

Electrochemical Corrosion Behavior of High Temperature Vacuum Brazed WC-Co-NiP Functional Composite Coatings

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Abstract. The present study aims to investigate the electrochemical corrosion behavior of high temperature vacuum brazed WC-Co-NiP coatings deposited onto 16MnCr5 (1.7131) case hardening steel in 3.5% NaCl (pH 7) electrolyte solutions. Corrosion resistance is appraised using the potentiodynamic polarization method at room temperature in a three-electrode cell configuration. The coating characteristics like morphology, microstructure and chemical composition before and after the corrosion tests have been analyzed by means of scanning electron microscopy (SEM) combined with energy-dispersive X-ray (EDX) spectroscopy. This coating technology makes possible the deposition of high quality hardfacings, with minimal influence on the metallic substrate. The electrochemical measurements resulted in a lower corrosion current density, correlated with a significant improvement in the corrosion behavior of the WC-Co-NiP coated samples, compared to the uncoated ones.

1. Introduction

In nearly every area of industry, corrosion and wear are phenomena of paramount concern. It is estimated that the costs of corrosion in the US surpassed 1.1 trillion dollars in 2016 [1]. Recent surveys express that the worldwide (direct) cost of corrosion is between 1.3 and 1.4 trillion dollars, that is 3.1% to 3.5% of a developed country's annual GDP. These figures represent only the direct costs of corrosion basically materials, equipment, and services involved with repair, maintenance, and replacement. They do not comprise the environmental damage, waste of resources, loss of production, or personal injury caused by corrosion. Both NACE and NASA corrosion experts have determined that a net of 15% to 35% of the annual corrosion-related expense can be reclaimed by applying presently accessible corrosion control methods. According, even though corrosion is a natural process, thus it cannot be completely stopped, five primary techniques namely: material selection, coatings, inhibitors, cathodic or anodic protection and design can be applied in order to control it [1-3].

Although the brazing process is usually employed as a joining technique, in this study the possibility of using this method as a coating technology was tested, with the purpose of bringing fresh and innovative solutions in the field of functional coatings. Applied as a coating technique, high temperature vacuum brazing of flexible tapes concludes in increased cohesion, and adhesion of the coating to the substrate. These coatings are usually employed as protection against wear in a wide variety of applications, most of which requiring at the same time high corrosion resistance [4].



Metallic matrix functional composite coatings are generally utilized to isolate the base material from the corrosive environment to protect it. Therefore, they are more noble than the substrate and offer protection by way of anodic or barrier action. In order to possess adequate corrosion resistance, the structure has to be as dense as possible, without pores, cracks or any other defects. If the deposit is porous or it contains micro-cracks, the corrosive media can reach down to the base material. In this case, the coating might detach, and the substrate will come in direct contact with the working environment [5]. The reinforcing material selected for the current study was cobalt cemented tungsten carbide (WC-Co). Cemented tungsten carbides possess a heterogeneous structure, where corrosion occurs predominantly in the metallic binder, because it generally has a lower corrosion resistance compared to the ceramic phase (WC). For example, cobalt (often used as binder) has relatively low corrosion resistance in sulfuric, hydrochloric, nitric and other strong acids. The corrosion behavior of cemented carbides is highly dependent on the nature and proportions of metallic binder constituents. For instance, the presence of nickel significantly improves the corrosion resistance, possessing lower corrosion rates compared to cobalt. Addition of chromium will improve the resistance to oxidation, nevertheless it can also severely affect particular mechanical properties through the formation of chromium-rich brittle carbides [6, 7].

2. Experimental

Manufacturing of the currently employed polymer bond hardfacing tapes involves mixing of 75 wt.% WC-Co (PA2), comprising of 7.5 wt.% Co, 5.7 wt.% C, and W as balance, recycled cermet powder with 25 wt.% NiP (Ni6), consisting of ≈ 11 wt.% P, max. 0.06 wt.% C and Ni as balance, brazing filler metal powder and an additional 2 wt.% water-based fugitive organic binder until the latter one fibrillates, and doing so, anchors the powder particles, allowing further processing steps. Both types of powders are commercialized by the Swedish company Högånäs AB. The mixture is subsequently rolled to a predetermined thickness, forming a flexible cloth, afterwards cut to the required shape and size.

