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COMPOSITE MATERIAL DEVELOPMENT TO PLASMA DEPOSITION FOR GEOTHERMAL TURBINE PROTECTION

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ABSTRACT

The composite materials are the actual solution for improvement corrosion prevention and have good reliability during the steam turbines life. Thermal spraying has emerged as a suitable solution and is widely used to apply wear, abradable and corrosion protective composites coatings for application in geothermal conditions. This work reviews the characteristics of the microstructure and physic and chemical properties of the complex material composites based on powders composition: Ni-Cr-Si-B-Al-W. The experimental procedure involves obtaining X-ray diffractometer patterns of the specimen and determined SEM investigation to detailed information about composites morphological modifications and method characterization of these composites classes.

Keywords*:* multi-composite powders, plasma composite deposition, geothermal power plants.

INTRODUCTION

Geothermal energy has the potential to play a significant role in moving the Europe and other regions of the world toward a cleaner and more sustainable energy system. In order to increase the reliability of geothermal steam turbines, the assessment of the materials life under geothermal environment conditions is very important [1]. The advanced corrosion is the main problem for geothermal components.

Thermal high velocity fuel spraying (HVOF) has emerged as a suitable and is widely used to apply wear, abradable and corrosion protective composites coatings for application in turbine protection. These surfaces can be obtained using ceramic or metallo-ceramic materials as coating layers of the blades, preventing corrosion and providing good reliability during the geothermal turbines life.

The composite materials are the option for improvement and corrective action to prevent corrosion and have good reliability during the life of the steam turbines. Current development efforts are concentrating around several problem areas including: powders and composite structures spray plasma-forming of graduate structures, wear resistant materials to rotors restoration and life extension of geothermal turbines. Some of the specific experiments [2] are related to the synthesis of new complex powder mixtures with different addition of Ni-Cr components and powder elements such as: Si-B-Al and 3.5 %WC to obtain complex-ceramic protective layers, with improved wear, thermal shock and abradable resistance.

METHODS AND MATERIALS

Formation of the protective coating oxide layer with HVOF plasma deposition is use to decrease their oxidation and corrosion rate and prevent the aggressive attack of chemical species, such as chloride and sulphides. Thermal plasma deposition of: Ni-Cr, Si-B or Al-B coatings form the stable oxides with low diffusion coefficients for oxygen. In spite of Cr, Al and Si-B having low affinity for oxygen, when formed the thin oxide layer resists oxygen diffusion and limits further oxidation of the alloy. Thermal spraying using a metallization HVOF jet was realized using propane and oxygen gases under variable pressures [3]. After combustion the gases flow a high speed through a nozzle beyond white the powder is injected by a carrier gas through the samples (Figure1).

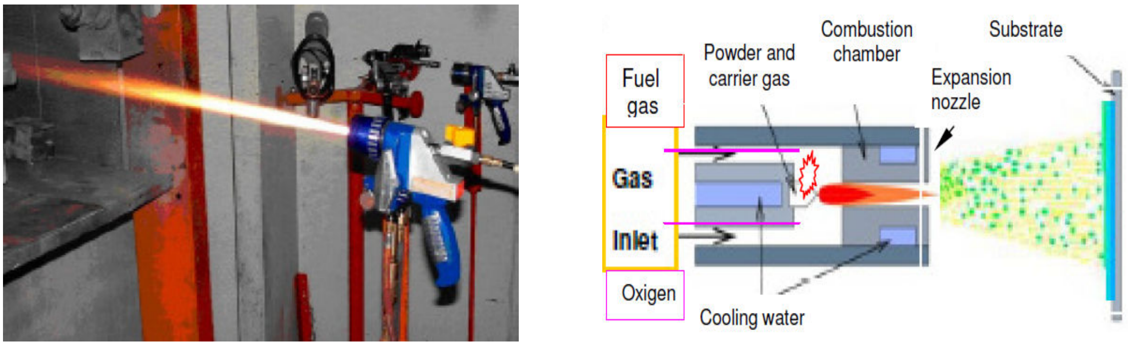


Fig. 1 - plasma spray HVOF process and schematic representational components of system METCO-4MP plasma jet metalizing device deposition.

