CHARACTERISTICS OF HIGH TEMPERATURE VACUUM BRAZED WC-Co-NiCrBSi FUNCTIONAL COMPOSITE COATINGS

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Abstract

The present work aims to investigate the characteristics of high temperature vacuum brazed WC-Co-NiCrBSi coatings deposited on 16MnCr5 steel substrate. The coatings characteristics like morphology, microstructure, chemical composition and the appearance of the interface with the substrate have been analyzed by means of Scanning Electron Microscopy (SEM) combined with energy-dispersive X-ray spectroscopy. The hardness profile of the cladding is evaluated with the help of a Vickers microhardness tester. Size, occurrence and distribution of pores and microcracks has been estimated using image processing of SEM micrographs. X-ray diffraction measurements performed on the on the brazed composite cladding, have been done in order to identify possible phase transformations during the thermal treatment. Tribological behavior is assessed with the aid of a tribometer utilizing a pin-on-disk testing arrangement. Corrosion resistance is appraised using the potentiodynamic polarization method in 3.5% NaCl solution at room temperature in a three-electrode cell configuration. This coating technology makes possible the deposition of high quality hardfacings, with minimal influence on metallic substrate. The achieved porosity degree (approximately 1%) is similar to the values reported in literature. It was found that the mean coefficient of friction is approximately two times lower for the WC-Co-NiCrBSi composite, compared to 16MnCr5. Consequently, the wear rate of the coating is more than 20 times lower than that of the unprotected substrate material. The electrochemical measurements resulted in a lower corrosion current density, correlated with a significant improvement in the corrosion behavior.

Keywords: Vacuum brazed coatings, WC-Co-NiCrBSi characteristics, wear and corrosion resistance

1. INTRODUCTION

In spite of the fact that brazing process is usually employed as a joining technique, this study aims to investigate the possibility of using this method as a coating technology, which brings fresh and innovative solutions for deposition of functional coatings on disparate surfaces. Brazing process exhibits the capability to generate joints with high strength, through the formation of a metallurgical bond between the components. Employed as a coating technique, this method concludes in higher cohesion and adhesion of the coating to the substrate [1, 2]. Moreover, the versatility of this process allows a wide variety of chemical compositions and final coating thicknesses to be deposited. These coatings may be applied as alternatives to a wide variety of applications, in which resistance to both corrosion and wear is simultaneously required [2, 3]. The properties of WC-based composite coatings obtained by high temperature vacuum brazing, such as their morphology as well as wear and corrosion behavior are still barely known [4].

This work aims to study the development of functional composite coatings with metallic matrix based on NiCrBSi self-fluxing alloy reinforced with WC-Co hard particles, using the high temperature vacuum brazing method. Employing this method, wear and corrosion resistance of various components can be successfully improved.

2. EXPERIMENTAL PROCEDURE

Flexible composite tapes were manufactured by mixing 75 wt.% NiCrBSi with 25 wt.% WC-Co powder with an additional 3.5 wt.% special formulated Nitrile based organic binder, followed by rolling of the mixture in order to form cloths with 3 mm thickness. Both types of powders are commercially available from Höganäs AB (Sweden). Chemical composition of the feedstock materials is presented in **Table 1**. The tapes obtained in this manner were cut to desired shape and fixed onto the substrate surface. As substrate material, a commercially available 1.7131 (16MnCr5) case hardening steel was machined to the corresponding dimensions and ground with SiC paper in order to remove potential oxides.

Table 1 Chemical composition of flexible tapes (wt.%)

	Ni	Cr	B	Si	Co	Fe	C	W	wt.%
WC-Co	-	-	-	-	7.5	-	5.7	Bal.	75
NiCrBSi	Bal.	14.42	3.23	4.36	-	3.83	0.72	-	25
Organic binder	Nitrile based special formulation								3 - 3.5

High temperature brazing process was performed in a HITERM 80-200 cold wall vertical vacuum furnace at a stable vacuum state of 3.5×10^{-4} mbar. Detailed procedure of brazing parameters and the optimization process was described elsewhere [5].

Microscopic investigations have been conducted utilizing a Philips XL 30 scanning electron microscope and elemental analysis of the coating was carried out by energy-dispersive X-ray spectroscopy with a EDAX XL-30 detector. Phase identification was performed implementing a Philips X' Pert X-ray diffractometer in the interval of $20° < 2\theta < 100°$.

