Morphological characterisation of complex powder used for protective coatings for geothermal plant components

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Abstract. This paper aims to review the morphological characteristics, microstructures, physical and chemical properties of two complex composite powders: Ni18Cr5Si2B and Ni21Cr11Al2.5Y. These powders will be used as an option for coating geothermal turbine blades to prevent corrosion. The corrosion process in the steam turbine results in damages being recognized as the leading cause of reduced availability in geothermal power plants and is depends on temperature, mechanical and vaporous carryover of impurities and water treatment. Thermal spraying is a suitable technique for coating layers with wear and corrosion resistance. Therefore this technique could be successfully used in geothermal applications for obtaining coatings layers from new complex composite powders protecting the turbine blades from corrosions and good control of steam chemistry. The composite powders were investigated using X-ray diffraction and electronic microscopy to provide detailed information about composites morphological modifications. The results obtained after morphological evaluation are encouraging for using these composite powders as an option for coating geothermal components using thermal spraying technique.

1. Introduction

The corrosion process in the geothermal turbine depends on temperature, pressure, chemistry, mechanical and vaporous carryover of impurities and water treatment (distribution between the vapours, the surface film and rotor blades material, heat transfer properties etc.). Corrosion is considered to be the most severe problem in geothermal power plants. The extreme high temperature and pressure conditions present in geothermal systems, as well as the existence of almost an entire periodic system of elements as corrosive salts [1,2] result in a high corrosion rate in geothermal power plants. In order to increase the competitiveness of the geothermal energy against the conventional energy resources, there is a great necessity for reducing the costs of geothermal power plant construction and providing safer and continuous energy exploitation. One of the major obstacles that
affect a stable and continuous energy production is the corrosion of constructional materials and equipment due to their interaction with an aggressive environment [3-6].

However, high-quality materials are inevitable for some process components when conventional materials have failed or are expected to lack performance. This includes equipment that is required to have a high reliability and near-zero corrosion allowance for reasons of performance, maintenance, and/or safety [7,8].

Multi-composite materials technology provides the construction of the main components exposed to very corrosive environment. Rating the principal technological measures already applied to current geothermal turbines is studied and discussed. The geothermal steam inlet pressure and temperature are relatively variable with time and a decreasing in geothermal steam initial parameters may appear. Even in the situation when the fluid reinjection is ensured, usually the source loses pressure, being necessary a period of time for renewing. The renewing time depends on the reservoir nature and its permeability [8].

A very important issue in the thermal spraying processes is the application of appropriate coating materials. The method of producing coating materials has a determining effect on the possibilities of their use for different thermal spraying technologies.

Producers of materials apply advanced technologies which make it possible to produce materials with the assumed and complex chemical and phase composition as well as of the specified particle morphology. The structure of such materials is optimized for the given thermal spraying method and it includes the specificity of the transformations taking place in the material during the process of thermal spraying, formation and use of the coating [9-15].

The corrosion process can be stopped with new materials, with a good steam chemistry control and new blades surfaces structure. These surfaces can be obtained using ceramic or metallo-ceramic materials as turbine blades coating layers, preventing corrosion and providing good reliability during the life geothermal turbines.

2. Materials and Methods

Elemental powders and composite structures used for plasma spray coatings are currently investigated due to their promising results regarding obtaining gradual structures and life extension of geothermal turbines.

The stainless steel represents an important segment of the powder metallurgy (P/M) industry, the cost of stainless steel and the potential application being very promising. More complex powder compositions have been investigated to determine the final composition and microstructure responsible for adequate geothermal turbine applications. In this context master alloyed metallic compounds with controlled particle morphology were used to determine the composite homogenization and densification. Commercial Sulzer Metco metal powders were used to design two compositions that probably will behave good regarding the corrosion protection: 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. The powders then placed into a sealed container and filled with argon gas to prevent oxidation of powders. The powders particles were mixed in a high velocity ball milling RETSCH type, using stainless steel vials and balls, shaped and bonded together. Samples were tapped for analysis for scanning electron microscopy (SEM) and X-ray diffraction (XRD).

The composite powders obtained are NiCrBSi and NiCrAlCoY.
3. Results and discussions

Aggressive corrosion in geothermal steam condition may be defined as an accelerated corrosion, resulting from the presence of many salt contaminants such as Na₂SO₄, NaCl, and silicates forming molten deposits, with a damaging impact on the protective surface of plant geothermal components.