Powder metals components such as Ni, Co, W do not form protective oxide layers. Aluminum has a relatively great affinity for oxygen and the constituents such as: W, Co, Mo and C can form volatile oxides which may accelerate the rate of oxidation. Due to the absence of a protective oxide layer, the metal can then lose weight when it oxides is contents. The presence of some elements such as S and Fe or Cu accelerate the oxidation rate even though they are present in a powders components or in alloys of plasma support deposition in only small amounts.

For producing good materials coatings, the stainless steel represents an important and growing segment in the Powder Metallurgy (P/M) industry. Due to the cost of stainless steel, the potential application should require least one of the following: corrosion resistance, oxidation resistance, good mechanical properties (ductility and impact strength) and wear resistance [4]. The criteria's selecting has been extensively studied since they determine the final composition and microstructure responsible for adequate geothermal turbine applications. In this context pre-alloyed metallic compounds with controlled particle morphology can be useful in assisting composite homogenization and densification. Commercial metal powders were purchased from Sulzer Metco© including Cr (7 - 12 µm - 99.5% pure); Ni (4 - 8µm - 99.5% pure); Al (4.5µm - 97.5% pure); B (2 - 4µm - 99.5% pure). The powder components were weighted according to the designed composition, and initially mechanically blended. The powders then placed into a container that was sealed and filled with argon gas to prevent oxidation of powders [5].

As a mechanical alloying process, the powders particles were mixed, shaped and bonded together. Small amount of samples powders were taken for analysis using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The obtained samples has been analyzed using a FEI Quanta Inspect F scanning electron microscope (SEM) equipped with a 1,2 nm resolution field emission gun (FEG) and a 130eV MnK resolution X-ray energy disperse spectrometer (EDAX) combined with X-ray diffraction (X-Ray Diffractometer Panalytical X'Pert Pro MPD D). As a substrate for coatings samples were used with stainless steel AISI/SAE 304 in different geometrical shape (cylindrically and prism like). For proper cleaning conditions, the samples to be coated, the surfaces were prepared by Al_2O_3 granules (G-22 grade) were grit blasted a distance of 150 mm and 3 bar air pressure, to obtain a roughness Ra around 5 microns.

RESULTS AND DISCUSSIONS

The properties of complex composites are determined not only by the nature and quality of the oxide and carbon content employed but also by the microstructure, porosity layers and homogeneity resulting from the processing plasma deposition and the depositions parameters. SEM has been used to study all aspects of particle morphology, including size, shape, surface topography, surface structure (crystal, grain and dendrite), coating or thin film characteristics, oxides, inclusion, void and agglomeration characteristics and satellite formation. The SEM has also been used to study final surface topography, effect of oxides or other coating, porosity, inclusions and other contaminant on P/M composite. Compacting-grade of stainless steel powder is produced by atomization the primary reason for selecting a stainless steel composition usually is its improved corrosion resistance.