Determination of tensile adhesive strength was carried out on an INSTRON 5584 universal testing machine, having in mind the indications of EN 582: 1993. The sample arrangement had a diameter of 20 mm, a total length of 62 mm, with a coating thickness of 2 mm.

Hardness of the composite coatings was determined with a Zwick/Roell YHVµ-S microhardness tester using a Vickers microindenter (ISO 6507). The applied load of the diamond pyramid was of 1 kgf for 15 s.

In order to compare the wear resistance of the WC-Co-NiCrBSi to that of the 16MnCr5 steel substrate, investigations were performed with a CSM Instruments tribometer with a ball-on-disk arrangement, following the instructions of DIN 50324. The total sliding distance was 1890 m (10000 laps) with a linear speed of 15 cm s^{-1} on a radius of 3 mm, and a normal load of 10 N was applied through a 6 mm cemented tungsten carbide ball (static partner). All tests were carried out under dry sliding conditions, at standard room temperature and pressure.

The electrochemical corrosion behavior was evaluated through potentiodynamic polarization, employing a IVIUM Vertex potentiostat/galvanostat in a three-electrode cell, according to ISO 13129 standard. Working electrodes were prepared from both types of materials, a platinum disk was used as counter electrode and a saturated calomel electrode as reference. The testing medium was a 3.5 wt.% NaCl neutral solution, at room temperature. All polarization studies were performed with a scan rate of 10 mV min^{-1}.

3. RESULTS AND DISCUSSIONS

During the high temperature vacuum brazing process, the organic binder decomposes at approximately 550°C, leaving behind numerous interconnected pores, favorable for the capillary action. Simultaneously with the rise in temperature, at 960°C, the Ni-based self-fluxing alloy reaches its solidus temperature. A stabilization hold at 10°C below this temperature for 10 min is mandatory to uniformly distribute heat and reach the set ΔT. The hold of 60 min at the brazing temperature of 1100°C provided sufficient time for the alloy

to melt, gain the optimum fluidity to infiltrate, fill the hollow spaces between the WC-Co particles and wet the substrate. Additionally, this hold ensures the propitious environment for the diffusion process between the braze alloy, cermet particles and substrate material in order to obtain high quality hardfacings with a strong metallurgical bond [5].

The coatings morphology and microstructure obviously has a major impact on the mechanical properties, tribological and corrosion behavior [6-8]. In connection with previously mentioned statement, microstructure of the substrate/coating system is shown in the cross-section micrograph (**Figure 1**). High temperature vacuum brazed coatings have a dense structure with a uniform cermet distribution. One can clearly observe that the melted self-fluxing alloy infiltrated between the WC-Co particles, cementing them with the metallic matrix. The maximum temperature to which the materials are exposed during brazing (1100°C) cannot melt tungsten carbides. Although, diffusion from the metallic matrix towards the cemented WC and substrate, as well as dissolution of Co into the matrix during brazing of WC-based coatings has been reported [6].
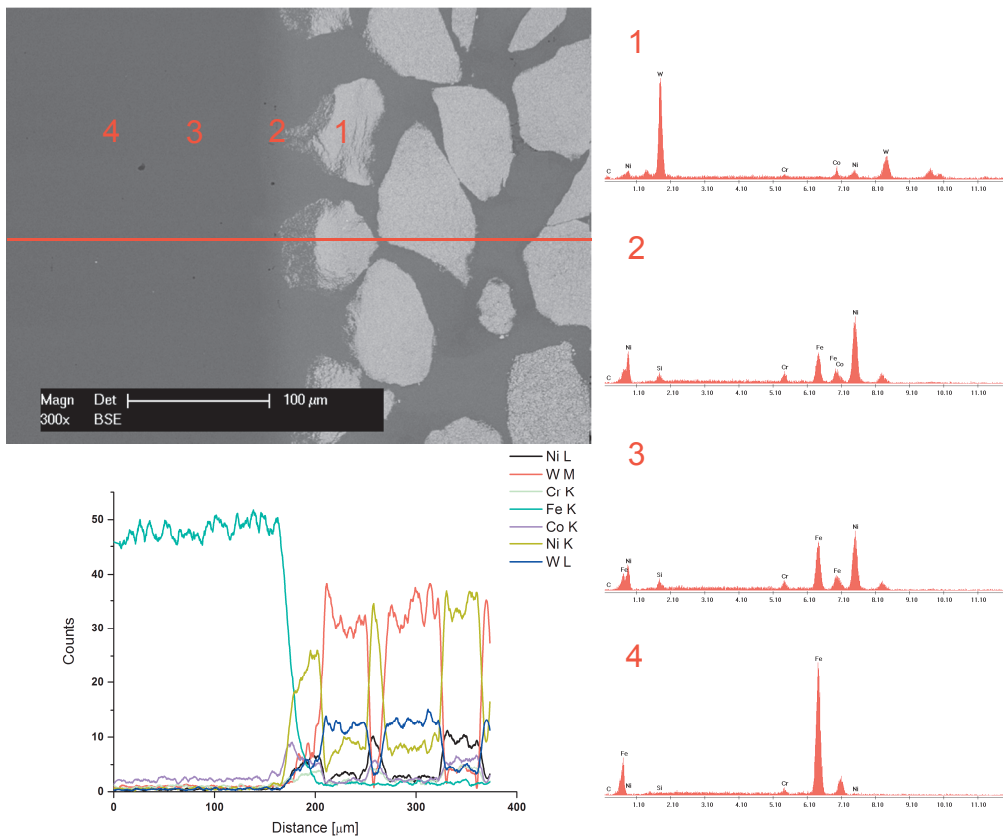

