

Îmbunătățirea performanței straturilor pulverizate de tip NiCrBSi prin retopire cu ajutorul inducției electromagnetice

Improvement of NiCrBSi sprayed coatings performance by electromagnetic induction remelting

## Teză de doctorat – Rezumat în limba română

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# 1. Introduction

The development of society is highly dependent on the providing of energy resources. Successive energy crises with major global impact require the identification of other measures such as streamlining and optimizing the technological processes of obtaining, processing materials. That include the identification of new technological manufacturing solutions, reducing costs related to maintenance, repair, rehabilitation, to increase the service life of the equipment.

A suggestive example is the development of new, more durable assemblies, with improved wear behavior and very high corrosion resistance in extremely aggressive environments (coal mines, marine environments, hydropower plants). The protection of the surfaces of these components subjected to the action of these environments can be achieved by several methods (electrolytic deposits, reworking of surface coatings, thermal and thermochemical surface treatments, application of protective coatings, etc.)

Coating techniques have been continuously developed so that almost any type of material (metals, oxides, cermets) can be used, helping a significant number of economic sectors (automotive, chemical, aerospace, food, Crude oil, medical, nuclear, textile or transport) [1], [2] Although the materials used and related technologies have progressed at an extremely fast steps, there is a great lack in the area of protection in various aggressive environments.

The service life of a component can be extended by various methods. An important part of these are aimed at reducing the wear of adhesive, abrasive, erosive or corrosion due to exposure of components in various aggressive environments that lead to damage to parts at undesirable costs [3,4]. Thermal spraying, along with other coating methods and subsequent treatments, helps to reduce these effects.

## 1.2 Aim of the work

The aim of the doctoral thesis is to obtain high quality coatings (in terms of corrosion and wear resistance) by going through two steps, using a simple and inexpensive procedure for depositing thermal spray coatings with flame (step I) and the application of a subsequent process of remelting them with the help of high frequency currents. (step II).

Of all the methods of flame deposition, the cheapest and most productive is the oxyacetylene flame deposition. Following the research of the literature, it is known that the coatings obtained by this process consist of several layers with lamellar structure, very high porosity and the imminent possibility of delamination [5]. In this case of powder deposition, the major disadvantage is that at the interface the particle has a mechanical bond to the substrate and has the risk of exfoliation when exposed to an external agent / force.

Under these conditions, the application of a post-deposition treatment is imperative. The coating was re-melted with the help of electromagnetic induction in order to improve the adhesion and considerably reduce the porosity. The specific objectives and related activities are:

- **development of high quality functional coatings** from the family of Ni-based auto fluxing materials, with good wear and corrosion resistance in aggressive environments and with improved adhesion to the substrate
- **parameters optimization** for the post-processing treatment (remelting by induction) in order to eliminate the porosity and improve the adhesion of the coatings to the substrate;
- process optimization for implementation on industrial production lines
- **obtained coatings characterization** by: optical microscopy (OM), scanning electron microscopy (SEM) combined with X-ray dispersive energy spectroscopy (EDX), X-ray diffraction (XRD), hardness (HV), evaluation of the adhesion to the substrate by interface indentation, tribological behavior assessment (POD) and corrosion resistance (NSS/LV).

## **2.** The current stage

Currently, more and more parts/components need a surface coating that gives them increased durability while working in aggressive environments and beyond.

These components may be subjected to various mechanical, chemical, thermal or thermochemical stresses. Individual stresses can be as follows and can lead to:

- chemical stresses: corrosion
- thermal stresses: aging and creep
- mechanical stress: fatigue and wear

In reality, most of the time, these tensions are combined with each other, resulting in the following types of tensions and their effects.

- Mechanical-chemical: corrosion by friction and cavitation
- Mechanical-thermal: fatigue at high temperature
- Chemical-thermal: corrosion at high temperatures.

The vast majority of coating processes have been developed for the same purpose: to lead to superior characteristics so that the protective coating meets the requirements and at the same time the process has high quality, efficiency and reproducibility.

Thermal spraying is considered to be one of the main methods of thermal coating to obtain functional coatings. It is a process by which a metallic, ceramic, cermet or polymer material is deposited on a substrate, providing a protective layer. The consumable spray material is fed into equipment that will turn it into a semi-molten state and accelerate it with a gas jet to the substrate. Several layers in the form of thin slats are deposited on the surface of the base material, which overlap and are mechanically anchored to each other.

a) Substrate preparation

In order to make a high quality product according to the customer's requirements, it is absolutely necessary to go through a set of operations presented in Figure 2.1.