The starting powders and processed powders were subjected to microscopic characterization using SEM and EDX analysis. Therefore, understanding the cohesion, adherence behavior and interfaces mechanism is absolutely necessary. In different manufacturing processes the powder result in different morphology, density, initial phases, particle size distribution and grain size within the powders. Powder with a spherical morphology has excellent flow-ability and feed-ability through the system. The powder particles shape influence the flow rate; as a result, very low deposition rates for angular powders are commonly observed. The effect of energy ball milling on the experiment is to obtain complex matrix composite powders and compare with the as-mixed powder. Diffusion and adhesion couple were formed during ball milling processing. The sizes of the composites the conglomerate and the diffusion metallic element was reduced by increasing the ball milling time of powders. The comparative powder mixtures were analyzed from the particles dimensions point of view by sizing. For analyze of the powder mixtures we used a sizing instrument RETSCH AS 200 type with sieves with dimensions starting from 125µm till 25µm. Sizing method used was volumetric dry sieving. The machine worked at a vibration power of 90 for 30 minutes. The rest on every sieve was weighted and the sizing curve was drawn. A determination of the flow rate of a powder is important in high-volume manufacturing which depends on rapid, uniform, consistent filling of the cavity. Poor flow characteristics results in low and un-uniform feeding and difficulty in ensuring powder plasma HVOF processing. The term free-flowing refers to the physical properties of powder, such as composition, particle fineness, and particle shape that allow the powder to flow readily into the die cavity. Flow characteristics are dependent on several variables, including surface friction, particle shape and size, type of material and bulk weight (Figure 2). Characteristics of powder surfaces, such as surface oxide films also affect flow characteristics. The presence of oxide films on powder particle surfaces alters the friction between particles and increase flow rate. Powders with lower surface oxide contents flow slowly than powders with higher oxide levels. In general reduced flow rates (Figure 2) are encountered with powders that exhibit one or more of the following characteristics: low specific gravity, low apparent density, high friction coefficient of fine particles, high specific surface area, a complex blend of different materials and high moisture content.

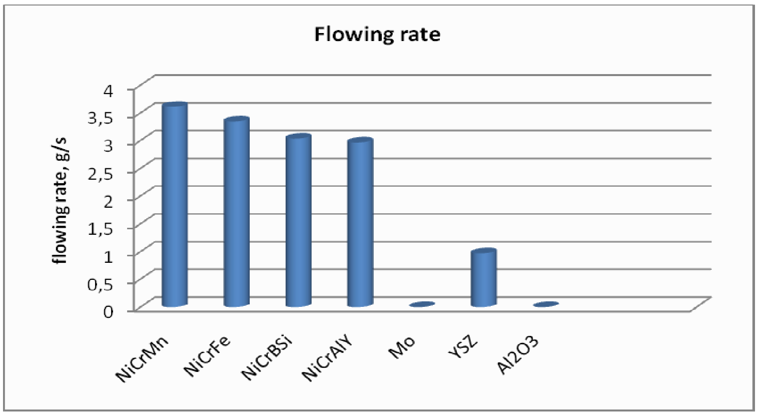


Fig. 2 - Graphical representation of the flow rate under atmospheric conditions.

Decreasing particle size generally lower apparent density and the smaller the particles are the larger the specific surface of the powder is (Figure 2). This phenomenon increases the friction between particles and subsequently decreases the apparent density. Complex Ni based powder composites coating shows good high-temperature wear and corrosion resistance. They have good wear resistance after adding percents of Si-B elements to the powders. Ni-Cr based coatings are used in applications when wear resistance combined with oxidation or hot corrosion resistance [6]. High nickel contents and low carbon contribute to good quality of the matrix. Complex matrix of Ni-Cr-Si-B-Al powders (Table 1) and 3.5%WC hard particles have been used as composite coatings (Figure 3). Addition of chromium promotes the oxidation and corrosion resistance at elevated temperatures and increases the hardness of the coating by formation of hard phases. In the presence of Al the nickel aluminide (NiAl) coatings exhibit system performance and excellent carburization resistance at high temperature.