Figure 1 BSE cross-section micrograph and EDX spectra that correspond to the line-scan and the four distinct regions across the interface

Furthermore, EDX spectra collected from four distinct regions are also presented in **Figure 1**. In spot 1 (bright grey), the corresponding EDX spectrum indicates the presence of Ni and Cr, which confirms the statement regarding the diffusion of elements from the brazing alloy into the cermet particles. Area 2 (light grey) is situated at the interface region, where the highest inter-diffusion reaction between the metallic matrix and the substrate takes place, as well as dissolution of the hard metal. A clean, inclusion and porosity free interface can be observed, while the EDX spectrum manifests peaks for Ni, Fe, Co, Cr and Si. At a distance of about 50 μm from the interface in the substrate, corresponding to region 3 (dark grey), the elemnts Ni and Si are still present. Deeper in the base material, (area 4, dark grey), EDX analysis indicates only the elements matching

the chemical composition of the 1.7131 steel. The EDX scan corresponding to the line drawn on the SEM micrograph, further consolidates the data obtained from the microscopic investigations and the affirmations regarding diffusion and dissolution processes.

X-ray diffraction measurements indicate a vast amount of possible phases due to the very complex nature of WC-Co-NiCrBSi brazed coatings. The XRD diffractogram presented in **Figure 2** reveals that the hardfacings consist predominantly of WC (35%), and $Cr_3Ni_5Si_2$ ternary metal silicide (31%), closely followed by $CrNi_3$ intermetallic phase (27%), with additional hard Cr_2B_3, wear resistant phase (7%).
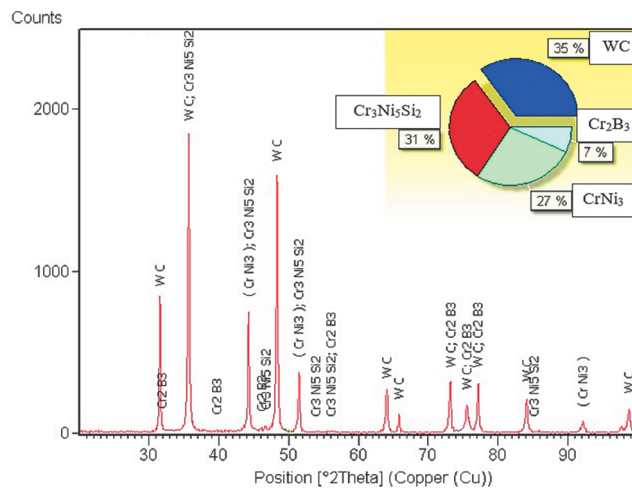

Figure 2 XRD pattern of high temperature vacuum brazed WC-Co-NiCrBSi coating

Presence of other phases is highly plausible because of the high number of involved elements. Due to the low process temperature (1100°C), compared to the melting temperature of tungsten carbide (~2850°C) and the lack of oxidizing elements, no decarburization of WC (normally resulting in the formation of the more brittle W_2C phase) was observed. Areas susceptible to stress concentration can appear while loaded under working conditions due to considerable differences in microstructure, physical and mechanical properties between the WC-Co cermet, Ni-based metallic matrix and the substrate material. Because of the high quantity of ceramic type reinforcement, tensile fracture of the functional coating was dominantly a brittle one, with cracks propagating through the carbide particles, leaving behind a small amount of plastic deformation in the ductile matrix. Tensile cohesive strength of the coating itself reached a mean value of 120 MPa, which is well correlated with the values reported by other researchers [7].