Figure 2.1 Surface treatments applied before thermal spraying

### b) Design of components for thermal spraying

Because that the spray jet is always in a straight line, only the parts in front of it can be sprayed. Depending on the spray process used, there are different angles of flame. The optimum angle of impact of the sprayed particles and the proximity of the base material is 80-90°. Deviations of up to 45° are possible in exceptional cases, but with a lower quality of the coating and some particles that do not reach the coating will be pulled into the aspirations machine.

If surfaces with 90 angles or grooves are sprayed, the coating will always be much more pronounced at the tip and sharp corner of the groove, which will not give stability to this coating and also the adhesion will not be standard. To eliminate this problem, the gun should always retract when it reaches this groove or 90° angle. Figure 2.2 shows the preferred sketches for thermal spraying in which there will be no problems during the process. It can be seen that it is desirable that the edges be rounded so as not to be stress concentrators and over time the coating will not crack. On the other hand, at angles of 90° it would be advisable for the deposited coating to always end in a groove at a distance of at least 5 mm from the shoulder. It is also not wise for these grooves to have straight edges, it is best for their exits to be in a circular arc, preferably as large as possible.



Figure 2.2 Design of thermal spray components

# c) Classification of thermal spray processes

Depending on the source of energy used, thermal spray processes can be classified into several main groups, of which we list: molten liquid energy, flue gas energy, kinetic energy, electric discharge or electron beams.

Each of the groups listed has its own distinctive characteristics such as enthalpy, the deposition rate of the layer, the thickness of the layer that can be deposited, the temperature at which the process takes place. These characteristics have a direct influence on the quality of the coating. These include the porosity, the adhesion of the coating to the substrate, the internal connection between the particles, the oxides present in each layer that form the final coating.

In many cases, a process that is easier to handle under the given conditions will be chosen, even if the quality is a little lower, but acceptable.

Figure 2.3 shows a classification of these processes according to the energy used.



Figure 2.3 Thermal spraying process classification according to the sources of energy

## d) Post-processing of spray coatings

In order to change the microstructure of the coatings, they must then be subjected to different surface treatment procedures after the spraying process. These processes aim to

improve density, reduce oxides, reduce internal stresses, etc. According to J.R. Davis, there are three main categories in which these processes can be divided to improve the quality of the resulting layer:

- Physico-chemical treatments: chrome plating, aluminization, sealing;

- Heat processes: fusion, heat treatments, diffusion, isostatic pressing, layer remelting

- Mechanical processing: milling, turning, sandblasting, polishing;

## e) Wear of materials

Wear is usually defined as the removal of material from solid bodies, caused by contact and relative motion, which alters the initial state of the contact surfaces. Consequently, wear is the result of tribological contact that takes place between two moving surfaces. Wear occurs in all cases where there is friction, whether it is useful or harmful. The result of the wear process is expressed in units of length, volume, mass, operating time until the product is decommissioned. The specialty literature offers a wide variety of classification of the types of wear and possible solutions to wear problems. The version proposed by Barwell in 1957 regarding 4 types of basic wear is generally accepted. These types of wear are as follows:

- abrasive wear

- erosion wear
- adhesion wear
- fatigue wear

In conclusion, this chapter of the thesis presents the current state of research in the field, the processes that are currently used in the machine building industry in the field of surface engineering and the problems that occur in the components of products that work in harsh regimes.

# **3.** Equipment and methodology

# a) Equipments

In the development stage of experiments and research, equipment from the following laboratories was used:

- Timișoara Polytechnic University,
- University of Applied Sciences, Westfaelische Hochschule, Gelsenkirchen, Germany

- The company's Karl Schumacher GmbH testing laboratory, Bochum, Germania The equipment necessary for the good development of this work is:

- Cut-off Machine (Discotom-2, Struers)
- Hot Mounting Press (ProntoPress-20, Struers)
- Grinding and Polishing Equipment (RotoPol-V, Struers)
- Scanning Electron Microscope (ESEM XL 30, Philips)
- Energy-dispersive X-ray Spectrometer (EDAX)
- Confocal Laser Scanning Microscope (VK-X, Keyence)
- X-ray Diffractometer (X'Pert, Philips)
- Thermogravimetric Analysis Instrument (STA 449 F1 Jupiter, Netzsch)
- Universal Hardness Tester (KB250, KB Prüftechnik)
- Micro Vickers Hardness Tester (ZHVµ, Zwick / Roell)
- Pin-on-Disc Tribometer (TRB, CSM Instruments)
- Potentiostat / Galvanostat (VoltaLab PGP201, Radiometer Analytical)
- turning machine (weipert)
- Thermal spraying pistole (Methaterm MPP 85)

- Induction system (Ambrell Ekoheat)
- Corrosion testing system (Liebisch S 1000 M-SC)

# b) Methodology

The experimental and research program included the following stages:

- selecting the three types of powder;

- the deposition by the process of thermal spraying with oxyacetylene flame of the material, in powder form, on a weekly alloyed steel;

- remelting the sprayed coating that required an optimization of the process parameters using a design of experiments via the Taguchi method.

- determining the characteristics and properties of the obtained coatings, including the materials used. Thus, differential thermal analysis (DTA) was used for the selected powders. Optical and confocal laser microscopy (CLSM) was used to determine porosity (pore size and distribution) by processing micrographs in a dedicated software. The morphology, chemical composition and quality of the coating-substrate region were examined using scanning optical microscopy (SEM) combined with X-ray dispersive energy (EDX) spectroscopy. The phase changes of the powder, the sprayed coating and the heat treatment were analyzed with an X-ray diffractometer (XRD). The hardness of the coating on the surface and in cross section was assessed by Vickers indentations. Tribological investigations using a pin-on-disc arrangement helped to compare the coefficients of friction and wear rates of the developed coatings with a chosen reference coating. Electrochemical tests were performed in a three-electrode cell to evaluate the behavior of the developed coatings compared to a reference coat.

# 4. Results and discussions

The first stage of the technological process is the deposition of the NiCrBSi-based powder coating.

# I. Oxy-acetylene flame spray

# 4.1 Feedstock powders

Nickel-based self-fluxing alloys are known for their high homogeneity of coatings and good wear resistance. For this work, 3 types of NiCrBSi-based powder from LSN Diffusion prepared specifically for Karl Schumacher were used. The chemical composition and the internal name of the material are shown in Tab. 4.1.

	Table 4.1 Chemical composition of NICIBSI powder										
	Trade name	Ni[%]	Cr[%]	B[%]	Si[%]	Fe[%]	C[%]	Grain Size [µm]			
	KS-IC-45	Bal.	6.02	1.12	4.19	1.5	0.25	+106-45			
I	KS-IC-55S	Bal.	10.10	2.49	3.51	4.0	0.40	+106-45			
Ī	KS-IC-55	Bal.	13.02	2.80	4.19	5.12	0.42	+106-45			

Table 4.1 Chemical composition of NiCrBSi powder

The manufacturer of the material atomized with water reported a powder size of + 106-45  $\mu$ m. In the SE micrograph shown in Figure 4.1 the powder appears to be spheroidized. The spherical geometry of the powder is considered an advantage, on the one hand it requires less energy from the deposition equipment for feeding and on the other hand there is uniform heating of the material.



Figure 4.1 Micrograph showing (left) topography and (right) EDX spectrum of NiCrBSi powder

The EDX analysis of NiCrBSi powder can be seen in Figure 4.1. The Ni element proves to be dominant in the spectrum. After Ni, the carbide-forming element Cr shows the strongest signals. Carbides are well known as hard compounds having a positive effect on the wear resistance of thermally sprayed coatings. Although Si and B are in relatively low amounts in the chemical composition, they are important elements in deoxidation and wetting phenomena. Silicon tends to form phases with both Ni and Fe, influencing the structure of the coating.

The melting range of the material is a particularly important aspect in the context of industrial applications. Also, the whole deposition process is adjusted according to the melting temperatures of the material, in this case being determined using a thermogravimeter. In the thermogram shown in Figure 4.2, the temperature region between 920 ° C and 1150 ° C is considered relevant. The melting range of the powder starts at 1009 ° C, the material being completely melted at 1068 ° C. Taking into account the identified temperatures, it can be assumed that the matrix will have to be heat treated at a temperature of at least 1050 ° C. Both B and B have the role of lowering the melting temperature of the powder and stabilizing it [7]. Moreover, the addition of Si to the alloy increases the self-fluxing property of the material.



