

**DEVELOPMENT OF HIGH TEMPERATURE VACUUM BRAZED WC-Co-NiP  
FUNCTIONAL COMPOSITE COATINGS**

**Teză de doctorat – Rezumat**

pentru obținerea titlului științific de doctor la

Universitatea Politehnica Timișoara

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pentru  
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## 1. Introduction, Background and Motivation

Surface degradation of structural and active components is a continuous concern of modern engineering. Recently, various technologies, including thermal spraying, laser cladding, welding and high temperature vacuum brazing have been implemented with the purpose of depositing thick wear and corrosion resistant coatings. Considering the present knowledge in the field of surface engineering, the main goal of this study was to develop, investigate and characterize infiltration braze claddings, deposited from Ni-base self-fluxing alloys reinforced with WC-based cermets. Nickel based coatings, are being successfully applied onto metallic substrates and show superior characteristics that make them more attractive compared to other types of coatings. Besides de large variety of technologies able to deposit WC reinforced hardfacings, infiltration braze coating is being noted as an effective method to overlay composite coatings with high density and superior bond strength, wear and corrosion resistance. Due to the vastness of possible chemical compositions, the properties of such coatings, obtained through high temperature vacuum brazing are still scarcely known. Therefore, this work aims to study the deposition process of functional composite coatings with metallic matrix based on NiP self-fluxing alloy reinforced with WC-based hard particles. Furthermore, it will investigate the influence of process parameters and the obtained coating characteristics like morphology, chemical and mechanical properties.

Several areas of application (components of pumps, mixers or extruders, mixing buckets, baffles and pipe bends) have been found to fit the particular properties and characteristics of brazed coatings.

Regarding the main limitations of the technique, fruitful means to overcome or at least mitigate them have been found, eliminating the use of hazardous organic binders and reducing the maximum process temperature. More than a few Ni-based self-fluxing alloy powders were considered and tested, and the initial Nitrile based glue was replaced with a nontoxic water-based fugitive binder. The flexible composite tapes have been placed on top of 16MnCr5 (1.7131) case hardening steel substrates and brazed with different parameters to finely optimize the thermal treatment. [1-3].

Recent research has led to the development of the brazing process [2, 3, 6], through which are obtainable relatively thick coatings (up to tens of millimeters), while other coating processes are still limited to much lower thicknesses [1-5, 7]. The classification of the high temperature vacuum brazed WC-Co-NiP functional composite coatings is schematically illustrated in Figure 1.

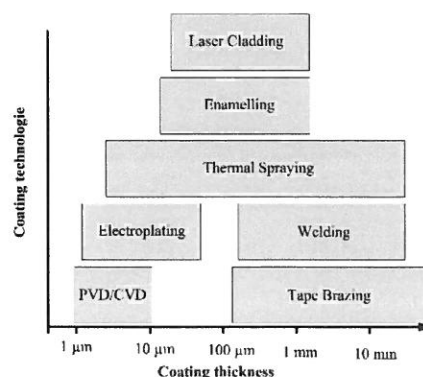


Figure 1 Coating techniques

In the current **state of the art, tape brazing** involves the use of flexible cloths rolled from mixtures of hard phase powders, filler metal powder and appropriate polymeric binders. The mats can easily be manufacture under diverse chemical compositions of base and filler metal powder, and formed to size and shape by cutting or stamping. After forming, the cloths are overlaid on top of the metallic substrate and fixed in place often with a small amount from the same polymeric binder. The coating process actually takes place at temperatures usually slightly above the liquidus temperature of the filler alloy, in vacuum or under protective atmosphere, with the aid of a furnace. During the brazing process, filler metal reaches liquid state and infiltrating the spaces between the hard phase particles wetting and enveloping them. Metallurgical interactions governed by diffusion and alloying appear among base powder and brazing alloy, as well as at the coating/metallic substrate interface, resulting in a strong metallurgical bond.

No universal reference for the brazing temperatures and holding times exists, because the values depend strongly on the chemical composition of the substrate material, reinforcing powder and filler metal, their ratio in the mixture and the metallurgical interactions. Considering that the majority of substrate materials are iron, nickel, chromium or cobalt alloys, base powders are usually ceramics or cermets and the metal matrix consists typically of self-fluxing nickel base alloys the furnace brazing temperature is approximately 1100°C. Brazed overlays with a thickness range of 150 µm to 20 mm have been successfully deposited, with theoretical possibilities of an even greater thickness interval. Due to the common high amount of hard phases (up to 70 wt.% or more in some cases) Ni-base matrix alloy, and generally low porosity (≈1%), these coatings can offer high wear and corrosion resistance under severe working conditions. The major limitation of this coating technique is the requirement to treat the whole substrate to the necessary high brazing temperature. This process can have a negative effect on the substrate material, leading to undesired grain growth or phase transformations. Another current disadvantage of the method is the use of potentially harmful chemical compounds in the polymeric binders, which need to be filtered, contained and neutralized.

The present study assessed the possibility of overcoming the afford mentioned limitations of the high temperature vacuum braze coating technique.

The original contributions of this study refer to the possibility of utilizing vacuum brazing as a non-conventional coating method in order to obtain WC-Co-NiP functional hardfacings with superior wear and corrosion resistance. In this regard, it explored the possibility of combining recycled WC-Co powder as reinforcing phase with NiP brazing filler metal as metallic matrix, to develop vacuum brazed composite coatings. A careful selection of feedstock materials in order to favorably combine a manufacturing process as accessible, economic, and environmentally friendly as possible, with the production of coatings with superior characteristics was also carried out. The successful employment of water-base fugitive glue as organic binder for the manufacturing of flexible cloths, which is safe to handle and harmless to the environment, and at the same time offers adequate flexibility and long shelf life was highlighted. The usage of BNi6 (NiP alloy) brazing filler metal as metallic matrix decreased the maximum temperature of the brazing process down to 1000°C, thus reducing production costs and thermal influence on the substrate material. Studies on the deposition mechanism, as well as investigations on the influence of the thermal cycle parameters on the morphology of the coatings have been accomplished. Consequently, the optimization of the brazing process parameters for the studied chemical composition was successfully performed. Experimental investigations revealed noteworthy characteristics and properties of the high temperature vacuum brazed WC-Co-NiP functional composite coatings (including wear and corrosion resistance).

Accordingly, the method presented in this thesis leads to a facile and cost effective way to develop metallurgically bonded functional coatings with improved wear and corrosion resistance, due to the dense, composite microstructure.

The main goal of the present study was to development and characterize high temperature vacuum brazed WC-Co-NiP coatings deposited on steel substrates.

The thesis has been structured into 5 chapters:

**Chapter 1** presents the background and motivation of the chosen topic.

**Chapter 2** deals with the state of the art in the field of brazing, presenting some theoretical aspects regarding, methods, current materials, classification and applications. Moreover, an introduction in the tribological and corrosion behavior of brazed coatings is made. Main advantages and limitations compared to other coating technologies are also discussed.

**Chapter 3** describes the methodology and equipment used to achieve the experimental study. This chapter offers an outline concerning the applied investigation methods and presents different experimental techniques, which can provide important information on the quality and performance of high temperature vacuum brazed coatings.

**Chapter 4** presents the experimental program concerning the infiltration hardfacing process, the results obtained during this study and highlight the most important aspects.