The high temperature vacuum brazing process was carried out in a HITERM 80-200 cold wall vertical vacuum furnace at the stable pressure of around $3.0 \cdot 10^{-4}$ mbar and a brazing temperature of 1000 °C for a soaking time of 30 min. During the high temperature vacuum brazing process, the NiP brazing filler alloy melts and infiltrates the WC-Co particles. Metallurgical reactions, governed by diffusion and alloying occur at the interfaces between the reinforcing particles (WC-Co hard phase) and metallic matrix (NiP alloy), as well as at the coating/substrate one. Consequently, the WC-Co-NiP/16MnCr5 systems possess a strong metallurgical bond [4]. The detailed procedure of manufacturing such hardfacings was reported in a different study [8]. The morphology and microstructure of the coating and coating-substrate interface is illustrated in the BSE cross-section micrograph of figure 1.

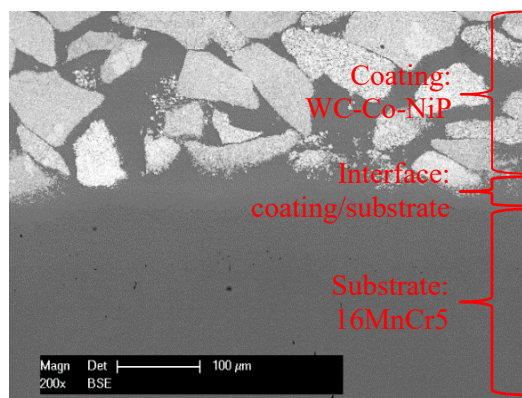


Figure 1. BSE micrographs of WC-Co-NiP/16MnCr5 system.

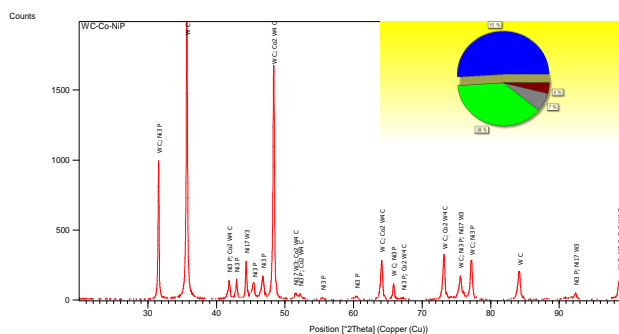


Figure 2. XRD pattern of WC-Co-NiP coating.

The high temperature vacuum brazed coatings display a dense structure, with uniform distribution of the cermet particles. One can clearly observe that the molten self-fluxing alloy infiltrated between the WC-Co particles, cementing them together, and at the same time bonding the entire system with the metallic substrate.

The X-ray diffractogram displayed in figure 2 reveals that the hardfacings consist of 51 wt.% WC, 38 wt.% Ni_3P , 7 wt.% Ni_{17}W_3 and 4 wt.% $\text{Co}_2\text{W}_4\text{C}$. Presence of other phases (in undetectable quantities) is plausible, because of the high number of elements involved.

The electrochemical corrosion behavior is evaluated through potentiodynamic polarization, employing a VoltaLab PGP201 potentiostat/galvanostat in a three-electrode cell configuration. For comparison purposes, working electrodes (WE) were prepared from the 16MnCr5 substrate material, WC-Co-NiP functional coatings developed throughout the present study, and two types of thermal sprayed coatings with similar chemical composition, namely WC-Co-Mo and WC-Co respectively. The chemical composition of the thermal sprayed coatings is only similar and not identical because at the present time there are no available methods of depositing thick coatings with the chemical composition of the vacuum brazed coatings, namely WC-Co-NiP. A platinum disk was used as counter electrode and a saturated calomel electrode (SCE) as reference. Prior to the investigations, the WEs have been ground with metallographic paper in order to remove potential oxides and to ensure as close as possible the same surface roughness (R_a 0.03). Subsequently, the specimens are rinsed with ethanol and dried under a stream of warm air. Polarization studies were performed at room temperature in the potential interval between -1000 mV and +1000 mV vs. SCE with a scan rate of 10 mV min^{-1} . The 1 cm^2 geometrical surface area of the sample allowed current readings to be directly expressed as current density (A cm^{-2}). The cathodic branch in the polarization curves corresponds predominantly to hydrogen evolution reaction, while the anodic branch features the most important information related to the corrosion resistance.

