Microstructural, Mechanical and Electrochemical Characterization of a Flame Sprayed NiFeCrBSi/WC Cermet Coating

Rabah AZZOUG, Yamina MEBDOUA, and Fatah HELLAL

Abstract− To increase the lifetime of drilling bits, these components are usually covered with hard metal matrix composites. Nowadays, nickel-based metal matrix composites arise as substitutes to cobalt-based ones. The challenge now is to provide an efficient coating with low cost. The aim of this paper is to exploit the characteristics of a newly designed flame sprayed NiFeCrBSi-WC composite coatings. The experimental activities were carried out using the scanning electron microscopy, for the microstructural analysis of coating. Additionally, micro-hardness and nano-indentation tests were carried out to evaluate the resistance of the coatings against penetration. Moreover, the electrochemical behavior was assessed in NaCl and Na_2SO_4 aqueous solutions. The ionic concentrations were varied between 1 g/l to 35 g/l. The results show that the microstructure is dendritic and characterized by the presence of hard chromium carbides and nickel grains in the inter-dendritic space. The coating was subject to a slight decarburization. The presence of carbides and the decarburization make the microhardness of the matrix fluctuates between 300 HV to 900 HV. For the electrochemical response, the increase in ion concentration induces a decrease in the corrosion resistance. In Na_2SO_4 aqueous solutions, the charge transfer is roughly constant for the concentrations above 1 g/l.

***Keywords*− Flame spraying, nickel composite coatings, indentation, corrosion.**

I. Introduction

In the oil and gas industry, the research for inexpensive versatile materials with a long longevity has become an essential task to increase the drilling bits efficiency and to alleviate the impact of the unsteady oil price fluctuations on the production progress. The nature of the encountered rock formations and the severity of the operational drilling conditions are decisive factors in the choice of materials that best matches the requirements. Therefore, one cost effective way of improvement is to develop a new generation of metal matrix composites that can adapt in various harsh fields due to their upgraded performance.

Over the past decades, tungsten carbides cermet, containing as binder phase a cobalt-based alloy, were the materials that had been settled to lessen the degradation of the implemented PDC cutters and to protect the drilling bit body against corrosion and erosion. In either sintered or in a sprayed coating form, these materials have shown high anti-tribocorrosion properties combined with excellent toughness, hardness and strength. Their characteristics may be improved either by varying their chemical composition and the nature of the processing techniques, or by applying post-processing treatments. This improvement possibility had put them forward as exceptional candidate materials for the extreme drilling operations.

More recently, and beside the ongoing optimization on this kind of cermet, the fierce critics beyond the noxious cobalt effects on health and environment have promoted the exploration of novel alternatives that can exhibit more enhanced features and assure better functionality to the sintered and the coated parts. However, owing to the remarkable similarities between cobalt and nickel, in term of their physical properties, and the gap between their prices, the nickel self-fluxing alloys reinforced with tungsten carbides have won the favor [1-5].

Researchers tackled the microstructure of nickel self-fluxing alloys. Reinaldo and D'Oliveira [6] showed that in the case of Colmonoy coatings, the chemistry of the used steel substrates has a strong influence on coating performance. Depending on the deposition parameters, the microstructure of coatings may be of eutectic, dendritic or martensitic type. The more the dilution is low, the more the microstructure is complex, the more the coating is harder.

Gil, et al. [7] examined the microstructure of NiWCrBSiC coatings processed on 1020 steel substrates using the HVOF technique. The results revealed that the coating consists of a multiphase microstructure with inhomogeneous distribution of precipitates in a γ nickel matrix. The coatings also contain a set of hard precipitates embedded in a nickel-based matrix.

Hemmati, et al. [8] inferred that the rapid cooling rate promotes the nucleation and the growth of floret shape of nickel and chromium borides. They have also established that the proportion of NiBSi eutectic is influenced by the type of borides and can be affected by varying the amount of boron that remain in the melting pool.

Rodriguez, et al. [9] demonstrated that the post heat treatment using either oxy-acetylene flame, vacuum or

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argon atmosphere can significantly affect the microstructure and increase the hardness and the density of NiCrBSiW (Colmonoy 88) coatings deposited via HVOF process.