**Chapter 5** points out the conclusions of this study and the original contributions accomplished through this work.

## 2. Experimental Program

For development of high temperature vacuum brazed functional composite coatings from polymer bond flexible tapes, the following main steps have been taken into consideration during the current study:

- materials selection;
- manufacturing of the polymer bond tapes;
- high temperature vacuum brazing;
- characterization of the obtained coatings;
- evaluation of the results and drawing the conclusions.

Main steps of the experimental program are schematically presented in Figure 2.

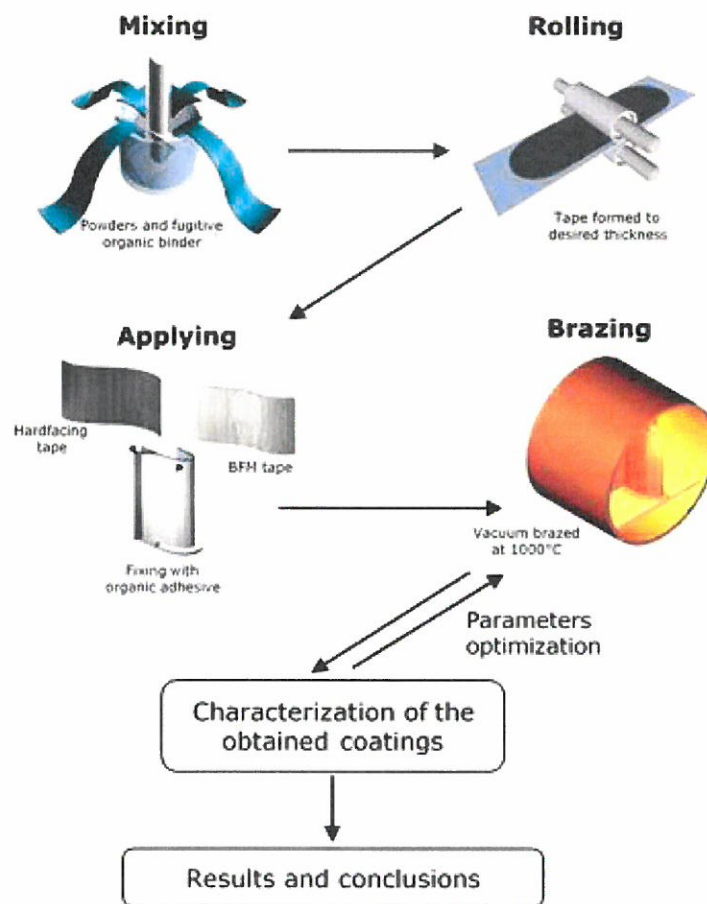


Figure 2 Schematic representation of the experimental program

Thermal behavior of the selected powders as well as organic binders was observed with the aid of Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) respectively. The morphology, microstructure, chemical composition of the coatings and the quality of the interface with the substrate have been analyzed by means of Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-ray Spectroscopy (EDX). Size, occurrence and distribution of pores and microcracks has been estimated using image processing of micrographs. Phase composition of the initial filler metal and reinforcing powders, and subsequent deposited coatings was determined using X-Ray Diffraction (XRD). Surface hardness and cross-section hardness profile was evaluated by Wickers indentation. Bond and adhesion/cohesion strength have been investigated through uniaxial tensile testing.

To assess and compare the wear resistance of the composite coating to that of the base metal, tribological investigations were performed with a ball-on-disk testing arrangement. The electrochemical corrosion behavior was evaluated by potentiodynamic polarization, employing a three-electrode cell.

Accordingly, **flexible composite tapes** were manufactured by mixing 75 wt.% WC-Co and 25 wt.% NiP powder with an additional 2 wt.% water based fugitive organic adhesive until the binder fibrillates, followed by rolling of the mixture in order to form cloths with 3 mm thickness. Chemical composition of the feedstock materials is presented in Table 1.

Table 1 Nominal chemical composition of the brazing cloth (wt.%)

	W	C	Co	Ni	P	wt. %
<b>WC-Co</b> 45-300 $\mu$ m	rest	5.7	7.5	-	-	75
<b>NiP</b> 20-55 $\mu$ m	-	max. 0.06	-	rest	10 - 12	25
<b>Organic binder</b>	Water based special formulation					+ 2-3

The **filler alloy** selected for further investigations and manufacturing of flexible tapes intended for the coating deposition is a BNi6 typ BFM. This filler metal is a gas atomized powder with a well-defined chemical composition. It is suitable for different applications, brazing conditions and braze properties. Applications are found in a wide range of industrial areas such as automotive, nuclear power and aerospace. The most established processing technique is vacuum furnace brazing, it can also be brazed in reducing atmospheres, or under inert gas. The Ni6 BFM powder presents a dense and homogeneous microstructure, with occasional satellite type formations on the surface of some particles and the granulometric fraction is situated between 20  $\mu$ m and 55  $\mu$ m.

Morphology and elemental composition of the NiP powder can be observed in the SE micrograph a), respectively EDX spectrum b) of Figure 3.

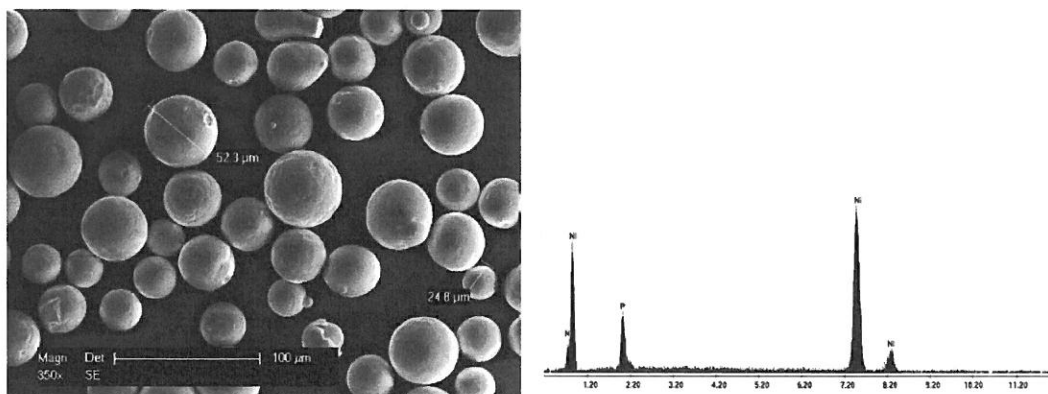


Figure 3 SE micrograph a), and EDX spectrum b) of the NiP powder



The **reinforcing material** selected for this study is a commercially available WC-Co powder obtained from recycling of hard metal tools. This is a crushed cemented carbide, with an angular shape and a granulometric fraction situated between 45 and 500  $\mu\text{m}$ , sold by Höganäs AB under the trade name PA2. The chemical composition given by the producer consists of 5.7 wt.% C, 7.5 wt.% Co and W as balance.

Morphology and elemental composition of the WC-Co powder can be observed in the SE micrograph a), respectively EDX spectrum b) of Figure 4.