Figure 3 illustrates typical polarization plots for the discussed samples subjected to potentiodynamic electrochemical corrosion in 3.5% NaCl solution (pH 7). As expected, the corrosion current density (i_{corr}) of the WC-Co-NiP brazed coating is substantially lower than that of 16MnCr5.

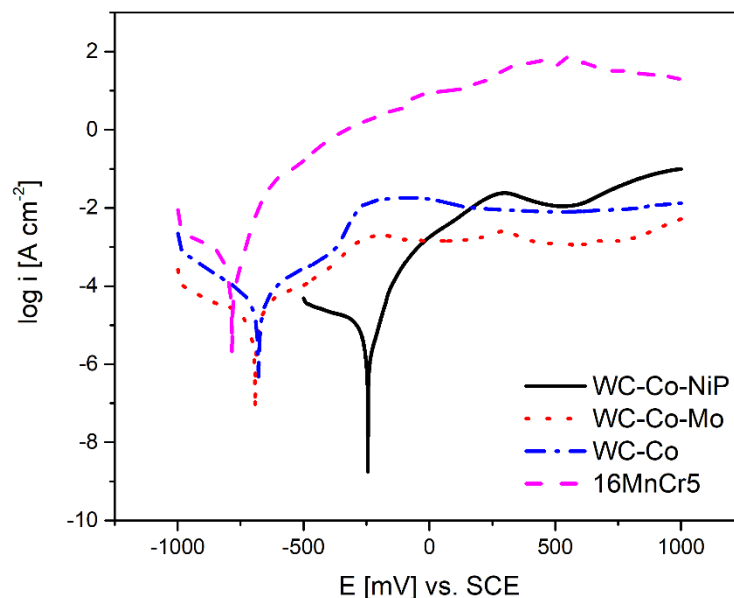


Figure 3. Polarization behavior of vacuum brazed WC-Co-NiP, thermal sprayed WC-Co-Mo, WC-Co and 16MnCr5 steel in 3.5% NaCl solution.

Correspondingly, the corrosion potential (E_{corr}) of the hardfacing is shifted to more positive potentials (-245 mV) in comparison to the uncoated sample (-780 mV), aspect associated with the

Ni-based chemical composition. The anodic branch (see figure 3) of the polarization curve shows an inclination to passivate, due to the high amount of Ni present in the brazing filler alloy. Adversely, the uncoated steel sample points no tendency towards passivation, due to the Cr content lower than 12 wt.%. Both corrosion current density (i_{corr}) and corrosion potential lean toward a lower reaction rate, and consequently, better corrosion resistance of the coated samples compared to the uncoated ones is to be expected [9].

The polarization curves of WC-Co-NiP coated samples show passive plateaus at values between 300 mV and 550 mV, indicating the formation of a passive oxide film. Further increasing the potential in the anodic direction, the passive film previously formed on the surface of the sample, brakes down and the nickel rich phase of the coating is subsequently dissolved. The values presented in table 1 indicate a corrosion current density around 45 times lower for the brazed coating in comparison to substrate material. Although both types of thermal sprayed coatings show a more stable behavior in the anodic branch, with a more pronounced tendency of passivation and a wider passive region, the brazed coating exhibits lower corrosion currents and the corrosion potential is shifted to more positive values, indicating a higher resistance of the material in this specific testing conditions. This fact can be attributed to the presence of the corrosion resistant Ni_3P phase revealed from the XRD patterns, which is formed during the vacuum brazing process [10].

Average corrosion potential and corrosion current density of the analyzed samples obtained from the electrochemical polarization investigations performed in 3.5% NaCl aqueous solution are summarized in table 1.

Table 1. Corrosion potential and corrosion current density values in 3.5 wt.% NaCl.

Sample	E_{corr} [mV] vs. SCE	i_{corr} [$A\ cm^{-2}$]
WC-Co-NiP	-245	$0.4 \cdot 10^{-5}$
WC-Co-Mo	-695	$0.6 \cdot 10^{-5}$
WC-Co	-685	$1.8 \cdot 10^{-5}$
16MnCr5	-780	$18 \cdot 10^{-5}$

The micrographs illustrated in figure 4 offer an overview (top-view) of the coatings' surface (testing area) a) before, and b) after the electrochemical investigation. It can be observed that the metallic binder is severely affected, while the reinforcing phase (WC) retains its structural integrity.