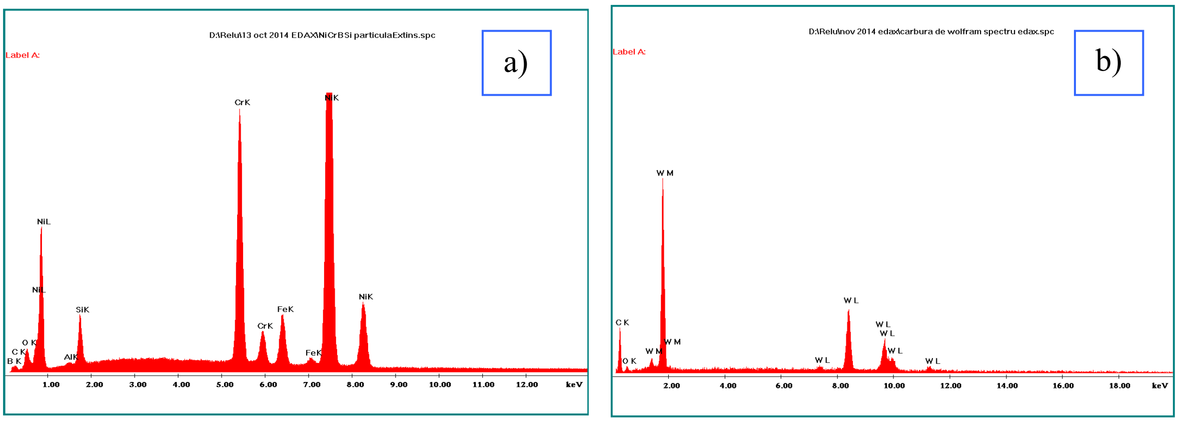


Fig. 3 - EDX-analysis of the (a) complex matrix Ni-Cr-B-Si-Al mixture and WC hard particles; (b) EDX profile of the WC powder samples.

The presence of carbon in the complex powder produces hard carbides with elevated hardness that promotes coatings wear resistance. Powders obtained by atomization have rounded to spherical shape with relatively smooth surface and the apparent density of the matrix is 4.2 g/cm^3. A better understanding of the service behavior of such coatings is needed in order to determine the mechanical and metallurgical changes, the interactions and the degradation mechanisms of these materials with energetic components [7]. The largely employed Ni-based powder belongs to the Ni-Si-B system, with the addition of other alloying elements is recommended. Addition of chromium promotes the oxidation and corrosion resistance at elevated temperatures and increases the hardness of the coating by formation of hard phases. Chemical composition of the hard particles is 99.9% W pure, apparent density is 18.5g/cm^3 and particle size diameters are 500nm-5µm. The tungsten particle size affected the morphology and mixing homogeneity of complex composites. The presence of nanoscale WC grain size (600-800 nm) result in an increase of abrasive and sliding wear resistance of complex protective composites coatings [6,7,8]. The EDX spectra of tungsten starting powders (Figure 3b) contained significant peaks of W however W_2C phase and correspondent peaks were found in the XRD spectra powder. Figure 4 is a SEM micrograph displaying typical rounded shape. Physical properties of powder depend on atomization condition. The finer grades 300-500nm of powder (Figure 5) require higher pressures and small molten metal streams complex mixture based on complex Ni-Cr-B-Si-Al powders (Table1).

Table 1 - Base complex powders chemical composition

Elements	Ni	Cr	Si	B	Al	Fe	O
Composition (wt %)	65.78	20.09	5.50	2.04	0.52	4.47	1.60

Table 2 - Characteristics of complex powders features

Characteristics of powder	Apparent density	Flow rate	Sizing
Ni20Cr5Si2B0.5Al and 3.5W	4.2g/cm^3	3.3s/50g	-43/+20µm (mesh -330//+20µm)

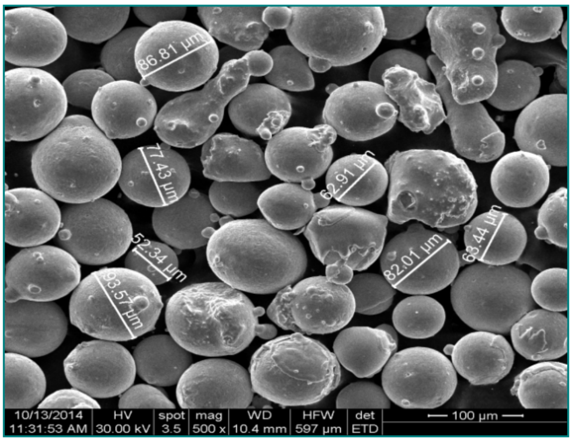


Fig. 4 - SEM of complex powders Ni-Cr-B-Si-Al base. Gas atomized, rounded to spherical in shape with relative smooth surfaces. X 500.

