Considerations regarding WC-cermets depositions by HVOF and ESD techniques used for reinforced steel components for geothermal turbines

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Abstract. The cumulative effect of erosion-corrosion process in geothermal turbines results in significant damages, especially for rotors and turbine blades; the degree in which they are affected depends on steam temperature, mechanical impact and the geothermal composition of the substances dissolved in steam. Layer composite materials are a feasible option to improve the erosion-corrosion resistance and the durability of turbine components. WC-cermet powders containing tungsten carbide are used for High Velocity Oxy-Fuel (HVOF) spraying and for Electro Spark Deposition (ESD) to obtain granular microstructure and to form local hard structures. Both techniques by WC-cermet depositions were found to be most suitable to improve wear resistance, to repair rotors and blades and to provide possible life extension of geothermal turbines. The paper presents a comparative assessment of tungsten carbide and the technological parameters used for HVOF and ESD cermet layers depositions. Also, the work presents the analysis of the micro chemical composition of the microstructure, the micromechanical characterization and erosion-oxidation resistance of HVOF and ESD coatings using WC-cerments on steel substrates. The experimental procedure involved X-ray diffraction of the samples, micro mechanical tests and SEM investigations to provide specifically information about micro-morphological modifications and grade of adhesion of protective layers.

1. Introduction
In the geothermal turbines the erosion and corrosion process take place always and the phenomena it interacting on the nature of geothermal steam enthalpy, pressure and chemical impurities brought by the geothermal steam sources [1]. Geothermal steam contains corrosive gas and various solid particles, which cause cumulative erosion-corrosion phenomena and very active scale deposits. High CO₂ content in geothermal fluid below about 140°C accelerates calcite scaling and promotes very active corrosion of geothermal plant components [2]. The solids content and composition is diversified, particularly as regards chloride and different trace elements, as: boron, fluoride etc. For example, in the most commonly situation the sources concerning high gas content in the geothermal steam: high Cl⁻ (10,000ppm as 1.8% NaCl); CO₂ (300ppm) and SO₄ (50ppm as Na₂SO₄). The most affected parts by erosion are normally the diaphragms, the labyrinths seals, the drain holes, the turbine casing, the rotor blades and the rotor discs [3-4]. Some classes of composite coatings applied onto steel turbine components, could help it withstand a variety of rough surface erosion and corrosion condition [5].
The oxygen fuel deposition (HVOF) process and electro spark deposition (ESD) technique has emerged as a suitable surface engineering technology, used to apply wear, erosion and corrosion protective coatings [6-8]. Multi-composite protective coatings technique is gaining acceptance in geothermal power plants industry, to improve reliability and life service of turbine rotors and bleeds. Tungsten carbide (WC) based cermented carbides and composite structures obtained by HVOF spray and ESD deposition are currently investigated due to their promising results in obtaining gradual structures [9,10]. HVOF and ESD are capable techniques of depositing wear and corrosion resistance coatings to repair, improve and extend the service life of important components in geothermal turbines.

2. Materials and method

As a substrate for coatings was used SS 304 stainless steel. Holding excellent mechanical properties, the high amounts of nickel and chromium in austenitic stainless steels also provide important corrosion resistance. Additionally, SS 304 are weldable and formable. For tungsten HVOF deposition coatings, were purchased the commercial powder Amdry 5843 from Sulzer Metco© as 86WC10Co4Cr. These materials are generally recommended for application where: were abrasion, erosion, fretting and erosion resistance are required. The CoCr matrix provides higher corrosion resistance than Co matrix. The apparent density of the powder was measured conformed of ASTM B212, and the flow rate was measured conformed ASTM B964. For sizing of the powder we used Retsch AS200 sizing machine, worked at a vibration powder of 45 minutes. Chemical composition of the hard particles is 99.9% W pure; flow density is 45g/cm³ in 19s and particle size distribution (granulometry) are -45+15μm. The tungsten particle size affected the morphology and mixing homogeneity of complex composites. An HVOF system Diamond Jet Gun supersonic jet (Figure 1), are used to protect steel samples (Figure 1). Flat specimens with 50x20x3mm, and sand blasted by alumina (Grit 45) were used before spraying. The parameter of process deposition and general condition regarding gas and flows pressures are thus suggested in the Table 1.

Table 1. Feature of the cermet depositing parameters of HVOF experiments.

| Powder Type  | Gas    | Volume flow [SLPM]* | Operating pressure [MPa] |
|--------------|--------|----------------------|--------------------------|
| 86WC10Co4Cr  | Oxygen | 250                  | 1.0                      |
|              | Propane| 40                   | 0.05                     |
|              | Air    | 430                  | 0.07                     |

*SLPM = Standard Liters per Minute Gas consumption.