Tokarev [10] studied the heat treatment of plasma sprayed coatings. The author inferred that the use of intense heat sources increases the efficiency of deposition for the treatment of the coatings.

Serres, et al. [11] proved that with diode laser source associated with an APS plasma gun induce a laser remelting that densify the deposits and promote the formation of dendritic microstructure. The laser remelting contributes to the increase of adhesion, hardness and elastic modulus of the coatings.

Zhang, et al. [12, 13] confirmed that the addition of tungsten carbides decreases the size of the dendritic crystal and the eutectic.

Liyanage, et al. [14] showed that the coatings obtained via plasma transferred arc welding exhibit a multiphase microstructure consisting of Ni dendrites with harder eutectics and chromium based borides. They demonstrated that the change in chemical composition of the NiCrBSi alloy could disturb the formation of different phases.

Sudha, et al. [15] revealed the existence of three regions in the overlays, depending on the distance from the interface.

Sidha, et al. [16] showed that thermally sprayed HVOF coatings on Fe-based superalloy. The study the coatings had a layered microstructure. For NiCrBSi, Cr_3C_2-NiCr, Ni-20Cr, the principal phase was a nickel-base phase while in the case of Stellite-6 coatings, the main phase was a cobalt-rich matrix. The coatings are also characterized by the presence of inclusions, porosities (<2%) and unmelted or partially unmelted particles.

Otsubo, et al. [17] concluded that Fe_2B borides of lumpy shape can be formed near the interface. Owing to the interdiffusion, the formation of this type of borides doesn't affect the increase of adhesion.

Currently, the focus of research is to improve the nickel based self-fluxing coating to be more efficient under the more severe and aggressive conditions [18].

The aim of this study is to characterize the microstructure, the mechanical and the electrochemical behavior of a flame sprayed nickel based composite coating which will be used to cover the drilling bits in the Algerian fields.

II. Experimental Procedure

A. Presentation of the studied materials

To carry out this study, we have used X18 carbon steel as substrates and MB40 powder as coating material for performing the bonding layer. We have also used a NiFeCrBSi-WC composite wire to realize the deposits. The feedstock wire contains WC particles that are embedded in NiFeCrBSi powder. The steel substrates have 50 mm in diameter and 5mm in thickness. They were cut from rods which had 60 mm in diameter.

B. Spraying conditions

Before the thermal spraying, the steel substrates were cleaned from any oxide, oil, grease, impurity or other material deposited thereon with a chemical solvent (acetone) so as to avoid the formation of defects.

The realization of coatings was performed in the open atmosphere using the acetylene as fuel. The selected processing parameters for both the bond layer deposition and the flame spraying are listed in Table I. The coating operation of samples for their protection against wear was carried out with an oxyacetylene torch, type TECHNOKIT T2000 (Fig.1). This type of coating is simple and economical and preserves the integrity and the integrality of the tungsten carbides.

Table. I
Flame Spraying Parameters

Parameters	Estimated values
Torch velocity (mm/s)	1
Spray distance (mm)	120
Acetylene pressure (bar)	0.2
Oxygen pressure (bar)	4

Fig. 1: TECHNOKIT T2000 torch.

C. Metallographic Characterization

The samples are first mechanically polished with a series of SiC silicon carbide abrasive papers and then on a felt paper impregnated with a dilute suspension of colloidal alumina.

A chemical etching in aqueous solution of Murakami reagent (10g $K_3Fe(CN)_6$ + 10g KOH/NaOH + 100 ml water) was performed at room temperature for a period of 180 seconds to reveal the coating microstructure. This chemical reaction reveals the nickel grains in dark gray, the nickel dendrites in light gray and the pores in black.

The micrographic analysis was carried out using a scanning electron microscopy (SEM).

D. Mechanical characterization

The micrographic examinations after spraying are supplemented with micro-hardness, and nano-indentation tests.

For the micro-hardness measurements, a charge of 0.1 Kgf was used to perform the filiation from the substrate to the top coating surface using a step of 50 µm. The dwell time was 15 s.

In our study, the nano-indentation tests were performed using a Vickers indenter according to Olivier and Pharr method. The maximum charge used for the measurements was 100 µN. The indentation velocity was kept at 2500 nm/min. At the maximum charge, the dwell time was 10 s. The charge and discharge velocity was 200 µN/min.