Active corrosion occurs when metals are heated in the temperature range 250-300°C in the presence of sulphate deposits formed as a result of the reaction between sodium chloride and sulphides compounds in the solutions phase.

Geothermal steam specifics chemistry include: high non-condensable gas contents, high total dissolved solids salts in steam and corrosive chemical composition. High H₂S content generally promotes metallurgical problems: stress corrosion, cracking and metal fatigue. The high CO₂ content in geothermal fluid below about 200°C accelerate calcite scaling and promote active corrosion. Also one of the most commonly problems regarding high gas content in the geothermal steam are high non-condensable gas contents, sulphur deposition and corrosion due to low PH and oxygen into the geothermal power components steam.

The most common problems concerning high gas content in the geothermal steam are: high Cl⁻ (10,000ppm as 1.8% NaCl); CO₂ (300ppm) and SO₄ (50ppm as Na₂SO₄). High CO₂ content in geothermal fluid below about 140°C accelerates calcite scaling and promotes very active corrosion of geothermal plant components. The solids content and composition is diversified, particularly as regards chloride and different trace elements, as: boron, fluoride etc. Geothermal fluids contains about 130g/kg (130,000ppm), mostly sodium chloride.

Formation of the protective coating oxide layer with plasma deposition is use to decrease their oxidation and corrosion rate. 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, after the formation of the thin oxide layer, resisted oxygen diffusion and limits further oxidation of the alloy.

Some powder metals components such as Ni, Co, W, and Mo do not form protective oxide layers. Ti has a high affinity for oxygen and oxygen is highly soluble in Ti, thus the oxidation rate is not limited. The W and Cr, Mo, C can form volatile oxides which may accelerate the oxidation rate due to the absence of a protective oxide layer and the metal could lose weight during oxidation process.

We investigated by SEM microscopy all the aspects regarding particles morphology, including size, shape, surface topography, coating or thin film characteristics, oxides and inclusions. In different manufacturing PM processes the powder results in different: morphology, density, initial phases, particle size distribution and grain size.

Powder with a almost spherical morphology has excellent flow and feed ability through the system. The powder particles shape influences 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 obtaining complex matrix composite powders, and these powders will be compared with the result reaction in 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 were reduced by increasing the ball milling time.

For powder mixtures analyse we used a sizing instrument type Retsch AS 200 with sieves with dimensions starting from 125μm till 25μm. Sizing method used was volumetric dry sieving. The results are shown in figure 1.
The apparent density decreased when the mean diameter for the powders was low and the small particles implies a large specific surface for the powder used. This phenomenon increases the friction between particles and subsequently decreases the apparent density. Complex powder Ni based composites coating shows good high-temperature wear and corrosion resistance. They have good wear resistance after adding percent of Mo elements to the powders [10,14]. Ni based coatings are used in applications when wear resistance is combined with oxidation or hot corrosion resistance. The primary reason for selecting a stainless steel composition usually is its improved corrosion resistance.

Ni based powders are widely used. We selected NiBSi powders system and additions of alloying elements are strongly recommended. Addition of chromium promotes the oxidation and corrosion resistance at elevated temperatures and increases the hardness of the coating by formation of the hard phases. The mean diameter of the complex powder was calculated. In figure 2 the results of average diameter of the complex composite powders is shown. The average diameter for the powder to be sprayed using plasma spraying technique or high velocity oxygen fuels technique is around 45 microns; figure 2 showing that the characterized powders are in the appropriate range.

Flowing rate and density were calculated for the studied powders and the results are shown in figure 3 and 4.

The complex composite powder NiCrAlCoY had a flowing rate lower than NiCrBSi powder and the apparent density and tap density was lower as well. The composite coatings will have different properties that will be assessed in future papers. Silicon is added to increases the self-fluxing properties, increasing the flowing rate of the NiCrBSi complex powder. The average diameter, flowing rate and density values for both powders are in the range of HVOF coating process.
Figure 5 reveals SEM micrograph displaying typical rounded shape of the composites powder. The finer grades of powder require higher pressures and small molten metal streams complex mixture based on complex Ni-Cr-B-Si powders. In SEM imagens, the particle shape and surface topography can be observed. A significant increase of equivalent diameter could be observed (Figure 6).