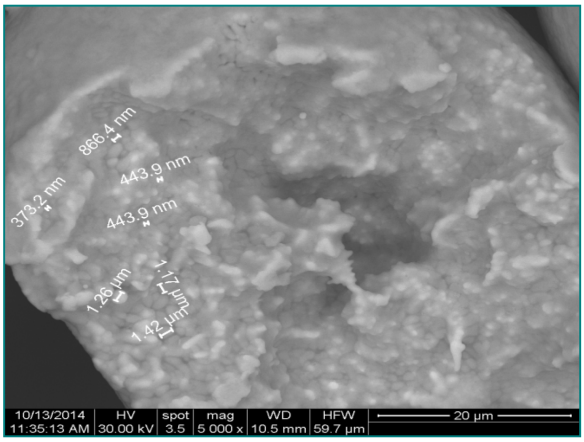


Fig. 5 - SEM image of the cross-section morphology of the particle powder. X 5000. The image revealing the nano-size elemental powder distributed in the atomized particle.

The SEM analyzed was performed in order to observe the particle shape and surface topography. The shape is round to spherical and the mean particles diameter is 65 µm. The spheroidization is detected and we can see a significant increase of equivalent diameter (Figure 5). The relative occurrence of the dimensions has been found to depend of the distributed of elemental powder on the particle surfaces). The effect of decreased particle size on density is particularly significant (apparent density 4.2g/cm^3) for particle sizes of then 20 µm (Table 2). Presence of boron depresses the melting temperature and contributes to the formation of hard phases. Silicon is added (Figure 6) to increases the self-fluxing properties and NiCrSiB alloys are widely used because of the good resistance of boride, carbide and silicide solid phase to wear and steam corrosion [9]. We found a significantly high oxygen concentration ability of the powder in its initial state.

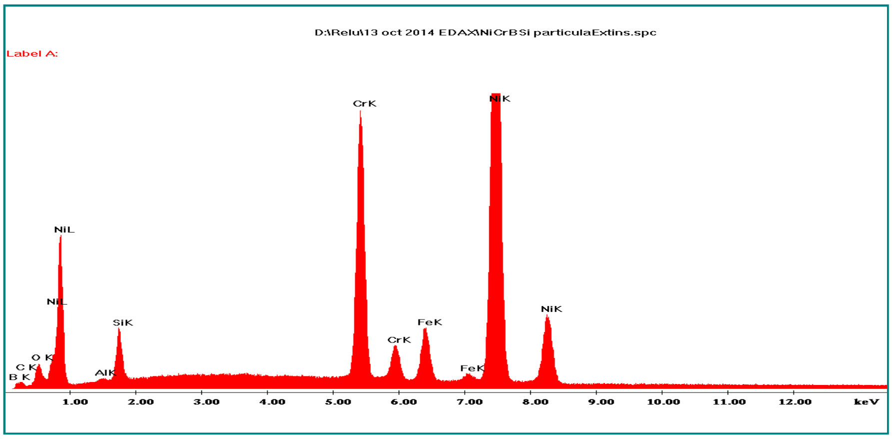


Fig. 6 - EDX spectrum analysis of complex Ni-Cr-B-Si-Al powders particle.

The parameter of process deposition and general condition regarding gas and flows pressures are thus suggested in the Table 3.

Table 3 - Feature of the characteristics of experimental HVOF samples deposition.