Figure 4.2 DTA curve of NiCrBSi matrix powder

Cross-sectional powder analysis revealed fairly large gaps inside them (Figure 4.3).



Figure 4.3 SEM cross-section micrograph of NiCrBSi powder: left KS-IC-45, right KS-IC-55

These voids lead to overheating of the particle during the spraying process, due to the fact that the volume of the material to be heated is much smaller, which indicates a more pronounced oxidation of the particles. The result is a coating with two types of porosity, interconnected porosity resulting from the coating formation process, layer by layer, and a closed porosity that is inside a percentage of the particles..

Due to this, a subsequent heat treatment is suitable which brings the coating into a molten state, closing not only the pores obtained during the process, but also the pores inside the particles.

#### 4.2 Substrate material

The substrate is the part of the assembly (component) on which the deposition coating will be applied in order to improve the surface properties.

The importance of the substrate material is crucial. The base material must be adapted to the application in which the component will be used. In the present experiments, 42CrMo4 steel (EN 1.7227) -a well-known alloy steel for a wide range of industrial applications was used as the substrate. The choice of a substrate that is widely used in industry ensures a wide use of the developed coatings.

The substrate was machined to a nominal diameter of 70 mm and 160 mm, this geometry allowing the ease of most tests. Substrate degreasing was performed to meet the cleaning standard set out in EN ISO 8501 [9]. A sandblasting of the substrate was performed to obtain a roughness Ra of approximately 75  $\mu$ m, as indicated in the American naval standard MS 2138 [6]. In order to protect the substrate from possible contaminants in the atmosphere, the blasting was carried out in a room specially designed for this process. Shortly after blasting, the spray coating was deposited.

4.3 Thermal spray process parameters

The process of spraying materials is an extremely important step in obtaining a highperformance coating. Deposition parameters have been carefully set according to the material layer and substrate and are described in Table 4.2.

Parameters	Materials /conditions/values
Feedstock powder	NiCrBSi
Substrate material	EN 1.7227
Substrate preparing	
Method	Sand blasting
Material used	Cast iron beads
Surface roughness	min. 75 μm
Gun manufacturer	Metatherm

Table 4.2 Main thermal spray parameters

Flame	
Combustion gas	Acetylene ( $C_2H_2$ )
Second gas	Oxygen (O <sub>2</sub> )
Flame stoichiometry C <sub>2</sub> H <sub>2</sub> :O <sub>2</sub>	1:2
Substrate temperature	105°C
Flame spraying temperature	aprox. 2650°C
Fusion temperature	aprox. 1050°C
Particle speed	100 m s <sup>-1</sup>
Coating deposition	
Deposit rate	2.5 kg h <sup>-1</sup>
Distance from the substrate	200 mm.

Prior to deposition, the substrate was degreased with water and alcohol, the steps being performed in accordance with EN ISO 8501. The sanding was performed in a dedicated chamber to avoid contamination of the substrate material.

### 4.4. Characteristics and properties of deposited coatings

In the microstructure of the coatings deposited by NiCrBSi, a network of interconnected pores and unbound particles can be observed, explained due to the impact, recoil and contraction of the particles once the substrate is touched (figure 4.10.a). All three types of powder have the same coating structure as a result of the process of thermal spraying with oxyacetylene flame, also having poor adhesion to the substrate, as shown in Figure 4.10.b. The adhesion is due only to mechanical anchoring on the support, which causes this coating to exfoliate with the action of a relevant external force. In the conclusions, it is necessary to apply a surface treatment that will lead to the improvement of the adhesion to the substrate and, at the same time, to the increase of the compactness of the coating.



Figure 4.10 SEM micrographs of the KS-IC-45 deposited coating: a) surface, b) interface

# II Melting of the deposited coating by electromagnetic induction

Electromagnetic induction heating is a previously unused process for remelting the deposited coatings. In order to carry it out, a series of analysis studies and experiments were required

### 4.5 Inductor geometry selection

As it is a process of heating by high frequency currents, the study started from the analysis of the surface hardening process by induction of steels. As can be seen in Figure 4.3, for the surface hardening of a steel bar, a resulting magnetic field will form which will

reach the surface of the part and heat it to the desired temperature.