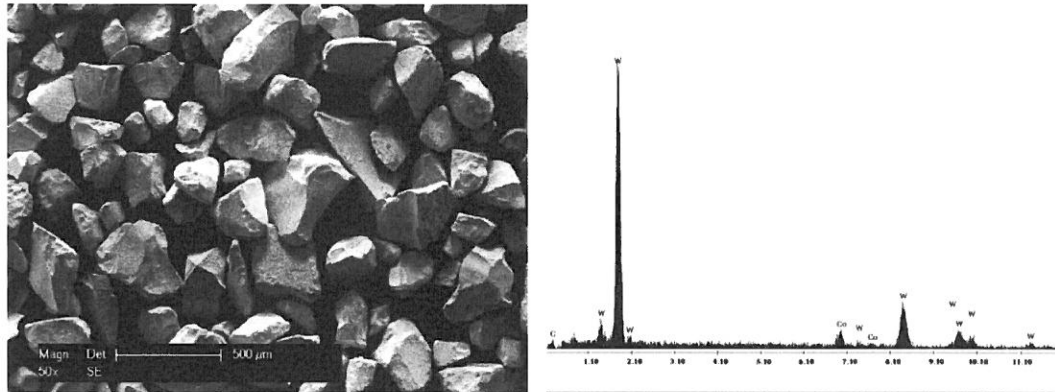


Figure 4 SE micrograph a), and EDX spectrum b) of the WC-Co powder

Figure 5 a) displays a SE micrograph of the brazing filler metal green tape, in which one can easily observe the fugitive glue fibrils that hold together the alloy particles. Complementary, Figure 5b) offers a magnified view of the WC-based hardfacing green overlay. This cloth contains additionally a small amount (around 2 wt.%) of NiP BFM particles in order to promote capillary action during the brazing process.

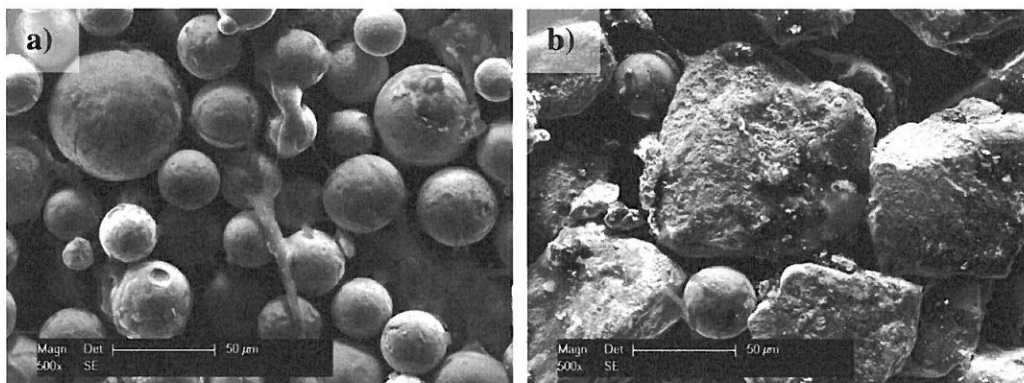


Figure 5 SE micrograph of: a) BFM tape, and b) hardfacing tape

During previous attempts of depositing WC-based composites via high temperature vacuum brazing on active areas of different parts a high amount of cracks appeared onto the surface and in the depth of the coatings. In order to overcome porosity and fractures or crack initiation that appear during the treatment due to different values for thermal expansion/contraction coefficient of the metallic and ceramic phases, optimization of the brazing process is mandatory.

From the **Thermogravimetric Analysis (TG)**, it was determined that the organic binder loses significant mass in two steps. The minor weight loss, between 100°C and 300°C represents the evaporation of liquids (water), solvents and other volatile compounds, about 3% of the total mass. The second and most relevant decline has a maximum at approximately 480°C, corresponding to the breakdown of around 92% of the entire matter, and relative total

decomposition. The maximum decomposition rate of the binder is achieved at around 400°C. The final mass corresponds to the non-flammable compounds existing in the material composition and represents roughly 2% of the initial.

The Differential Thermal Analysis (DTA) displayed the solidus and liquidus temperature of the NiP brazing alloy. The temperature stays relatively constant until the minimum that occurs at 880 °C, corresponding to the solidus temperature, followed by an endothermic event with a maximum at 890 °C, equivalent to the liquidus temperature of the sample.

In the case of this study, 1.7131 (16MnCr5) case hardening steel was utilized as **substrate material** due to availability and its importance as a structural material. Prior to the coating process, the substrate material was machined, in order to obtain several distinct geometries, each of them specific to subsequent investigation requirements. Only necessary preparation involved grinding in order to remove potential oxides or scale from the surface, without the requirement of reaching a specific roughness. Afterwards, the specimens are rinsed with a degreasing solution (ethanol) and dried in a stream of warm air.

Although, contrary to other coating techniques, like CVD, PVD and the thermal spraying processes, adhesion of vacuum brazed coatings is not influenced by the substrate roughness, oxide free and dry surfaces are compulsory to ensure braze joints of high quality [2, 3, 6-8]. On top of the clean metallic substrates, a cut to shape overlay was positioned and fixed with the aid of a small amount from the same water based organic binder (see Figura 6). In the case of the current study, initial thickness of the multiple tape arrangement was approximately 3 mm.

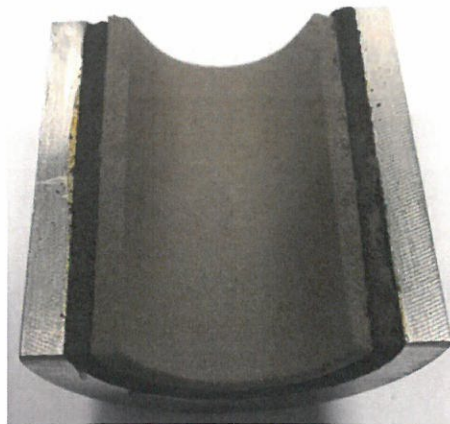


Figure 6 Macroscopic images of the sample arrangement

The high temperature vacuum brazing process was carried out in a HITERM 80-200 cold wall vertical vacuum furnace. The stable pressure of around  $3.0 \cdot 10^{-4}$  mbar was achieved with the aid of an oil-sealed rotary vane pump assisted by a turbo molecular pump. In order to determine the **optimum parameters** for the thermal cycle, a process parameter optimization was performed. Different values for the heating ramps, soaking time, cooling rate and intervals were applied. The four dissimilar heat treatment programs are illustrated in Figure 7.

Vacuum brazing was performed in the absence of reducing agents, therefore the basic oxide removal mechanism is by dissociation, according to Eq. 1 [20]:



A standard, extremely basic set of parameters was utilized as guideline. For this first set of parameters (*Program 1*), heating was performed with the rate of  $15^{\circ}\text{C min}^{-1}$  up to  $1000^{\circ}\text{C}$  followed by a 30 min brazing hold. Finally, a rate of  $30^{\circ}\text{C min}^{-1}$  was applied for cooling the sample down to room temperature.