E. Electrochemical characterization

To characterize the corrosion behavior of the coatings in the NaCl and Na_2SO_4 solutions potentiodynamic measurements were conducted at different concentrations (1 g/l, 10 g/l, and 35 g/l) and that, at ambient temperature.

We carried out tests of polarization in a conventional three-electrode cell (Figure 9). Data acquisition from the potentiostat is done via the VoltaLab software.

In each manipulation, we waited for the measurement of open circuit potential for a period of 30 minutes before starting the test. For these tests, the potential range chosen is between [-1000, 0 mV]. The scanning speed is 0.2 mV/s which implies a duration of 30 min.

The electrochemical impedance measurements were performed at open circuit potential at a sine perturbation amplitude of 10 mV and that between 100 kHz and 1 Hz of frequency. For these measurements, the acquisition rate was fixed at 5 per decade and the open circuit stabilization time was set at 30 min.

III. RESULTS AND DISCUSSION

A. Microstructural Analysis

Fig.2 represents the microstructure of the coating matrix. It appears from this microstructure that the feedstock material was propelled to form a dendritic nickel matrix, in which, the tungsten carbides are embedded. The dendritic matrix was completely melted and the presence of dendrites (light grey color) is due to the slow cooling rate. During the cooling, the dendrites were preferentially initiated around tungsten carbides. They then grow before the solid precipitation took place. This solid precipitation is the cause of formation hard chromium carbides (grey color) which take place in the nickel grains (dark grey color). Due to the optimized processing parameters, no micro-cracks were observed. The pores that appear in black color have an irregular form and are distributed in-homogeneously within the matrix. Due to self-fluxing effect of boron and silicon, the oxides are not present in this matrix. The inter-splats boundaries were completely eliminated. Indeed, the spraying torch moves at low speed which provide an excessive heat to remelt the coating.

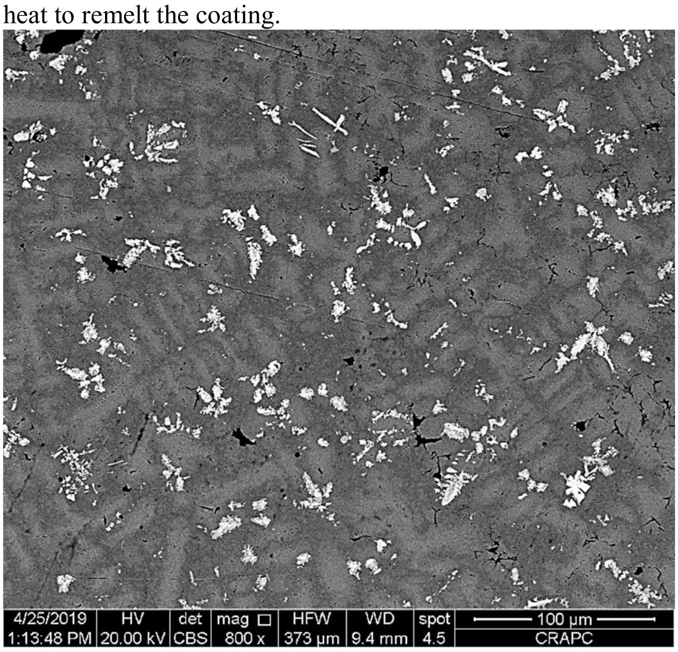

Fig. 2: Microstructure of the coating matrix.

B. Mechanical characterization

Fig. 3 illustrate the results of the microhardness measurement undergone on the cross section of coatings B. The results demonstrate the inhomogeneity of the coatings due to the presence of carbides. Even though the mean hardness of the matrix doesn't exceed 470 HV, the matrix is characterized by the presence of zones of carbides with relatively high hardness (500HV to 700 HV). During these tests, the indenter was not able to touch the WC carbides. However, the areas which surround the WC particles are characterized by high hardness (900 HV).