Figure 4.3 Magnetic lines and temperature distribution in a cylinder heated by a 4-spiral inductor



Figure 4.4 a) Melting with an inductor with a circular section with 3 turns, b) Rough melted coating in the form of rings

Consequently, the first step is to design an inductor (consisting of a water-cooled copper pipe) connected to the secondary of a transformer, which ensures a high power of the induced magnetic field.

Figure 4.4a shows such a 3-spiral inductor. From a technical point of view, this type of element is good for inductive hardening where the steel must be brought into the austenitic field, this phase being a solid one. In this case - of the remelting of the NiCrBS layer - the heating temperature must be brought above the liquid line. It is specified that the maximum temperature is obtained in the middle of the length element. With this type of inductor, it was not possible to obtain properly remelted coatings. Due to the irregularly distributed heating temperature, combined with the translation of the element from left to right, rings of molten material were obtained (Figure 4.4b). In the case of parts with sharp edges or shoulders (tension concentrators) or at the ends of the bars, these areas will overheat which will lead to rapid melting and leakage of the sprayed material. In the case of the shoulders, it was observed that the part did not melt until the intersection of the cylinder with the difference in diameter (see figure 4.5). This is due to the fact that the magnetic field is concentrated towards the inside of the inductor; if the heating and melting has been done to

the edge, the layer inside the inductor spiral is disintegrated and will flow



Figure 4.5 non remelted shoulder part with 3-coil inductor

The experiments thus led to the variant of the inductor with a rectangular section and a single coil. It was tested and the results were very good. The surface is heated and melted evenly, due to the fact that inside the inductor spiral, the magnetic field lines are in the form of an ellipse which in the case of magnetic induction leads it in the center of the inductor at an angle close to 0 degrees with the workpiece. This eliminates the risk of damage to the melt layer. Following the experiments, the use of a rectangular pipe inductor with a rectangular section measuring 20 mm x 10 mm was adopted in order to have a larger working surface under the spiral.

### 4.6 Optimization of the parameters of the remelting process

In the case of remelting coatings there are a multitude of factors that influence the process, including: preheating temperature, shaft rotation speed, distance between element and workpiece, power applied by the transformer, etc. which leads to a very large volume of experiments After a brainstorming session it was concluded that a method should be found to reduce the number of tests and include all possible options. At the same time, the porosity was chosen as a factor in determining the quality of the remelted coating.

In statistics, a complete factorial experiment is an experiment consisting of two or more factors, each factor having several possible values or levels [8]. The experiment considers all possible combinations that result in a number of  $N^{K}$  where n is the number of factors influencing the process and k is the number of levels on which the respective factors are divided.

The full factorial design method requires a large number of experiments to be performed, so the work becomes unreasonable and also difficult if the number of factors is greater than two and has more than three levels. To facilitate the optimization work, Taguchi suggested a special method of orthogonal design matrix to study the whole set of parameters, but with the benefits of a much smaller number of experiments.

In this paper, this method was chosen because for these 3 types of powder would have generated a number of 243 experiments, by the Taguchi method they were reduced to only 48 experiments to find the optimal parameters for each type of powder. According to the procedure, the following steps are followed:

 a) Identification of the primary function and its effects: Main function: Heating at remelting point Side effects: decreasing the porosity

Table 4.7

Control Factors	Noise factors
Applied Power	Substrate material
Preheating temperatures	Length of substrate
Process remelting temperatures	Operator skills
Piece rotation	Room temperatures
Linear feed of the melting element	Noise

b) Identification of noise factors, test conditions and quality characteristics Quality characteristics: low porosity