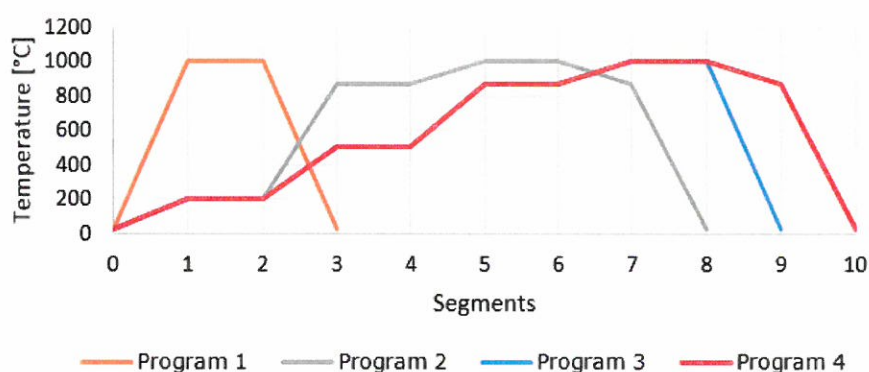


Figure 7 Experimental brazing process parameters

The optimized parameters of *Program 4*, followed the exact heating steps and soaking periods of *Program 3*, but the cooling was performed in to stages. Consequently, the samples were cooled down to  $870^{\circ}\text{C}$  by slowly reducing the temperature with a rate of  $10^{\circ}\text{C min}^{-1}$ . This temperature was set  $10^{\circ}\text{C}$  below the solidus temperature of the NiP BFM, in order to allow the molten alloy to solidify in place. This initial low cooling rate also prevents generation of residual stresses caused by the high temperature gradient, due to the difference in thermal conductivity of ceramic and metallic constituents and phase transformations that occur during rapid solidification.

The final cooling ramp was performed with a higher rate. In the case of this study, a cooling speed of  $30^{\circ}\text{C min}^{-1}$  was applied until the vacuum furnace chamber reached a stable temperature of  $25^{\circ}\text{C}$ . These settings ensured the required metallurgical properties and production needs, while avoiding part distortion and at the same time reducing the process duration.

The characteristics of the obtained specimens were investigated by means of Scanning Electron Microscopy (Philips XL 30 ESEM) and 3D Confocal Laser Scanning Microscopy (Keyence VK-X) combined with an Image Analysis and Processing Software (ImageJ)

Based on the results of the TGA, DTA, selected bibliographic references, suggestions from the NiP powder manufacturer and experience gained from practice of numerous experiments, the initially basic brazing cycle was meticulously optimized.

During the heating up process, the organic binder decomposes at approximately  $500^{\circ}\text{C}$  creating numerous small interconnected pores favorable for the capillary action. As the temperature increases, at  $880^{\circ}\text{C}$  the self-fluxing alloy reaches its solidus temperature. It is mandatory to keep the samples at approximately  $10^{\circ}\text{C}$  below this temperature for a pre-determined soaking time (depending on different factors, like the size, shape and chemical composition of the components to be brazed) in order to have a uniform heat distribution. The final brazing step performed at  $1000^{\circ}\text{C}$  for 30 min assured the high fluidity of the Ni-based alloy necessary for wetting, infiltrating and filling the micro voids. This temperature is also required for the diffusion process along the interface region between the coating and base metal in order to obtain high quality coatings and a strong metallurgical bond.

**Microstructure.** All the final properties of vacuum brazed coatings depend strongly on the microstructure. Mechanical properties, tribological behavior, corrosion resistance and many other aspects are all influenced by the size and distribution of the carbides, amount of pores, metallurgical interactions, as well as formation of specific phases. Accordingly, microscopic investigations are conducted utilizing a Philips XL 30 ESEM scanning electron microscope and a Keyence WK-X 3D confocal laser scanning microscope. The porosity degree is evaluated with the aid of the ImageJ open access image analysis and processing software. Elemental analysis of the coatings is carried out by energy-dispersive X-ray spectroscopy with a EDAX XL-30 microanalyzer. Phase identification is performed implementing a Philips X' Pert X-ray diffractometer.

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.

In connection with the previous statements, the morphology and microstructure of the coating and coating-substrate interface is illustrated in the BSE cross-section micrographs of Figure 8.

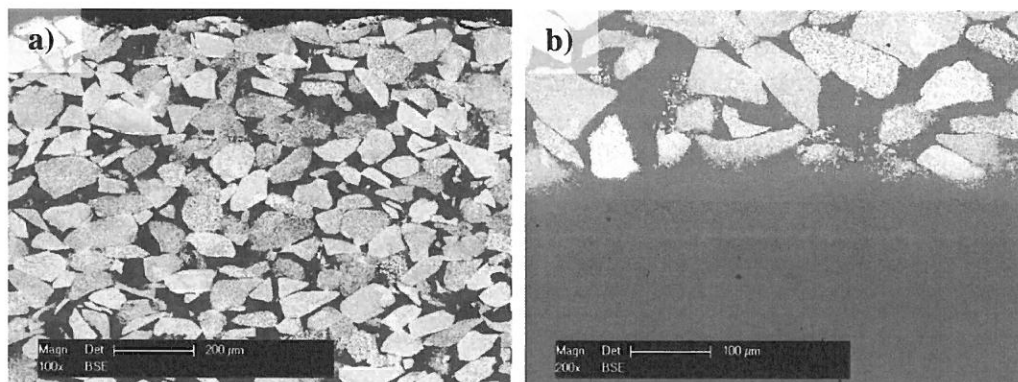


Figure 8 BSE micrographs of: a) coating, and b) coating/substrate interface

**Porosity degree** has a drastic influence on the mechanical properties (e.g. hardness, cohesive and adhesive strength) as well as the tribological and corrosion behavior. Vacuum brazed overlays are barrier coatings, protecting the substrates by isolating them from the aggressive medium, rather than using sacrificial action. That is why the deposit must be as much as possible free of pores and other defects.

The optimized heat treatment leads to deposition of high quality hardfacing coatings with low porosity, a good distribution of both large and small hard phases, excellent metallurgical bond and minimal dilution. Simultaneously, the optimization process has eliminated the initial problem of cracks and fracture building and reduced by almost 20 times the size and occurrence frequency of interconnected and individual pores. This work highlights the crucial importance of optimizing the brazing process parameters for each chemical composition, thickness and combination of flexible composite cloth and substrate material.

Amount and distribution of pores in the coatings obtained with the optimized parameters are illustrated in Figure 9.



Figure 9 Processed micrograph illustrating the porosity degree

**Phase composition.** A comparative representation of the XRD patterns collected from a) as-received NiP (Ni6) brazing filler metal powder, b) NiP alloy obtained from heat treating the Ni6 BFM powder with the optimized brazing thermal cycle, c) as-received WC-Co (PA2) reinforcing powder, d) WC-Co powder heat treated with the optimized brazing thermal cycle, and e) the high temperature vacuum brazed WC-Co-NiP functional coating is given in Figure 10.