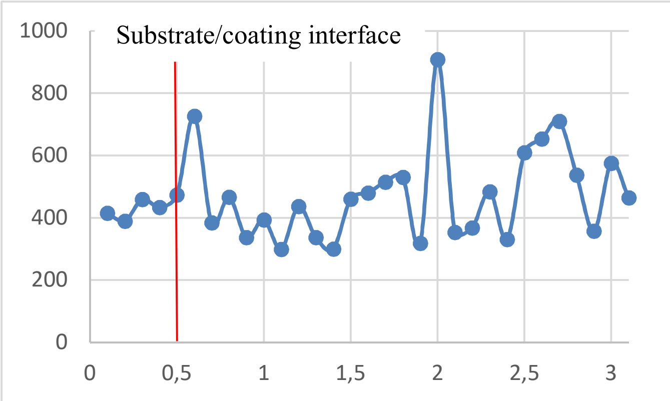

Fig. 3: Micro-hardness evolution profile of the cross section of the coating.

Fig 4. represents the load displacement curve obtained after nanoindentation of the coating matrix.

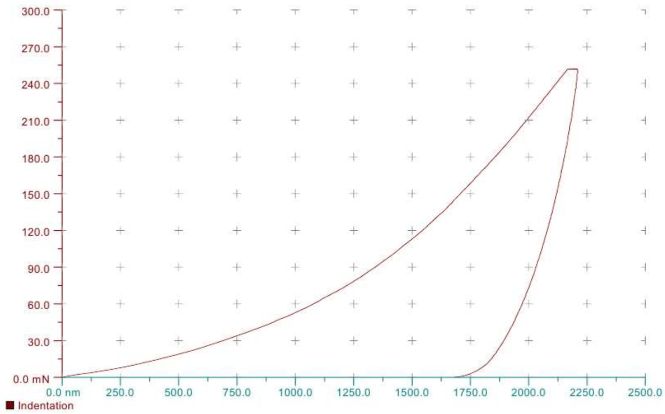

Fig. 4: Load displacement curve obtained after nanoindentation of the coating matrix.

The elastic modulus of the matrix is equal to 112.87 GPa. The hardness was about 272.29 HV.

C. Electrochemical characterization

Fig.5 and Fig.6 represent the potentiodynamic polarization curves obtained after the electrochemical characterization.

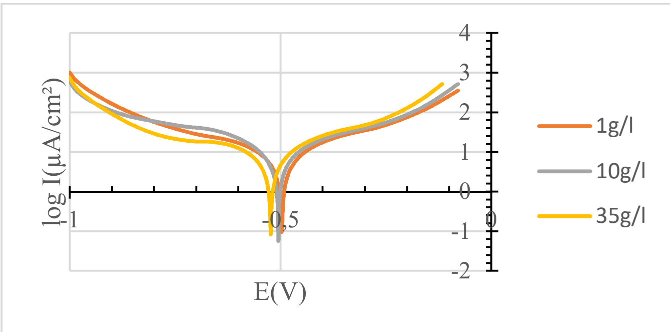

Fig. 5: Potentiodynamic polarization curves gotten in NaCl solutions.

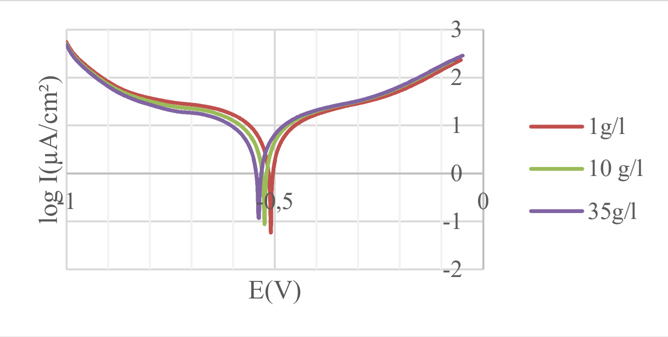

Fig. 6: Potentiodynamic polarization curves gotten in Na_2SO_4 solutions.

The extracted electrochemical data from the previous curves are summarized in Table II and Table III. It's clear that the corrosion current increased with the increase of the ionic concentrations. The corrosion potential shift from –505 mV in NaCl solution with 1g/l of concentration toward the more negative values to reach -524.2 mV with 35 g/l NaCl of concentration. The corrosion rate varies between 5.983 µm/year and 28.78 µm/year in this range of concentration.

In Na_2SO_4, the corrosion potential decreased from -509.5 mV at 1g/l of concentration to 524.5 mV at 10 g/l to reach a value of -539.5 mV. The corrosion current increased gradually and is between 1.3750 µA/cm² and 2.2501 µA/cm². In the given range of concentration, the corrosion rate increased gradually from 16.98 µm/year to 22.63 µm/year.