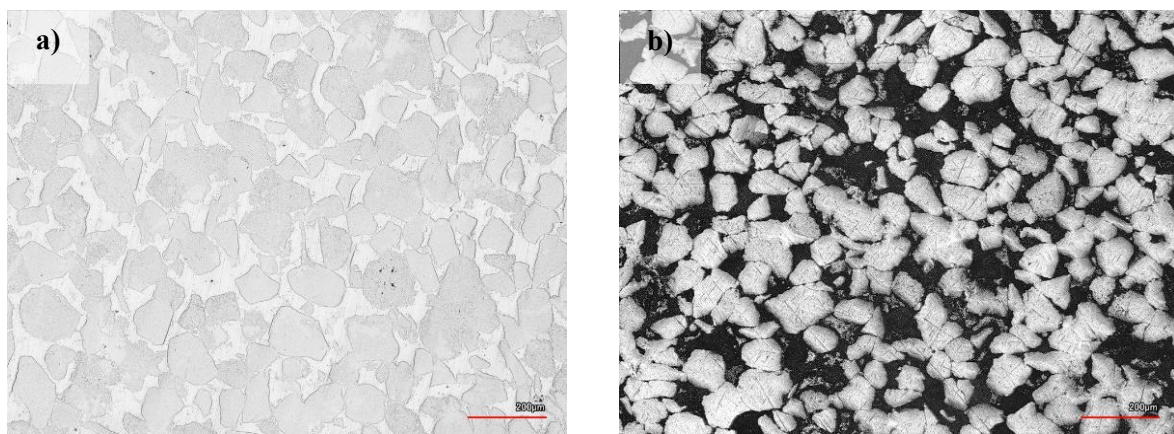


Figure 4. Optical micrographs of: a) coating surface before electrochemical investigation, and b) after electrochemical investigation.

Because transition metal carbides have high resistance to chlorine containing solutions, corrosion of WC-based composite coatings manifests predominantly through the dissolution of the metallic binder. Subsequently, the metallic matrix is depleted, leaving behind only a skeleton of WC particles with severely affected properties, as shown in the scanning electron micrograph of figure 5.