Operating machine: Ambrell Ekoheat 35/25 + lathe machine

Testing equipment: DM RM-E Leica light microscope

Remelting element: copper spiral element/ section 20x10 mm

Work piece material: 42CrMo4 steel coated with NiCrBSi

c) Identify the objective function that needs to be optimized

It is desired: closing the pores, increasing the adhesion to the substrate resulting in a compaction of the coating

d) Identifying controllable factors and their levels

Table 4.8

Factor [Unit]	Level					
	1	2	3	4		
Temperature[°C]	980	1010	1050	1080		
Power [KW]	40	60	80	100		
Preheating [°C]	25	100	250	350		

e) Selecting an appropriate orthogonal array and constructing the matrix

• By fully factorial design the number of tests required is 81

• An L 16 type matrix was chosen by the Taguchi method

f) Performing experiments

g) Defining the optimal factor and its performance

Average signal-to-noise ratio for each factor

Table 4.15
------------

	Temperature	Power	Preheating		
1	-21.627	-17.403	-24.423		
2	-17.663	-20.981	-16.037		
3	<mark>-16.202</mark>	<mark>-17.211</mark>	-19.965		
4	-17.190	-17.308	<mark>-12.478</mark>		
Δ	5.425	3.770	8.386		
Influence [%]	30.86	21.44	47.70		

Due to the fact that a lower porosity is required, analyzing Table 4.15 it was observed that the optimal parameters for the melting process are those presented in Table 4.16.

Tabelul4.16							
Parameters	Level	Optimum Value					
Temperature	3	1050°C					
Power	3	80 KW					
Preheating	4	350°C					

#### Additional hardening

In order to increase the hardness and the compactness and quality of the deposited coating, a process of hardening the surfaces of the shafts by applying pressure with a ceramic balls at a pressure of 200 bar was applied.

## 4.7 Characteristics and properties of remelted coatings

### 4.7.1. The thickness of the remelted coating

Optical microscopy determined a thickness of the deposited and remelted coating of more than 1 mm. Such thicknesses have been studied as the implementation of these coatings in the hydraulic cylinder manufacturing industry and requires further mechanical processing of the coating. It was also considered to ensure superior corrosion behavior.

#### 4.7.2. Microstructure of the coating

XRD analysis reveals the presence of 4 important phases in the composition of remelted coatings: -nickel phase, which is predominant in all 3 types of powder, as observed in the XRD analysis of the powder. Following the remelting, the nickel phase was reduced from 70% to 62% for KS-IC-45 powder, from 48% to 45% for KS-IC-55S powder and for type KS-IC-55 from 53.5% to 46%. This soft phase also explains the much lower corrosion behavior of KS-IC-45 powder, the matrix being prone to corrosion.

- the dark zone marked B corresponds to phase CrB (chromium boride),

- the phase of nickel boron (Ni3B) is the bright area marked with A. These two phases are very hard phases which, at the same time, can be observed in the hardness tests. In powder type KS-IC 55 it can be seen (Figure 4.8) that these two phases are very finely distributed which leads to an increase in hardness.

- the presence of silicides (Cr6Ni16Si7) in the coating structure increases the stability of the coating at high temperatures, at the same time this phase increases the corrosion resistance. The silicones are denoted by C and represent the dark phase shown in the following images (Figure 4.6 - Figure 4.8)



Figure 4.1 XRD Diffractogram of KS-IC-45 inductive remelted (left) and cross-section LMmicrograph (right)



Figure 4.2 XRD Diffractogram of KS-IC-55S inductive remelted (left) and cross-section LMmicrograph (right)



Figure 4.3 XRD Diffractogram of KS-IC-55 inductive remelted (left) and cross-section LMmicrograph (right)

### 4.7.4 Coating hardness

Microhardness measurements were performed along the cross section of the NiCrBSi coatings using a Zwick micro hardness tester. Determining the hardness of the coatings, from the parts that were inductively melted with optimized parameters were extracted 3 samples obtained from different parts of the material and prepared metallographically. On each sample, 7 measurements were made from the outside to the substrate. Table 4.18 shows the average values for each indentation.

Distance [mm]	0.05	0.2	0.35	0.5	0.65	0.8	0.95	HRC
KS-IC-45	380	381	380	380	381	371	365	38
[HV 0.3]								
KS-IC-55S	573	591	636	639	585	584	590	53
[HV 0.3]								
KS-IC-55	733	753	695	702	695	748	720	60
[HV 0.3]								

Table 4.18

It is observed that a high proportion of chromium leads to a higher hardness but a high hardness brings problems in further processing.

It should be noted that following the application of the ceramic ball hardening process, increases in hardness of up to 10 HRC were observed.