Table. II

THE EXTRACTED ELECTROCHEMICAL DATA FOR THE COATING IN NACL

C_{NaCl} (g/l)	1	10	35
E_{corr} (mV)	-505.0	-506.1	-524.2
I_{corr} (µA/cm²)	0.7471	2.1748	2.5970
V_{corr} (µm/year)	5.983	25.53	28.72

Table. III

THE EXTRACTED ELECTROCHEMICAL DATA FOR THE COATING IN NA_2SO_4

C_{NaCl} (g/l)	1	10	35
E_{corr} (mV)	-509.5	-524.5	-539.5
I_{corr} (µA/cm²)	1.3750	2.1378	2.2501
V_{corr} (µm/year)	16.98	20.30	22.63

Fig.7 shows the Nyquist plot gotten after an Electrochemical Impedance Spectroscopy in NaCl solutions. The semi-circles are capacitive, suggesting that there was adsorption of ions during the tests.

It results from the same figure that the increase in ion concentration decreases the charge transfer at the interface between the coating and the electrolyte.

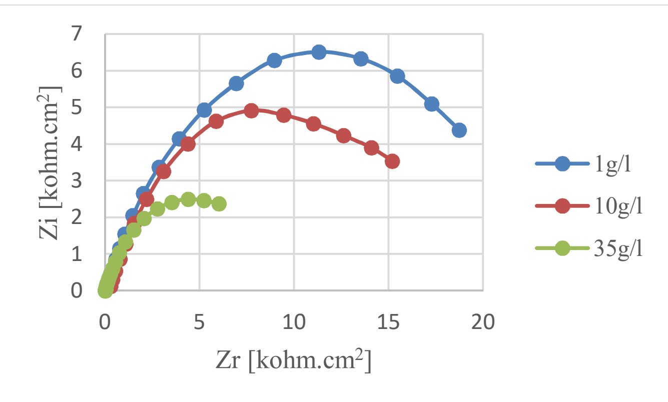

Fig. 7: EIS spectrum obtained in NaCl solutions.

From Fig.8, it results that the increase of ion concentration induced an increase in the radius of the impedance semi-circles toward a constant value due to passivation of coating. The coating forms then a compact passive film that protects it against the sulfur ions.

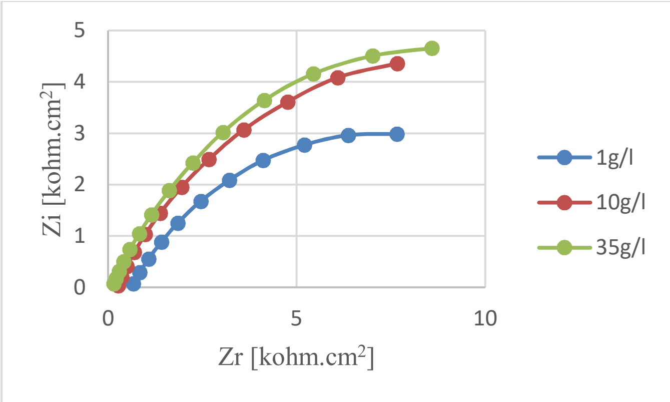

Fig. 8: EIS spectrum obtained in Na_2SO_4 solutions.

As compared to Rabah et al [19] findings, it results that the corrosive behavior of this coating is better.

IV. CONCLUSION

It can be concluded that the coating is composed of dendritic γ nickel matrix which is characterized by the presence of chromium carbides and γ nickel grains in the inter-dendritic regions.

The mechanical indentation behavior is governed by the plasticity of the indented phases. The microhardness of the matrix is about 470 HV. However, it can reach 900HV due to the decarburization of WC particles. The elastic modulus of the matrix is about 112.87 GPa.

The coating shows good resistance in NaCl and Na_2SO_4 aqueous solutions due to the presence of WC particles as reinforcement. For that reason, it can be used to cover the drilling bits in the exploited Algerian oil and gas fields. Nevertheless, actual tests must be carried out, using these coated drilling tools, in different prospecting sites, taking into account the rock encountered formations and the operational drilling conditions.

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