For ESD deposition is used a pulsed arc micro-welding on short-duration process; associate of a high-current electrical pulses and very low heat-input. The short electrical pulse produces very rapid solidification of the deposited material resulting by melting a consumable WC-electrode material on a steel substrate (Figure 2).

In the experimental depositions was used as the electrode material. Coating materials were chosen based on similar tungsten compositions being qualified for HVOF applications. A tungsten carbide (Table 2) was used as electrode material, and 85WC9Co5Cr1Ni was selected as cermets that show excellent wear and corrosion resistance; it can be applied by ESD in a smoother than average deposit and the deposition can be done in strictly indicated areas.

Substrates require no special surface preparation. In the experiment, flat samples 50x20x3mm, sand blasted by alumina (Grit 45) was used before spark deposition. The process parameters affecting the quality of the ESD coating include optimum values of variables (voltage, operating current, capacitance, current peak, spark frequency, and coating rate) in Table 2. The electrode is a 4 mm diameter and 30 mm long cylinder. The frequency and the rotation speed of the electrode were kept...
constant at 350 Hz and 2500 rpm, throughout the experiments. The estimated cooling rate of the ESD process can be range from $10^4$ as $10^5$ degree C per second. This low net heat input and the rapid solidification process are beneficial to the homogeneity and mechanical properties of the deposition.

**Figure 1.** HVOF equipment spraying operation to obtained cermet layer.

**Figure 2.** ESD operational equipment (hand-held applicator to obtained cermet layer deposition.

| Electrode composition (Sinterid powder) | Applied voltage | Operating current | Capacitance | Current peak | Coating rate | Spark frequency |
|----------------------------------------|-----------------|--------------------|-------------|--------------|--------------|----------------|
| 85WC9Co5Cr1Ni                         | 60 V            | 5 A                | 50 μF       | 230 A        | 0.9 mm$^2$/s | 350Hz          |

The structural investigation, involved X-ray diffraction patterns and analyses by X-Ray Diffractometer Panalytical X’Pert. Scanning Electron Microscopy analysis (SEM) and energy dispersive spectroscopy (EDX) was used to analyze by Quanta Inspect FEI microscope equipped with a 1.2 nm resolution and field emission 130eV. The Nano-Mechanical Tester CSM Instrument indentation is used to measure the mechanical properties.

The Nano Indenter enables to measure Young’s modulus and hardness in compliance with ISO 14577.

Tribological characterization was to determine roughness (Ra), friction coefficient and wear rates, with Ball-on disk tribometer. On average of 10 tests were used as an indicator of the hardness and war resistance. The hot corrosion environment of mixed NaCl-Na$_2$SO$_4$ has been selected for the tests. The salts molten are extremely corrosive and are on good substitute for the geothermal high enthalpy steam environmental systems. The 10% mass NaCl and 90%Na$_2$SO$_4$ with a 655°C, provides a very aggressive environment for hot corrosion of steel.

The samples where oxidizing in 10 furnace cycles, each cycle consisting of 1h of heating at 655°C in furnace, followed by 60 min of cooling in air. The weight of specimens was measured at the end of each cycle an electronic balance. Before tests, on surface of layers, was applied uniformly a salt mixture (salt was kept in the range of 0.5mm with of hair brush by repetitive action).

3. Results and discussion

3.1. Coatings produced by HVOF and ESD process

The content of Co element plays an important role on the density and hardness of the powder and sintered WC-Co-Cr products. In case of increase in the Co content results a decrease of the density and the hardness value [11]. On HVOF processing spraying, the WC-Co-Cr spheroid powders are exposed to the flame and reaction causing possible decomposition of powder particle [12]. This leads to
dissolution of WC into the liquid Co-binder, loss of carbon by oxidation. On the deposition layer, the porosity is generally associated with a high number of unmelted component powder particles that became prepared in the coating. In the case of ESD depositions are possible some advantages: the coating material is metallurgical bonded to the steel substrate and the low heat input allows the substrate, remain at low temperature. The rapid solidification of the deposits produces a nano-structured or possible amorphous structured coating.

As a result, the most common application of the ESD process is to apply local wear resistance coating [13]. Because the coating/substrate bond is applied very precisely with an electrode, no effluent chemical process occurs, and different metals or different faces of the same work piece can be successfully coated. Successive layers of different metals could also be coated creating multi-composite layers.