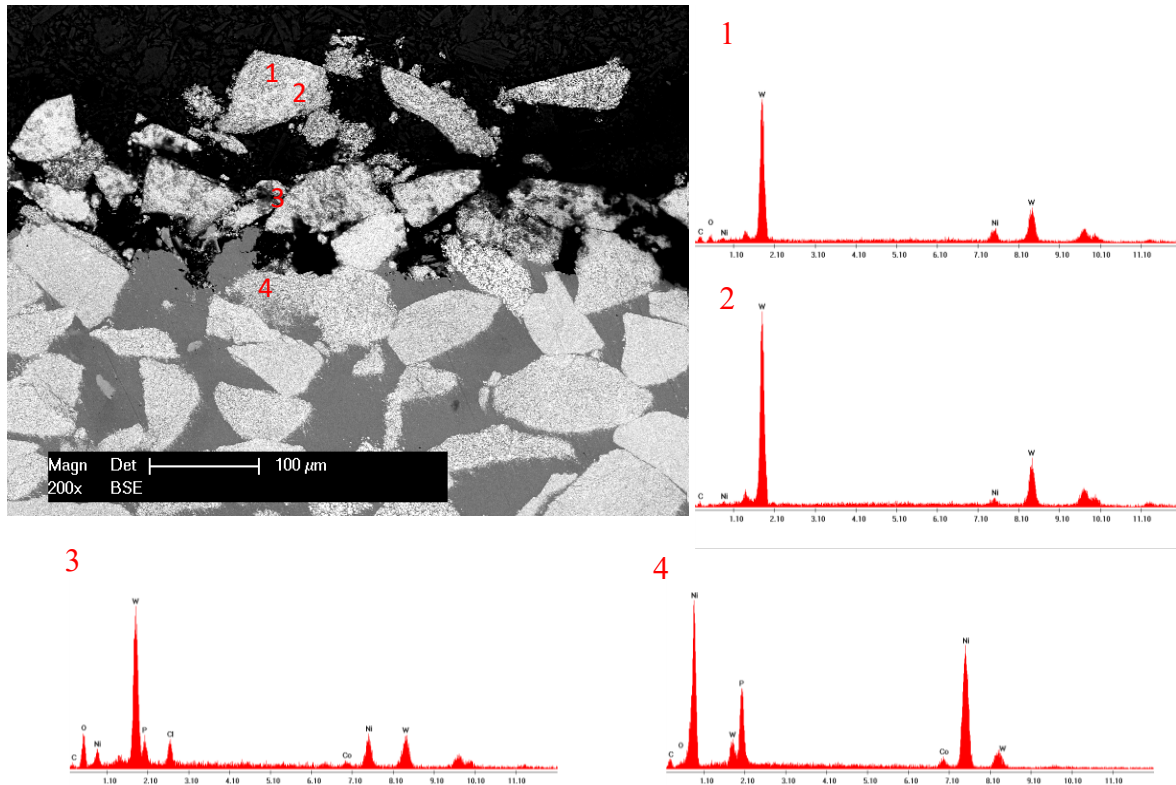


Figure 5. SEM cross-section micrograph and EDX spectra corresponding to the marked regions, after electrochemical corrosion.

The selective corrosion mechanism is experienced by the majority of (metal-matrix) composite coatings and it was observed in several studies conducted by other researchers [11-15]. The superior corrosion resistance of WC-Co-NiP coatings compared to the 16MnCr5 case hardening steel substrate is attributed to the formation of the nickel passive layer. This film forms willingly in contrast to the development of the passive films on iron. Dissimilarities in the nature of the oxide layer grown on Fe and Ni are accountable for this phenomenon. The layer thickness on Ni is between 0.9 mm and 1.2 mm, while the Fe oxide layer is situated in the interval 1 mm and 4 mm and has an elevated predisposition to chemical dissolution. There are two theories regarding the morphology and chemical composition of the nickel passive film. One theory stipulates that the layer is completely NiO with a small quantity of nonstoichiometric nickel, producing Ni^{3+} cation vacancies. In the case of the second one, it comprises of an inner film of NiO and an outer one of anhydrous $\text{Ni}(\text{OH})_2$. Once generated, the oxide film of nickel, neither cathodic treatment nor chemical dissolution can easily remove it [16]. The passive film of nickel will not offer protection against corrosion in strongly oxidizing media, for instance in nitric acid. Alloying with chromium will generate a denser, more stable film, increasing the corrosion resistance to a variety of oxidizing environments. However, these alloys are susceptible to attack in atmospheres containing chlorides or other halides, particularly if oxidizing compounds are present. Corrosion will manifest mostly in the form of pitting and occasionally as stress corrosion cracking. Addition of molybdenum, titanium and/or tungsten should improve the behavior under all working conditions [17]. The EDX spectra of figure 5 confirm the formation of Ni oxides and possibly W oxides as well as the dissolution of the metallic binder. The corrosion behavior of the present high

temperature vacuum brazed WC-Co-NiP functional coatings was found to be in good compliance with those of WC-based claddings tested under similar conditions by other researchers [11, 18].

3. Conclusion

The corrosion behavior of high temperature vacuum brazed WC-Co-NiP functional composite coatings, potentiodynamic polarized in 3.5% NaCl was found to be similar to the one observed in the case of thermal sprayed WC-Co-Mo and WC-Co respectively. The corrosion current density (i_{corr}) of the WC-Co-NiP brazed coating is lower than that of thermal sprayed WC-Co-Mo and WC-Co. The corrosion potential (E_{corr}) of the brazed hardfacing is shifted to more positive values in comparison to that of thermal sprayed coatings, which is associated with a lower reaction rate. The electrochemical polarization curves illustrated a 45 times lower corrosion current density in the case of WC-Co-NiP coatings compared to 16MnCr5 case hardening steel samples in the 3.5% NaCl electrolyte solution. The superior corrosion resistance of WC-Co-NiP functional coatings is assigned to the chemical composition of the metallic matrix, namely the Ni-P alloy (Ni₃P phase), which is able to readily generate a passive layer, stable up to the potential of around ≈ 600 mV vs. SCE. The corrosive attack onto vacuum brazed WC-Co-NiP coatings is characterized by selective dissolution of the metallic matrix, compared to the generalized corrosion observed in the case of the unprotected substrate material. Accordingly, the present work proved vacuum brazed WC-Co-NiP coatings are highly effective in the anodic protection of the 16MnCr5 substrate material against the 3.5% NaCl corrosive media.

4. References

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