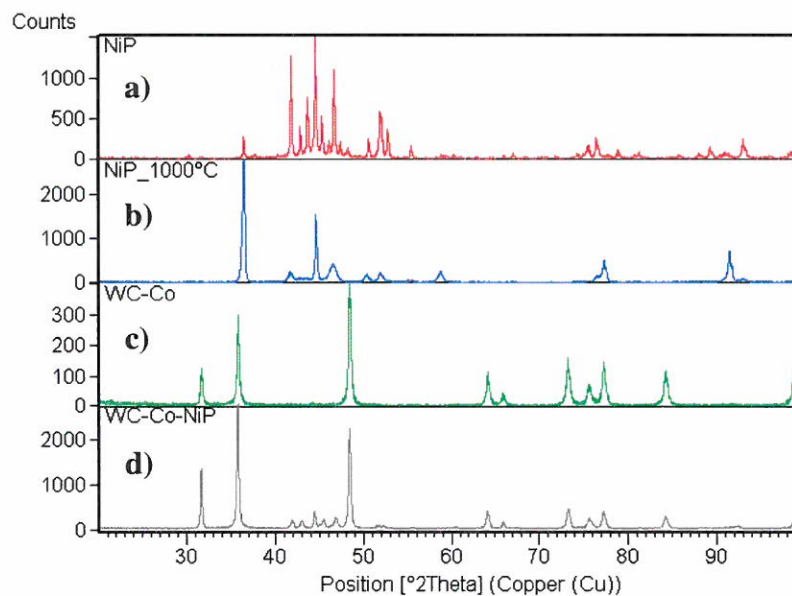


Figure 10 XRD patterns of: a) as-received NiP BFM, b) heat treated NiP BFM, c) as-received WC-Co powder d) heat treated WC-Co powder, and e) WC-Co-NiP brazed coating

From the superimposed XRD patterns it is clear that the as-received gas atomized NiP BFM powder experiences during the brazing process noteworthy phase transformations. From the initial composition consisting of 76.8 wt.% Ni<sub>3</sub>P, 16.2 wt.% Ni, 4 wt.% NiP, 3 wt.% Ni<sub>2</sub>P and 1 wt.% P, after the heat treatment performed with the parameters of the optimized brazing process (Program 4), the phases detected and quantified in the bulk alloy (nugget) comprised of 60 wt.% Ni<sub>3</sub>P and 40 wt.% Ni. This accentuated transformation is mainly attributed to dilution. Contrary, the X-ray diffraction performed on the brazed WC-Co-NiP functional coatings do not indicate any presence of free (elemental) Ni. Instead, this element has formed an intermetallic phase with W, more exactly 7 wt.% crystalline Ni<sub>17</sub>W<sub>3</sub>. Meanwhile, the free

Co (metallic binder of the cermet powder) has diffused, forming 4 wt.% of the tougher tungsten rich  $\eta$ - complex carbide  $\text{Co}_2\text{W}_4\text{C}$ .

**Hardness.** Coating surface macrohardness was determined with the aid of a KB 250 BVRZ universal tester, while the microhardness was assessed with Zwick/Roell ZHV $\mu$ -S tester equipped with a Vickers microindenter.

The vacuum brazed WC-Co-NiP composites, deposited during this study exhibit a variable microhardness in the coating cross-section. The values range from a minimum of 650HV1 (metallic matrix) up to a maximum of 1130HV1 (cermet particles), with a mean of 890HV1. Lower hardness values are attributed to pores located in the tested areas. Additionally, the mean value of the WC-Co-NiP coating surface hardness was assessed at 1010HV10.

The substrate material (1.7313) is known to have 470HV if case hardened and 170HV when soft annealed.

Determination of **tensile adhesive strength** was carried out on an INSTRON 5584 universal testing machine, having in mind the indications of EN 582 and EN 10002. The sample arrangement had a diameter of 20 mm, a total length of 62 mm and a coating thickness of 2 mm.

Tensile cohesive strength of the coating itself reached a mean value of 150 MPa (determined after three tests), with a mean value for the maximum load of 50 kN, which is well correlated with values reported by other researches [1, 2]. Unfortunately, tensile adhesive strength of the coating-substrate system was unable to be directly determined through this method. Although, according to similar studies, and having in mind that the coating technique is in fact a vacuum brazing process employing the Ni6 BFM and a low alloy steel substrate it is expected for the adhesive strength to reach values around double that of the cohesive one.

The relatively high elongation (strain) visible on the stress-strain curve of Figure 11 is a result of the plastic deformation of the metallic screws used to tension the samples.

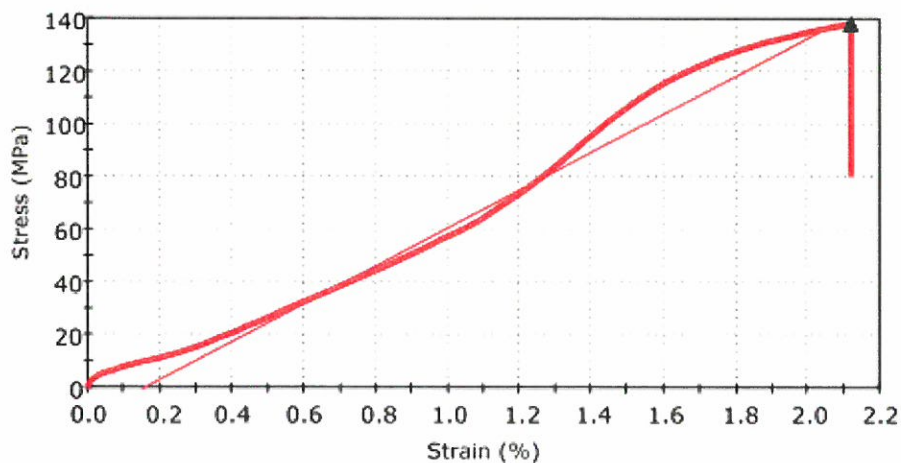


Figure 11 Typical Stress-strain curve of the samples

In order to compare the **tribological behavior** of the WC-Co-NiP coating to that of the 16MnCr5 steel substrate, investigations were performed on a CSM Instruments tribometer with a ball-on-disk arrangement. The total sliding distance was 1890 m (100000 laps) with a linear speed of  $15 \text{ cm s}^{-1}$  on a radius of 3 mm, and a normal load of 10 N applied through a 6 mm 100Cr6 ball (static partner). All tests were carried out under dry sliding conditions, at ambient temperature and pressure.

The coefficient of friction ( $\mu$ ) was monitored and registered during the entire testing period and can be observed in Figure 12, and Table 2 respectively.

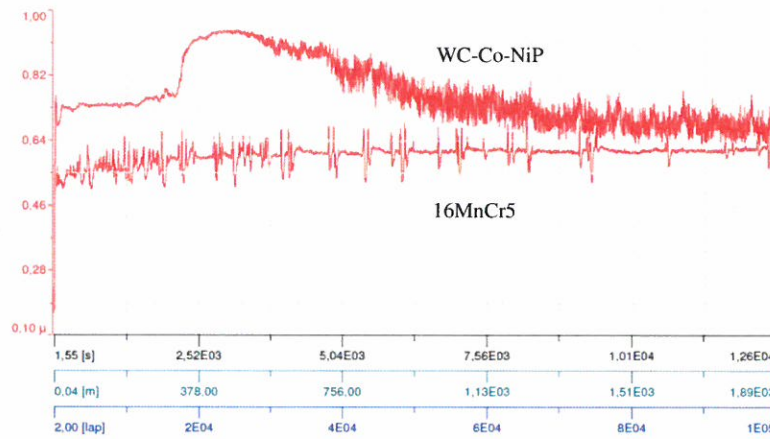


Figure 12 COF evolution for 16MnCr5 and WC-Co-NiP vs. 100Cr6

The considerably wider and deeper worn track found on the surface of 16MnCr5 base metal concluded in numerical values for the wear rate of  $\approx 9.10 \cdot 10^{-2} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ , compared to only  $\approx 5.40 \cdot 10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$  in the case of the composite hardfacing. Furthermore, the formation of an unstable oxide film and galling causing additional friction and adhesion between the static partner and the sliding steel specimen was observed.