### 4.7.5 Coating adhesion

The performance and quality of a thermal spray coating depends on the coatingsubstrate interface. A possible delamination would inevitably destroy the entire coat and the quality of the deposit would be practically useless. The anchoring mechanisms in the thermal spray depend on the bond between the deposited particles and the bond between the particles and the substrate.

To investigate the adhesion of the coating indentation tests were performed at various

points on the interface using the Brinell and Vickers indenters (fig. 4.9)



Figure 4.9 Micrographs of indentations (a) Vickers and (b) Brinell

In the region of the coating interface, several indentations were made until a force of 1200N on the HV scale and 187.5 kgf on the HBW scale was reached. Although the size of the plastic deformations was considerable, no cracks were observed at the edge of the indentations. This result shows excellent adhesion to the interface region, low internal stresses and high resistance to crack propagation. The indentations without cracks also confirm other technical aspects: good preparation of the substrate (cleaning, roughness), optimal deposition parameters, good selection of materials as well as optimization of the applied remelting treatment.

### 4.7.6. Tribological behavior

Several equipments were used to perform a complete analysis of the wear behavior. Inductively fused NiCrBSi coatings deposited with the three types of powder were used to compare NiCrBSi samples. The comparison is extremely important because it can give us an analysis of how the developed coatings behave and the choice of the optimal one.

When using bore cylinder parts, it is desirable that the coefficient of friction be kept to a minimum. A high coefficient of friction leads to the introduction of additional energy into the tribological system. This energy can be translated over time by damaging the whole assembly due to micro deformations on the surface of the coating, introducing vibrations as a whole or damaging the wear of the surfaces. A pin on disk assembly was used to determine the coefficient of friction. The parts were polished to obtain a flat surface, then they were cleaned with acetone, a static ball made of WC-Co with a diameter of 6 mm and a pressing force of 10N were chosen for the tested sample. The test was performed with a sliding speed of 15 cm / s on a circle with a diameter of 12 mm and the test stopped after 25000 rotations equal to 942 linear meters, almost double the parameters used for as-sprayed coatings. The results of the coefficient of friction and the wear mark are shown in Figure 4.10 to Figure 4.12







The Pin-On-Disk tribological investigation revealed a wear rate of  $1.11 \times 10^{-5}$  mm<sup>3</sup> / Nm for the KS-IC-55S remelted NiCrBSi coatings compared to a higher value of  $1.35 \times 10^{-5}$  mm<sup>3</sup> / Nm in the case of IC-KS-45.

As it is observed that the IC-KS-55S type coatings have a better resistance to slip wear, it can be concluded that they have a more compact structure due to the melting process, compared to the IC-KS-55 type coatings. and a higher hardness than IC-KS-45

#### 4.7.7 Corrosion behavior

A set of samples was prepared for electrochemical testing. Prior to electrochemical corrosion tests, the coated surfaces were polished to a flat surface due to the fact that the samples were extracted from the 160 mm diameter cylindrical surface deposition. After preparing the flat surface, they were polished until they reached a specified roughness (Ra $\approx$ 0,1) and then covered with resin to obtain a tested working surface of 1 cm<sup>2</sup>. The corrosion behavior of NiCrBSi coatings was investigated by electrochemical testing in aqueous solution with a concentration of 3.5% NaCl + 5% H2SO4. A saturated calomel electrode (SCE) was used as the reference electrode, a platinum electrode as the auxiliary electrode, and the samples represented the working electrode. The samples were polarized in a potential range from -1000 mV to +1000 mV, applied between the platinum electrode and the working electrode.S-a realizat o clasificare a rezistenței la coroziune a aliajelor de pulbere NiCrBSi.

Following the process of remelting by electromagnetic induction, the coating formed by the powder KS-IC-55 is nobler compared to KS-IC-45. The polarization curves shown in Figure 4.51 show that it has a more positive potential and a lower total current density. Powders with a higher Cr content have the ability to passivate after passing through the critical point. The low chromium coating has a reduced ability to form a passivation layer which leads to more intense corrosion.



Figura 4.5 Polarization curves of NiCrBSi coatings

### 5. Concluzii și contribuții personale

The experiments were based on the introduction of a new process for remelting NiCrBSitype coats sprayed with oxyacetylene flame in the case of new parts or in the case of replacement for worn coatings deposited by other types of processes. The experiments took place on three different types of powder with the aim of optimizing the remelting process for different hardness requirements from the hydraulic cylinder industry.

