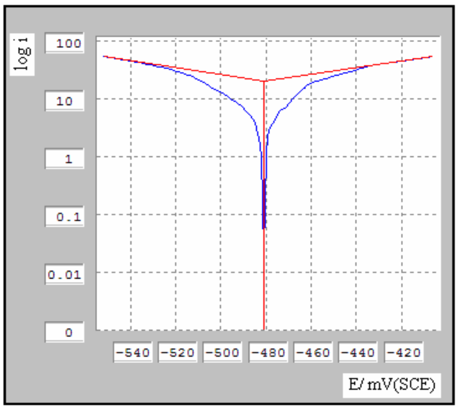

Fig. 8. *Tafel method applied for corrosion in 3%NaCl*

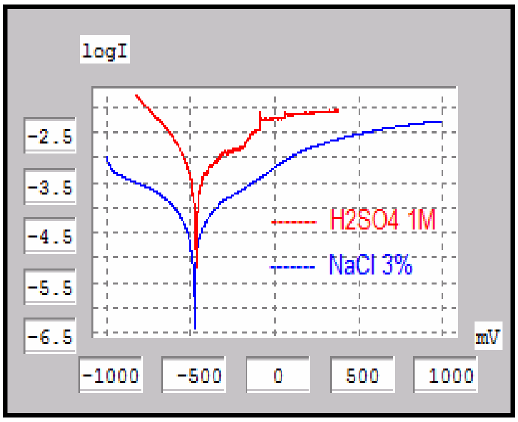

Fig. 9. *Tafel curves in two corrosive environments 3% NaCl solution and 1M H_2SO_4*

obtained in two corrosive environments tested. Corrosion potentials are very close but the corrosion current is higher in H_2SO_4 solution [9].

The parameters from Tafel curves are summarized in table 3.

Table 3. *Electrochemical parameters of the corrosion process*

Corrosive environments	**E_{corr}**	**i_{corr}**
	[mV]	[μA/cm^2]
3%NaCl	-480.7	0.0209
1M H_2SO_4	-467.0	0.0966

Figure 10 shows the anodic polarization curve in case of NbC layer immersed in 3%NaCl. This curve presented the specific zones: active, passive and trans-passive. The corrosion process take place into active zone, respectively the metal passes into corrosive media as ions [10].

In this interval the current density is increased up to a critical value (i_{crt}) and then start to decline until the passivation potential (app. 250mV). The passivation is the result of formation of corrosion products film [11]. In transpassive zone, the oxide film starts to dissolve oxidative.

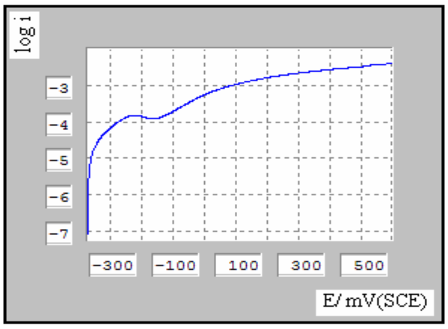

Fig. 10. *Anodic polarization curves in 3% NaCl solution*

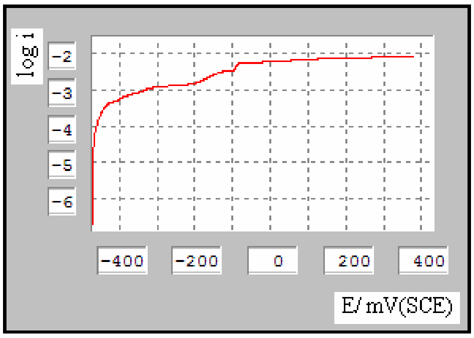

Fig. 11. *Anodic polarization curves in 1M H_2SO_4 solution*

Figure 11 shows the anodic polarization curve in case of NbC layer immersed in 1M H_2SO_4 solution. This curve shows the absence of passivation process and quickly corroded to 480mV. At increase the potential, above 400mV, continue the corrosion process slowly but constantly [12]. Test results shows a good corrosion behaviour of the NbC layer in corrosive environments tested. Higher polarization resistance and lower corrosion current shows better corrosion behaviour in 3%NaCl solution.

4. Conclusions

These coatings have good wear resistance, abrasion resistance, corrosion resistance and a strong stratum -substratum interface. We would like to underline that our condition tests are rather severe for the coated samples and lead to high corrosion rates. Nevertheless, long immersion duration does not alter the morphology of the NbC coating.

The coating is fine grained, adherent, dense and fee from cracks. However, some porosity is observed in the coating layer.

For NbC coatings, new open porosity appears and induces the peeling off of the coating due to corrosion products accumulation. These pores essentially come from the detachment of droplets previously deposited during the CVD process.

The NbC layers presented good corrosion behaviour in two corrosive environments: 3%NaCl solution and 1M H_2SO_4 solution, tested at room temperature. Corrosion potentials are very close but lower corrosion current shows better corrosion behaviour in 3% NaCl solution. The later coating should be considered for corrosion applications only if the porosity, inherent to the CVD process, is post-sealed (for instance oxidation, treatment). The niobium carbide coating would provide a very efficient protection against corrosion in saline solution.

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