Vacuum brazed WC-Co-NiCrBSi composites exhibit a variable hardness in the coating cross-section. The values range from a minimum of 647HV1 (corresponding to the matrix) up to a maximum of 1132HV1 (cermet particles), with a mean of 896HV1. The relatively low hardness values are attributed to pores located in the tested areas. The substrate material (1.7313) is known to have 470HV if case hardened and 170HV when soft annealed.

Dry sliding wear measurements were performed for both materials (substrate and coated sample) under identical conditions. The coefficient of friction was monitored and registered during the entire testing period and can be observed in **Figure 3**. The lowest value for both types of samples coincided with the start of the investigation (0.159 for the steel and 0.207 in case of the coating). However, it quickly changes, when the systems enter kinetic friction, increasing up to approximately 0.55. Concomitant with the completion of the first couple of laps, a decrease is observed. This phenomenon lasting only a very short period is due to reduction in surface roughness, being more visible for the substrate material because of the lower bulk hardness. Subsequently, after ~1500 laps, the coefficient of friction rises again for the next ~50000 laps. Contrary, after ~1000 laps, the WC-Co-NiCrBSi coating shows a lessening in friction, which reaches steady state at ~40000 laps, and remains generally stable, with a coefficient of around 0.28 until the end of the test. When the

coefficient for 16MnCr5 sample reaches approximately 0.85, it also enters steady state, that lasts until the surface degrades and the friction becomes highly unstable, behavior which is accordant with sever wear. Meantime, the hardfacing shows only a few deviations, attributed to pull-out of metallic matrix caused by adhesion [8]. Decisively, a maximal friction coefficient of 0.931 was measured during the ball-on-disk testing of the steel substrate, with a mean of 0.670. Significantly lower values were determined in the case of the functional coating, registering a maximum of 0.573 and an average of 0.329.
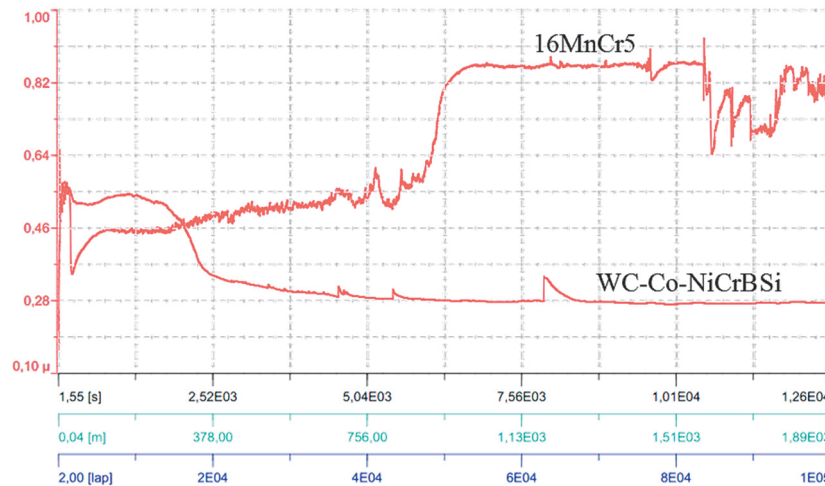

Figure 3 Coefficient of friction evolution for 16MnCr5 substrate material and WC-Co-NiCrBSi coating