The chemical composition of the NiCrBSi composite powder is shown in Table 1.

| Elements | Ni   | Cr   | Si   | B    | Al   | Fe   | O    |
|----------|------|------|------|------|------|------|------|
| Composition (wt %) | 67.78 | 18.09 | 5.52 | 2.02 | 0.52 | 4.47 | 1.60 |

In figure 6 the electronic microscope image of the surface morphology is investigated. On the spherical particles in zone 1 a small coating from the same powder could be observe. The powder homogeneity is very good and the chemical composition in zone 1 is shown in figure 7, on the EDS analyses results. In the EDS analyses all the designed species were identified and the coating on the particle placed in zone 1 are from the same powder composition.

The presence of boron lowers the melting temperature and contributes to the formation of hard phases. The alloyed elements such as: Ni, Cr and Fe were relatively uniform distributed over the composite (zone1 and zone2 are similar in the EDX - quantitative examinations). Electron diffraction
powder patterns (XRD) are difficult to analyse and experimental data must be carefully select (Figure 8). In the samples were observed the major cubic Cr$_{0.25}$Ni$_{0.75}$ and tetragonal phases Cr$_{0.25}$Ni$_{0.75}$ with the effects in carburizing and chlorination resistance. The minor orthorhombic phases Ni$_3$B were also observed. The presence of complex Ni$_3$B peak shows the formation of intermetallic compounds. Ni$_3$B with similar structure of cementite and similar properties of stable and inert chemically silicides, the Si in excess cause the formation of Ni$_3$Si.

Complex matrix of Ni-Cr-Al-Co-Y powders could be use as alternative composite coatings. In the presence of Al, NiAl compounds appear and coatings exhibit system performance and excellent carburization resistance at high temperature. The Y addition for this powder may act as a corrosion resistance increaser and Co addition could affect positively the coatings adhesion properties. Also Al added to this complex powder could promote oxide formation and Al$_2$O$_3$ layer could protect the coating at high temperature. In figure 9, SEM microstructure images are shown and the homogeneity of the sample could be observed.

In this case, the EDS analysis (Figure 10) is a technique for the rapid determination for samples homogeneity degree. This analyse displays the spectrum of composition existing in a given inhomogeneous phases from the shape of diffraction peak broadened by a range of lattice phase parameters. In table 2 the complex powder chemical composition is shown.

| Elements | Ni  | Cr  | Al  | Y   | Co  | O   |
|----------|-----|-----|-----|-----|-----|-----|
| Composition (wt %) | 58.42 | 21.47 | 11.71 | 2.36 | 2.02 | 3.02 |

Figure 9. SEM of gas atomized complex Ni-Cr-Al-Co-Y powders.

Figure 10. EDS mapping micrography of the matrix complex Ni-Cr-Al-Co-Y powders.

Figure 11. X-ray diffraction pattern (Cu Kα) of: a) matrix Ni$_{21}$Cr$_{11}$Al$_{2.5}$Y$_2$O$_3$.

The major cubic Cr$_{0.25}$Ni$_{0.75}$ and orthorhombic FeAl$_{2.7}$ phases and the minor cubic phase Cr$_{0.25}$Co$_2$Al were observed in the samples. In the XRD spectrum (Figure 11) was observed with low
intensity and broadened width, indicating that Y_{2}O_{3} particles into the complex-powders samples. The XRD pattern showed the brooded multiple diffraction peaks with low intensity, confirming the crystalline and fine size of the NiAl and Y_{2}O_{3} components in the composites. The Y_{2}O_{3} improves adherence and appalling resistance of oxide layer, and hence improves oxidation, sulfidation and carburization resistance of surfaces composites.

4. Conclusions

Several complex composite powders were studied to determine the final composition and microstructure responsible for adequate applications in geothermal power plants. Two sets of complex alloying powders were prepared by the P/M process. The new complex composites syntheses have been correlated with the elemental powders of B, Si, Co, Y and Al with different additions of NiCr powder.

The analysis and the results suggested that for the NiCrBSi complex powder were observed the major cubic Cr_{6}Ni_{16}Si_{7} and tetragonal phases Cr_{0.7}Ni_{0.3} and the minor orthorhombic phase Ni_{3}B were observed.

The complex powder matrix increases the corrosion and oxidation resistance and maintains the hardness and wear resistance of the materials.

The major cubic Cr_{6.25}Ni_{0.75} and the minor cubic phase Cr_{0.25}Co_{2} were observed in the samples Ni21Cr11Al2.5Y_{2}O_{3}.

The existence of the ternary compounds and the mutual crystallographic orientation relationship of this ternary phase with the matrix were also reported.

The morphological study of these complex powders suggested that these powders are suitable for high temperature corrosion resistance coatings realised by HVOF process.

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