Gas	Volume flow [SLPM]*	Operating pressure [MPa]
Oxygen	250-350	1.0
Propane	40-80	0.05
Air	450-600	0.07

** **SLPM** = Standard Liters per Minute Gas consumption.*

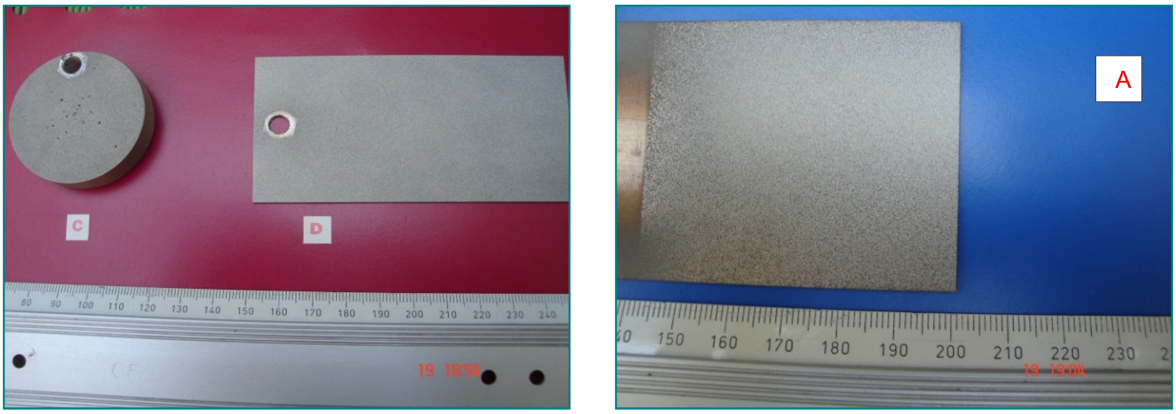


Fig. 7 - The coating HVOF spray samples on substrate stainless still 4307 (304L) to test the complex matrix composites deposition in different geometrical shapes.

Figure 7 shows the experimental results regarding the thermal deposition of the ceramic layer. The total ceramic layer thickness is between 60-70 microns and the thickness of the bonding layer is about 18-20µm (Figure 7). We found a correlation between the composition reported and the results of the tests performed in this study. Micro-hardness was determined by microidentation in the cross-section and different measurement was performed along the samples. Figure 8 shows the results of micro hardness on the different HVOF tests distance spray. The hardness indicate values between 450-800 HV, higher average values then those reported in the literature for composites coatings deposed by HVOF technique [2,7,10].

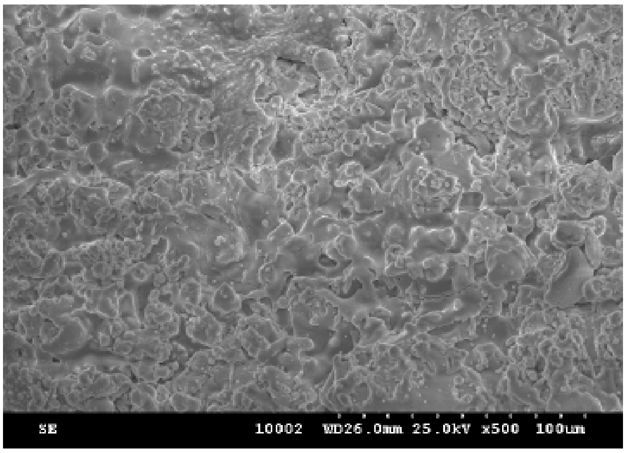
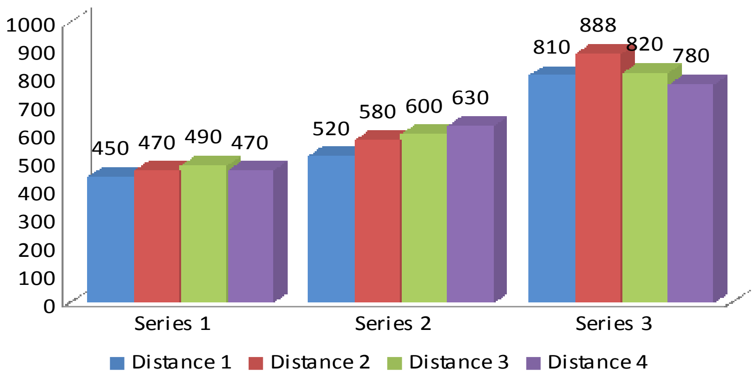