Attempts to improve NiCrBSi-type layers by heating them with high frequency currents have led to the following conclusions:

- As a feedstock material, the powder used was in the dimensions + 106-45 having a spheroidal shape due to the method of obtaining (by the gas atomization with water collection process), in the cross-section having very high encapsulated holes or porosity. The substrate used was a quenched and tempered 42CrMo4V type steel, with a mechanical strength of 911 MPa (N/mm2)

- The spraying of the three types of powder was done with the help of a specialized company in repairing used hydraulic cylinders. Calculating the necessary deposition parameters, resulted for the samples of diameter 160mm a deposition speed of 833mm/s, the rotation of the shaft being 95 rotations and an advance of 4mm per rotation, the deposition being made in 6 passes with a final coating thickness of 1.3mm

- After deposition, the coatings showed a porosity of up to 15% and a low adhesion to the substrate.

- The inductor type used for remelting these coats were chosen as a rectangular section of 20x10 mm with a wall thickness of 1 mm, continuously cooled with distilled water at a cooling temperature of 15 degrees Celsius.

- The optimization of the three types of layers was done considering the DTA curves obtained in the laboratory and compared to those given by the powder manufacturer. Using the Thaguchi method, was reduced the number of tests from 81 tests (as is normal for an arrangement of 3 factors influencing the process distributed on 4 levels) at only 16 experiments plus the verification experiment, for each of the three types of powder.

- The optimal working distance between the inductor and the heating piece was obtained as 7mm, with an influence on the substrate on a maximum depth of 7 mm and a lamellar sorbitic structure on the first 20 microns at the coating-substrate interface.

- After remelting, the coats were investigated in respect of the developed microstructure with a coat thickness higher than 1 mm and a reduced porosity from 15% down to 0.5% in the case of the coating obtained from the KS-IC-45 powder.

- The presence of chromium boride and nickel boride phases brought a high contribution to achieved hardness. Hardness increasing from 38 HRC in the case of KS-IC-45 powder which has the lowest chromium content of only 6 wt .% to a hardness of 60HRC in the case of KS-IC-55 powder with a content of 13% Cr

- Very good adhesion following the inductive melting process

- Similar friction coefficient of 0.64 was observed in the case of KS-IC-55S powders compared to 0.68 in the case of less hard KS-IC-45 powders.

- At the same time, a good corrosion resistance of the alloy formed after the remelting process was observed, in the case of KS-IC-45 type powder after the neutral salt spray test of 1000 hours, a corrosion penetration depth of only 3.5 micrometers was observed and in the case of testing in an acid environment a penetration of only 75 microns, which at a coating of 1000mm does not present a problem in terms of corrosion. In the case of the other 2 types of powder, no local corrosion attack was observed on the surface of the coating when tested in neutral salt spray.

In conclusion, the KS-IC-45 powder is suitable for use in industry with a hardening process applied before the polishing process, because the surface of the first 10 micrometres will be hard and meet the quality requirements of hydraulic cylinder industry. Inside, is the coating is ductile and presents an exemplary machinability in comparison with the coatings obtained from the other two types of powder. The remelting parameters can be extrapolated up to 1000mm diameters, which in the case of coatings obtained from hard powders, due to the internal stresses that form during cooling, it is not possible to realize it without a preheating in the furnace of the entire part.

### Personal contribution

- Carrying out a synthesis on the methods of deposition of functional coatings with accent on the critical analysis of thermal spraying processes
- Selection of powders according to chromium concentration and determination of deposition parameters for components with a given diameter of 160 mm
- Promoting the subsequent melting process by electromagnetic induction applied to NiCrBSi coatings
- Optimization of the inductor geometry taking into account the particularities of the coating remelting process
- Choosing the Taguchi method in order to determine a minimum number of attempts necessary to optimize the remelting process
- Determination of an optimal inductor-piece distance taking into account the specific features of the remelting process applied to the coatings deposited on worn parts
- Structural, mechanical, chemical characterization of the obtained functional coatings.
- Promoting the use of KS-IC-45 powder in the industrial process.
- Implementation in industry of the technological process developed within the experiments with direct applicability, obtaining coatings for new hydraulic cylinders and for the reconditioning of used ones,

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