The wear rates assessed after measuring the depth and width of the tracks left behind by the WC-Co static partner are in good agreement with the results of previous investigations (microhardness, coefficient of friction). One can clearly notice the difference in sliding wear behavior between 16MnCr5 substrate material and WC-Co-NiCrBSi functional coating in the micrographs of **Figure 4**.
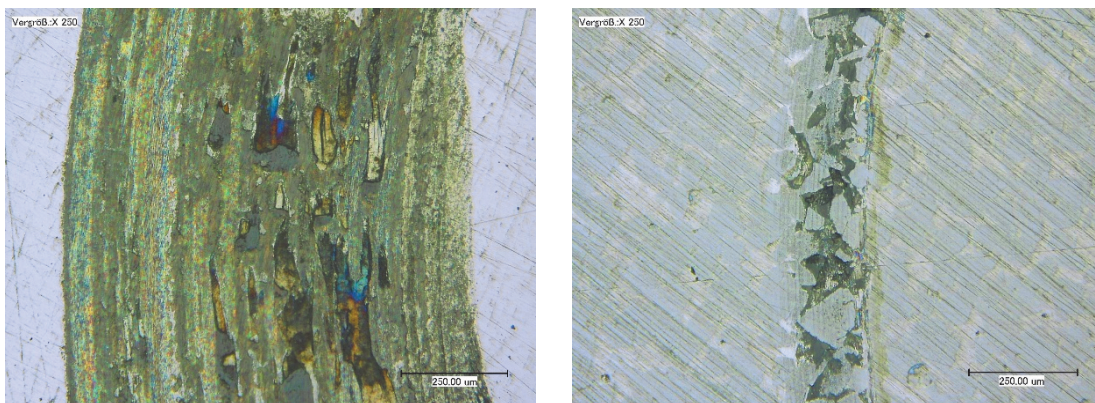

Figure 4 Digital micrographs of the sliding wear track for 16MnCr5 (left) and WC-Co-NiCrBSi (right)

The considerably wider and deeper worn section found on the metallic surface concluded in numerical values for the wear rate of $2.087 \cdot 10^{-6}$ mm^3 N^{-1} m^{-1}, compared to only $1.561 \cdot 10^{-8}$ mm^3 N^{-1} m^{-1} in the case of the composite hardfacing. Furthermore, the formation of an oxide film and galling causing additional friction and adhesion between the static partner and the sliding (rotating) steel specimen can be observed. The digital micrograph of the coating's surface displays sporadic areas where the pull-out occurred.

Figure 5 illustrates typical Tafel plots for the discussed samples subjected to potentiodynamic electrochemical corrosion in 3.5 % NaCl solution. It is clear that the corrosion current density (i_{corr}) of the brazed coating is substantially lower than that of the 16MnCr5 steel. The corrosion potential (E_{corr}) of the hardfacing is shifted to

more positive potentials (-250 mV), due to the chemical composition of the Ni-based metallic matrix. The anodic Tafel slope of the coating shows an inclination to passivate, due to the presence of a relatively high amount of chromium (~14%) in the alloy. Adversely, the steel sample points no tendency towards passivation.
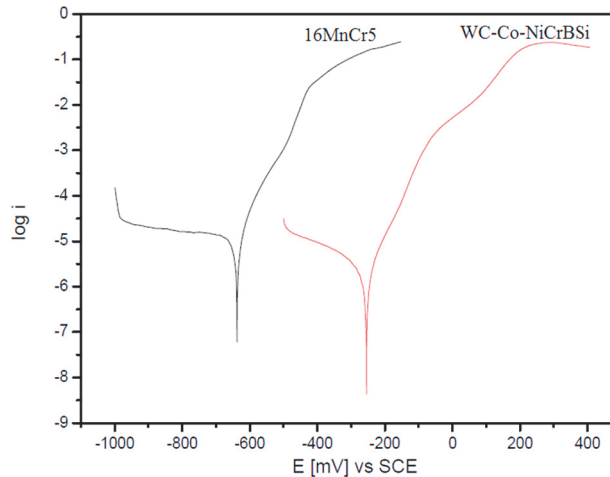

Figure 5 Tafel plot of 16MnCr5 and WC-Co-NiCrBSi in 3.5 % NaCl solution

Both corrosion current density and corrosion potential lean toward a lower reaction rate and consequently better corrosion resistance of the coated sample compared to the uncoated one is expected. Due to the fact that transition metal carbides have high resistance to NaCl solutions, corrosion of WC-based composite coatings manifests throw the dissolution of the metallic binder. This creates an area in which the metallic matrix is depleted, leaving behind only a skeleton of WC particles with severely affected properties.

4.   CONCLUSIONS

The investigations performed in this study underline a mean hardness of 896HV1, which is almost 2 times higher than that of case hardened 16MnCr5 steel. The mean coefficient of friction was more than 2 times lower, correlated with a ware rate more than 20 times lower compared to 16MnCr5 values. Adhesion strength was found to be higher than 120 MPa, fact which confirms a good metallurgical bond between the coating and the substrate. Moreover, a lower corrosion current density was measured for the WC-Co-NiCrBSi functional composite coating, leading to a significant improvement in corrosion resistance.

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