Fig. 8 - SEM image of multi-composite protection surface coating 65Ni20Cr5Si2B0.5Al and 3.5W deposit protective coating oxide layer. X 500.

The regions of high hardness seem to be correlated to formation of hard components, with tungsten carbide formation. Optimization of spraying parameters (Table 4) and stress relaxation processes will be as important as fixed thickness of steel deposition and properties cermets composite.

Micro hardness (HV 3000)



Results of HVOF spray distance employed: 1 = 100mm; 2 = 150mm; 3 = 200mm; 4 = 250mm.

Fig. 9 - The micro hardness of multi-composite coating 65Ni20Cr5Si2B0.5Al and 3.5W obtained in variables spray distances and operating pressures conditions.

In this condition it can be seen that results of the samples. The Series 3 sprayed from at distance of 150 mm has the highest values of micro-hardness followed by the sample Series 3 that was sprayed at 200 mm.

Table 4 - The experimental powder deposition and main specification of HVOF process

Oxygen [l/sec]	Propane [l/sec]	Air [l/sec]	Carrier gas pressure **Series 1** [atm]	Carrier gas pressure **Series 2** [atm]	Carrier gas pressure **Series 3** [atm]
4.5	1.2	8	8.8	10.2	11.5

The spray distance is an important parameter to be considered for tuning the processing conditions and thus to maintain or even improve the adhesion of the coatings. Additionally, bending samples adhesion tests (45 degree) were performed with different tilt, to observe how this parameter affects the adhesion of the coatings. For this test the distance was 250mm because it shows the best properties in the above tests carried out in this work. In this experiment the XRD analysis is a technique for the rapid determination of the samples homogeneity (Figure 10 and Figure11). It displays the composition spectrum existing in a given inhomogeneous phases from the shape of diffraction peak broadened (Figure 10) by a range of lattice parameters in the phase.