Table 2 Coefficients of friction and wear rates for the POD tests vs. 100Cr6 static partner

Sample	COF min.	COF max.	COF mean	Wear rate [ $\text{mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ ]
16MnCr5	0.17	0.70	0.60	$9.07 \cdot 10^{-2}$
WC-Co-NiP	0.16	0.95	0.77	$5.36 \cdot 10^{-4}$

Because friction is not merely a material property, but a system response, tribological POD investigations have also been performed against a WC-Co ball, maintaining the rest of the testing parameters identical as in the previous case.

Accordingly, the coefficient of friction was once more monitored and registered during the entire testing period and can be observed in Figure 13.

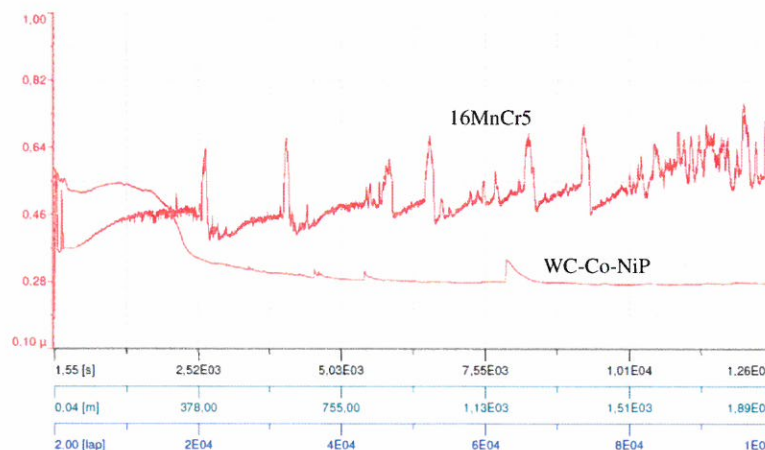


Figure 13 COF evolution for 16MnCr5 and WC-Co-NiP vs. WC-Co

Decisively, a maximal friction coefficient of 0.76 was measured during the ball-on-disk testing of the steel substrate, with a mean of 0.50. Significantly lower values were determined

in the case of the functional coatings, registering a maximum of 0.57 with an average of 0.33 (see Table 3)

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 the previous investigations (microhardness, coefficient of friction). The considerably wider and deeper worn section found on the metallic surface concluded in numerical values for the wear rate of  $1.03 \cdot 10^{-3} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ , compared to only  $1.55 \cdot 10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$  in the case of the composite hardfacing. Furthermore, the formation of an unstable oxide film and galling causing additional friction and adhesion between the static partner and the sliding (rotating) 16MnCr5 case hardening steel specimen was observed.

Table 3 Coefficients of friction and wear rates for the POD tests vs. WC-Co static partner

Sample	COF min.	COF max.	COF mean	Wear rate [ $\text{mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ ]
16MnCr5	0.18	0.76	0.50	$1.03 \cdot 10^{-3}$
WC-Co-NiP	0.21	0.57	0.33	$1.55 \cdot 10^{-4}$

The main mechanisms that govern the surface degradation in the currently investigated sliding systems are adhesion and tribo-oxidation. If the tribological system comprises third-bodies, namely hard particles (much harder than the two surfaces in contact), abrasive wear might also occur. This was found to be the case of the coupling between 16mnCr5 and WC-Co, which lead to the formation of abradable WC particles. Thus, the wear mechanism changed from an adhesive and tribo-oxidative one to a process that encompasses also abrasion.

During sliding between the two bodies in contact, the wear volume (removed material), increases with the sliding distance. Consequently, several stages of wear can be observed.

The running-in (run-in or break-in) stage, which is typically quite short in dry sliding, is usually characterized by very high wear rates. In actual fact, the counter-surfaces are worn out in order to eliminate the surface roughness (asperity peaks) and to compensate for possible misalignments. Furthermore, during this stage the surfaces get cleaned, completely or incompletely, by removal of contaminants.

After running-in, often a steady state stage is arrived. Throughout this period, the wear rate is habitually less than during running-in. Frequently, this is the predominant stage of the tribological process and it persists up to the end of the components service life. It is generally governed by adhesion, tribo-oxidation or a combination of the two.

Occasionally, a wear transition may take place after a certain sliding distance. During this stage wear rate can increase, but in many cases it can also decrease, and subsequently enter a different steady state regime. These types of transitions are generally caused by changes in the wear mechanisms, often accompanied by formation of third bodies or tribo-oxide layers, leading to deviations in the coefficient of friction.

In case of dry sliding against the 16MnCr5 steel counterface, the specific wear coefficient, of the WC-Co static partner is quite low. In the case of couplings with the similarly hard WC-Co-NiP material, it is even lower. Therefore, it can be concluded that through the optimal selection of a tribological pair it is possible to achieve very low wear rates for both tribo-partners.



The **electrochemical corrosion behavior** was evaluated through potentiodynamic polarization, employing an IVIUM Vertex potentiostat/galvanostat in a three-electrode cell. Working electrodes were prepared from both types of materials, a platinum disk was used as counter electrode and a saturated calomel electrode 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 -750 mV and +1000 mV versus SCE for the 16MnCr5 material and from -500 mV to +1000 mV for the coated sample, both with a scan rate of  $10 \text{ mV min}^{-1}$ . The  $1 \text{ cm}^2$  geometrical surface area of the sample allowed current readings to be directly expressed as current density ( $\text{A cm}^{-2}$ ).

The cathodic branch in the polarization curves corresponds to hydrogen evolution reaction, while the anodic branch features the most important information related to the corrosion resistance.

Figure 14 illustrates typical Tafel plots for the discussed samples subjected to potentiodynamic electrochemical corrosion in 3.5 % NaCl solution (pH 7). It is clear that the corrosion current density ( $i_{corr}$ ) of the WC-Co-NiP brazed coating is substantially lower than that of 16MnCr5 steel. The corrosion potential ( $E_{corr}$ ) of the hardfacing is shifted to more positive potentials (-250 mV) in comparison to the uncoated sample (-640 mV), which is associated to the chemical composition. The anodic Tafel slope of the coating shows an inclination to passivate, due to the nickel based chemical composition of the brazing filler alloy. Adversely, the uncoated steel sample points no tendency towards passivation.

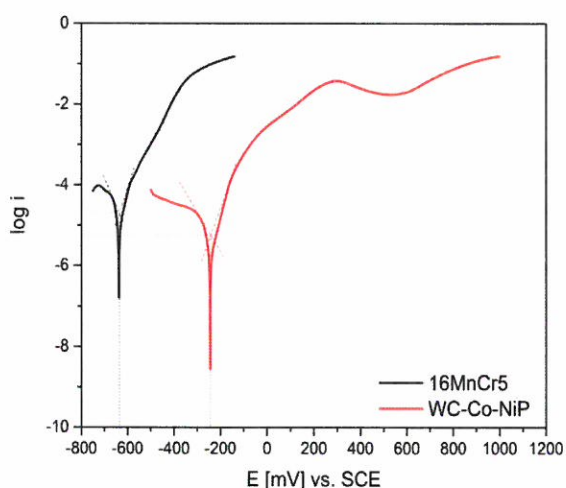


Figure 14 Tafel plot of 16MnCr5 and WC-Co-NiP in 3.5 % NaCl solution

Typical corrosion potential and corrosion current density of the analyzed samples obtained from the electrochemical polarization investigations performed in 3.5 wt.% NaCl aqueous solution are summarized in Table 4. The values indicate a corrosion current density around 10 times lower for the brazed coating in comparison to substrate material.

Table 4 Corrosion potential and corrosion current density values in 3.5% NaCl

Sample	$E_{corr}$ [mV] vs. SCE	$i_{corr}$ [ $\text{A cm}^{-2}$ ]
16MnCr5	-640	$10^{-4.3}$
WC-Co-NiP	-250	$10^{-5.3}$

Similar to the electrochemical investigations performed in the 3.5 % NaCl solution, corrosion current density ( $i_{corr}$ ) of the WC-Co-NiP brazed coating is substantially lower than that of 16MnCr5 steel in 0.5 M HCl solution. Likewise, the corrosion potential ( $E_{corr}$ ) of the

hardfacing is shifted to more positive potentials (-300 mV) compared to the substrate material (-500 mV). The anodic Tafel slope of the coating shows an inclination to passivate, due to the nickel based chemical composition of the brazing filler alloy. Adversely, the uncoated steel sample points no tendency towards passivation.

Both corrosion current density ( $i_{corr}$ ) and corrosion potential lean toward a lower reaction rate, and consequently, better corrosion resistance of the coated sample compared to the uncoated one is to be expected. Figure 15 illustrates typical Tafel plots for the discussed samples subjected to potentiodynamic electrochemical corrosion in 0.5 M HCl solution (pH 0).

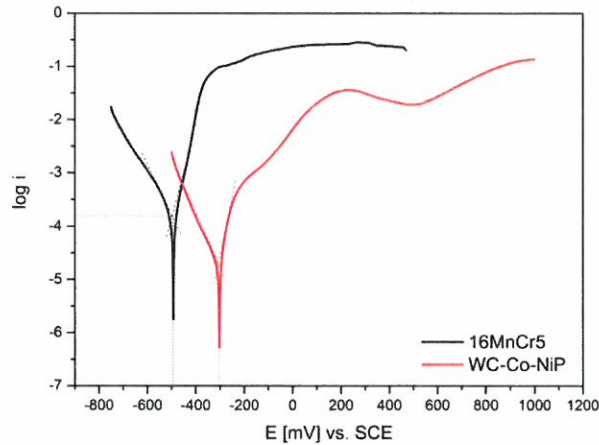


Figure 15 Tafel plot of 16MnCr5 and WC-Co-NiP in 0.5 M HCl solution

The corrosion potential and corrosion current density of the analyzed samples obtained from the electrochemical polarization investigations performed in 0.5 M HCl aqueous solution are summarized in Table 5. Correspondingly, the corrosion current density of the coating is approx. 10 times lower than the values obtained for the base material.

Table 5 Corrosion potential and corrosion current density values in 0.5 M HCl

Sample	$E_{corr}$ [mV] vs. SCE	$i_{corr}$ [ $A\ cm^{-2}$ ]
16MnCr5	-500	$10^{-3.8}$
WC-Co-NiP	-300	$10^{-4.7}$

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 film of iron. Dissimilarities in the nature of the oxide layer grown on Fe and Ni are accountable for this phenomenon. The film thickness on Ni is between 0.9  $\mu m$  and 1.2  $\mu m$ , while the Fe oxide film is situated in the interval 1  $\mu m$  and 4  $\mu m$ . 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, giving rise to  $Ni^{3+}$  cation vacancies. In the case of the second one, it comprises of an inner film of NiO and an outer one of anhydrous  $Ni(OH)_2$ . Once generated, the passive oxide film of nickel, neither cathodic treatment or chemical dissolution can easily remove it.

Because transition metal carbides have high resistance to chlorine containing solutions, corrosion of WC-based composite coatings manifests through 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.

### **3. Conclusions**

The original research described in the present work consists in a theoretical study on available literature data regarding functional coatings, fabrications methods and applications. The focus was directed to aspects concerning the production of high temperature vacuum brazed composite coatings, the optimization of deposition process parameters and characterization of such hardfacings.

In the current state of the art, tape brazing involves the use of flexible cloths rolled from mixtures of hard phase powders, filler metal powder and appropriate polymeric binders. The mats can easily be manufactured under diverse chemical compositions of base and filler metal powder, and formed to size and shape by cutting or stamping. After forming, the cloths are overlaid on top of the metallic substrate and fixed in place often with a small amount from the same polymeric binder. The coating process actually takes place at temperatures usually slightly above the liquidus temperature of the filler alloy, in vacuum or under protective atmosphere, with the aid of a furnace. During the brazing process, filler metal reaches liquid state and infiltrating the spaces between the hard phase particles wetting and enveloping them. Metallurgical interactions governed by diffusion and alloying appear among base powder and brazing alloy, as well as at the coating - metallic substrate interface, resulting in a strong metallurgical bond. No universal reference for the brazing temperatures and holding times exists, because the values depend strongly on the chemical composition of the substrate material, reinforcing powder and filler metal, their ratio in the mixture and the metallurgical interactions. Considering that the majority of substrate materials are iron, nickel, chromium or cobalt alloys, base powders are usually ceramics or cermets and the metal matrix consists typically of self-fluxing nickel base alloys the furnace brazing temperature is approximately 1100°C. Brazed overlays with a thickness range of 150 µm to 20 mm have been successfully deposited, with theoretical possibilities of an even greater thickness interval. Due to the common high amount of hard phases (up to 70 % or more in some cases) Ni-base matrix alloy, and generally low porosity ( $\approx 1\%$ ), these coatings can offer high wear and corrosion resistance under severe working conditions. The major limitation of this coating technique is the requirement to treat the whole substrate to the necessary high brazing temperature. This process can have a negative effect on the substrate material, leading to undesired grain growth or phase transformations. Another current disadvantage of the method is the use of potentially harmful chemical compounds in the polymeric binders, which need to be filtered, contained and neutralized.

Considering that WC is one of the most suitable materials for protection against wear and corrosion, due to its mechanical and chemical properties. The main attention was focused on utilizing this compound for its advantages, and simultaneously overcoming its limitations (low ductility and complex deposition processes), in order to obtain coatings with superior characteristics.

The present work dealt with the development of functional composite coatings based on cemented tungsten carbide reinforcement and nickel-based filler alloy using the high temperature vacuum brazing method. Cemented WC particles provide the hardness and low coefficient of friction, improving the wear resistance. Simultaneously, the Ni-based metallic matrix offers toughness and impact resistance to the final coating. Moreover, the brazing process provides a compliant support for the WC-Co particles and strong adhesion between the coating and the metallic substrate, through a metallurgical bond.

This technique delivers a simple fabrication way for the functional overlays and guarantees low porosity of the coatings.