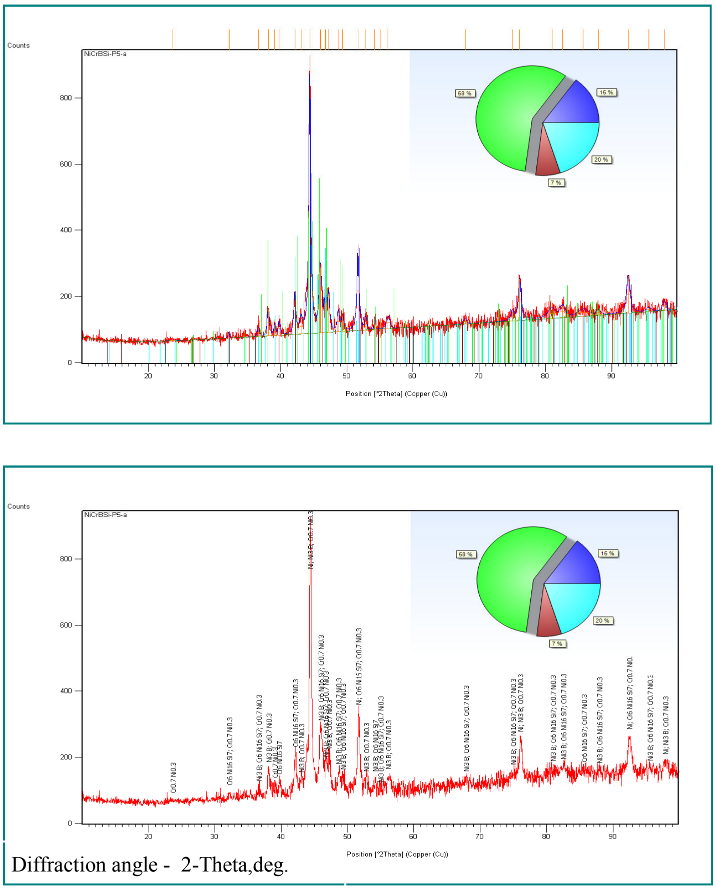


Fig. 10 - Indexing of the X-ray diffraction pattern of textured matrix sample of 65Ni20Cr5Si2B0.5Al X-ray diffraction pattern (Cu Kα).

Diffraction powder patterns XRD are difficult to analyze and experimental data must be carefully select.

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No.	Visible	Ref. Code	Compound Name	Chemical Formula	Score	Scale ...	Display Color	Quality	Subfiles	Crystal System
1	☑	04-003-7263	Nickel	Ni	39	0,638	Blue	I;ALT	Alloy,...	Cubic
2	☑	04-013-2478	Nickel Boride	Ni3 B	26	0,505	Lime	H;ALT	Alloy,...	Orthorhombic
3	☑	04-001-7368	Chromium Nick...	Cr6 Ni16 Si7	25	0,132	Mar...	I	Alloy,...	Cubic
4	☑	04-007-4101	Chromium Nickel	Cr0.7 Ni0.3	36	0,276	Aqua	P	Alloy,...	Tetragonal

Fig.11 - The identification and the colors code in the XRD diffractograms of composite matrix for the four major composite compounds distribution.

By the XRD analysis of the samples were observed the major cubic $Cr_6Ni_{16}Si_7$ (*Blue color cod in the difractogram Figure 10 & Figure 11*) and tetragonal phases $Cr_{0.7}Ni_{0.3}$, (*Aqua color cod in the difractogram Figure 10 & Figure 11*) with the effects in carburizing and chlorination resistance. Another phase that has been observed is the minor orthorhombic phase Ni_3B (*Lime color cod in the difractogram Figure10 & Figure 11*). The presence of complex Ni_3B peak shows the formation of intermetallic compounds Ni_3B with similar structure cemented and similar properties of silicides stable and chemically inert. Silicon is present almost entirely in the form of mixed crystals. The increase of Si content up to 5.50%, results in the presence of chromic silicides Cr5Si3. A higher content of Si and B significantly lowers the plastic properties of the composite layers. The most effective influence of the B and WC hardness can be explained by their participation in the formation of carbides and borides. The XRD pattern showed the brooded multiple diffraction peaks with low intensity, confirming the crystalline and fine size of the: silicide, boride and WC in the experimental composite. The $Cr_{0.7}Ni_{0.3}$ improves adherence and appalling resistance of oxide layer, and hence improves oxidation, sulphidation and carburization resistance.

CONCLUSIONS

Formation of the protective coating oxide layer with plasma deposition is a practical way to decrease their oxidation and the corrosion rate of the geothermal turbines components. Thermal plasma deposition of Ni, Cr, B, Si or Al coatings form the stable oxides with low diffusion coefficients for oxygen. In spite of Cr, Al and Si-B having affinity for oxygen, when thin oxide layer is formed, resists oxygen diffusion and limits further oxidation of the alloy. Small rounded particle size of hosting powders such as Ni and Cr would improve the homogeneity of alloying powder with WC mixture and construct a smooth film around the hosting particles. In the complex matrix composites Ni-Cr-Si-B were observed the major cubic $Cr_6Ni_{16}Si_7$ and tetragonal phases $Cr_{0.7}Ni_{0.3}$, and were observed the minor orthorhombic phase Ni_3B.The complex matrix composites greater corrosion and oxidation resistance and maintain hard hardness, strength and wear resistance up to operating geothermal steam conditions.

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