The **original contributions** of this study refer to:

- utilizing vacuum brazing as a non-conventional coating method in order to obtain **WC-Co-NiP functional hardfacings** with superior wear and corrosion resistance;
- exploring the possibility of combining **recycled WC-Co powder** as reinforcing phase with **NiP brazing filler metal** as metallic matrix, to develop vacuum brazed composite coatings;
- careful selection of feedstock materials in order to favorably combine a manufacturing process as **accessible, economic, and environmentally friendly** as possible, with the production of coatings with superior characteristics;
- the successful employment of **water-base fugitive glue** as organic binder for the manufacturing of flexible cloths, which is safe to handle and harmless to the environment, and at the same time offers adequate flexibility and long shelf life;
- the usage of **BNi6** (NiP alloy) brazing filler metal **as metallic matrix**, in order to decrease the maximum temperature of the brazing process down to 1000°C, thus reducing production costs and thermal influence on the substrate material;
- studies on the deposition mechanism, as well as investigations on the influence of the thermal cycle parameters on the morphology of the coatings;
- **optimization** of the **brazing process parameters** for the studied chemical composition;
- investigations on the **coatings characteristics and properties** (including wear and corrosion resistance).

In this regard, several aspects can be highlighted:

- A careful selection of the brazing filler metal and reinforcing powders with specific chemical compositions, bonded together by certain organic binders, in order to produce superior coatings was performed;
- Commercially available WC-Co recycled material was utilized as reinforcing powder;
- Commercially available BNi6 brazing filler metal was selected for the role of metallic matrix;
- Water-based fugitive glue was utilized as organic binder;
- Flexible cloths were manufactured from both types of powders; The 1.7131 (16MnCr5) case hardening steel was utilized as substrate material due to availability and its importance as a structural material;
- As filler material, initially 6 types of Ni-based powder were proposed; due to its superior properties, the NiP based powder was selected to take the role of metallic matrix for the brazed coatings;
- NiP powder presents a dense and homogeneous microstructure, with occasional satellite type formations on the surface of some particles; moreover, it possesses the lowest melting temperature (900°C) due to the high P content (10 - 12 %);
- As tungsten carbide (WC) is well known for its exceptional hardness and wear/erosion resistance, it was chosen as hard phase material;
- The reinforcing material selected for this study was a commercially available WC-Co powder obtained from recycling of hard metal tools;
- WC-Co was found to be an ideal reinforcing material for the manufacturing of functional composite coatings due to its superior wear resistance, compressive strength, good elevated temperature and corrosion resistance;
- A water-based fugitive adhesive was used as binder for the manufacturing of the flexible tapes; its special formulation was found to offer a clean alternative to the conventionally used organic binders;

- Manufacturing the polymer bond hardfacing tapes involved mixing precise amounts from the selected powders and organic binder until the latter one fibrillated;
- A ratio of 75 wt.% WC-Co, 25 wt.% NiP and additional 2 wt.% organic binder was found to offer the optimum composition for preparing highly flexible composite tapes;
- The high temperature brazing process was carried out in a HITERM 80-200 cold wall vertical vacuum furnace at a stable pressure of  $3.0 \cdot 10^{-4}$  mbar;
- 4 experimental brazing programs were tested in order to find the optimum process parameters;
- The brazing cycles were adjusted according to data provided by the thermal analysis correlated with the recommendations of the BMF manufacturer;
- It was found that Program 4, which was also the most complex, delivered the best results, regarding the required microstructure, morphology and low porosity observed from the SEM investigations;
- The optimized program was composed of 10 segments representing heating ramps, soaking times, cooling rates and intervals;
- The final brazing step performed at 1000°C for 30 min assured the high fluidity of the Ni-based alloy, necessary for wetting, infiltrating and filling the micro voids in order to obtain high quality coatings;
- As Program 3 and Program 4 differed only in the cooling stage, it can be mentioned that the additional cooling segment down to 870°C, with a lower rate, avoided the formation of microcracks in the coating;
- Results of the electron microscope investigations proved that the initial problem of high porosity, crack evolution and fracture occurrence was eliminated; the porosity degree decreased from an initial value of around 19 % to a final value of approx. 1 %;
- The high temperature vacuum brazed coatings displayed a dense structure, with uniform distribution of the cermet particles;
- Diffusion from the metallic matrix towards the cemented WC and substrate was highlighted using EDX line scan method; moreover, EDX mapping identified the elements and showed their distribution and relative proportion in the coating;
- The presence of Fe was limited to the substrate and also was found in smaller amounts in the interface region; W appeared to have diffused towards the interface; Co migrated towards the substrate and Ni replaced part of Co in the WC-Co cermet; P was concentrated in areas with high Ni concentrations;
- A phase composition consisting of 51 wt.% WC, 38 wt.% Ni<sub>3</sub>P, 7 wt.% Ni<sub>17</sub>W<sub>3</sub> and 4 wt.% Co<sub>2</sub>W<sub>4</sub>C was determined from the XRD patterns of the functional coating;
- Coating cross section microhardness ranged from a minimum of 647HV1 (metallic matrix) up to a maximum of 1132HV1 (cermet particles), with a mean of 896HV1; the substrate material (1.7313) is known to have 470HV
- The adhesion of the coating to the substrate was determined from tensile adhesive strength tests; the coating itself reached a mean value of 150 MPa;
- Fracture occurred only through the coating, without any noticeable trace of delamination;
- A higher adhesive strength, compared to the cohesive one was confirmed, hence a superior metallurgical bond between coating and substrate;
- The coatings experienced a mean friction coefficient of 0.77 under dry sliding friction against a 100Cr6 ball with an average wear rate of  $5.36 \cdot 10^{-4}$  mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>, value which was 170 times lower than that of the substrate material;

- The coatings experienced a mean friction coefficient of 0.33 under dry sliding friction against a WC-Co ball with an average wear rate of  $1.55 \cdot 10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ , value which was around 7 times lower than that of the substrate material;
- The superior wear behavior was attributed to the presence of hard WC phase and self-lubricating  $\text{Ni}_3\text{P}$ ;
- The electrochemical polarization curves illustrated a 10 times lower corrosion current density in the case of WC-Co-NiP coatings compared to 16MnCr5 case hardening steel samples in both 3.5 % NaCl and 0.5 M HCl solutions;
- The superior corrosion resistance of WC-Co-NiP functional coatings is credited to the chemical composition of the metallic matrix, namely the Ni-P alloy ( $\text{Ni}_3\text{P}$  phase), which is able to readily generate a passive layer, stable up to the potential of around 600 mV vs. SCE.
- The corrosive attack of vacuum brazed WC-Co-NiP coatings is characterized by selective dissolution of the metallic matrix, compared to the general corrosion observed in the case of the substrate material.

Using the described method, high quality hardfacing coatings with low porosity, a good distribution of both large and small hard phases, excellent metallurgical bond and minimal dilution have been deposited. Simultaneously, the optimization process has eliminated the initial problem of cracks and fracture evolution and reduced by almost 20 percent the size and occurrence frequency of interconnected and individual pores. Moreover, significantly lower dry sliding wear rates of the WC-Co-NiP, compared to that of 16MnCr5 case hardened steel were found against 100Cr6 static partners (170 times lower) and WC-Co (7 times lower) respectively. Furthermore, the corrosion behavior was also ameliorated (around 10 times lower corrosion current densities) with the application of the functional coating.

Accordingly, the present work highlights the crucial importance of optimizing the brazing process parameters for each chemical composition, thickness, and combination of flexible composite cloth and substrate material. At the same time, it proves once more the feasibility of using high temperature vacuum brazing as a practical technique of generating high quality WC-Co-NiP functional coatings.

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