3.2. Microstructural characterization

Figure 3 and Figure 4 shows SEM imagines observed at the surface deposited are not free of defects, some cracks are present and little WC particle are not included onto the layer. The both coatings had a fairly porous structure in the near-surface region, however this porosity was expected not to be very critical for corrosion resistance, as the pores were shallow and disconnected [14]. The pores were specifically shown to be disconnected in the bottom region of the coating, where the coatings were shown to be well-attached to the substrate.

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**Figure 3.** SEM micrograph of surface cermets deposited by HVOF process. Note the dark oxide inclusions and porosity.

**Figure 4.** SEM micrograph of ESD surface cermets. Note the dark oxide inclusions and porosity. Wait particle are inclusion of WC.

**Figure 5.** SEM image of HVOF cross-section of layer deposition.

**Figure 6.** SEM image of ESD cross-section of layer deposition.
Porosity in wear coatings can also lead to the generation of coating fragments that break away and became abrasive cutting agents, increasing coating wear rates. The microstructure and compositions of the coating cross sections were examined using SEM. In the HVOF experiment the coating thickness was approx 260-300μm for 150mm sprayed distance and as resulted a stable deposition (Figure 5). For the ESD coating depositions, the thickness can range from 30-40μm based on the material combination. The coating thickness of hard 85WC9Co5Cr1Ni materials, such as the refractory metal carbides and the hard facing alloys, is generally limited from 60μm (Figure 6).

XRD cermets patterns, as shown in Figure 7 indicated the main constituent WC phases. For the samples XRD patterns are similar and have main WC phase and low W2C phases. During the HVOF spraying process, the WC phase was dissolved into the matrix and C was oxidized to CO and CO2. Due to its small volume fraction (Co,Cr,W)7C3 cannot be identified from XRD data. After EDS deposition, have detectable additional phases WC and W2C, but due to the small volume of Ni fraction, the presence of Ni phase could not be identified. The diffraction peak of W2C, located at 2θ ≈ 39.94°, is slightly shifted from the theoretical position (2θ ≈ 39.57° as listed).

This means that the W2C phase contains some Cr, formed as a result of metallurgical interactions during the HVOF spray process. The cermet (W,Cr):C composition is formed from the peak positions and from the corresponding lattice parameters. In this case, the samples are possible contained detectable W2C and components with peaks belonging to a f.c.c. Co-based solid solution and to the (Co,Cr,W)7C3 carbide. In this EDS experiments, there were no discernable peaks from intermetallic phases Co3W2C or for tetragonal phases Cr7Ni3. Figure 7b show that mixing of Co-Cr-Ni was only physical present and the powder components acting minimal only as binders for WC powder in EDS layer depositions. The XRD indicate the crystallization of the layer deposition. For (110) Bragg peak is found to be relatively broad indicating the smaller grain sizes for layer.

3.3. Mechanical properties
The hardness measured values are reported in Table 3. The mechanical properties have been correlated with the characteristics of the coatings. Using the nanoindentation technique and the small indentation of 5N force (500gf), provides an ideal non-destructive mechanical testing solution. Values of the Young's modulus (E) are calculated from the load-displacement data usually following the Oliver and Pharr procedure [10]. The wear rate of coatings exhibited better tribological behaviors than the uncoated steel. Tribological characterization by Ball-on disc tests and determination of the friction coefficient (load: 5N) and specific wear rate are presented in Table 3 and Figure 8.
Table 3. Comparative mechanical properties and erosion results for HVOF and ESD layers.

|               | Average values | Wear rate (mm³N⁻¹m⁻¹) | Roughness Rₐ (μm) | [HV] hardness (GPa) | Young’s Modulus [E] (GPa) | Friction Coefficient (μ) | Volume loss (mm³) |
|---------------|----------------|------------------------|-------------------|---------------------|--------------------------|------------------------|-------------------|
| SS 304 steel  | 2.65 x 10⁻⁴    | 4.95                   | 3.22              | 180.12              | 0.852                    | 1.32                   |
| HVOF layer    | 2.36 x 10⁻⁶    | 5.03                   | 10.32             | 260.28              | 0.673                    | 1.23                   |
| ESD layer     | 2.25 x 10⁻⁶    | 5.22                   | 12.54             | 294.43              | 0.591                    | 1.18                   |

Figure 8. Curves for friction coefficient for bottom specimens.

Owing to the heterogeneous and porous microstructure, all collected experimental data were analyzed by statistic method. The Young’s modulus (E) in boarded coating varies with ranging from 260 to 295 GPa due to the cermet phases. A specific wear rate of HVOF and EDS layer coatings was as low as 2.50 x 10⁻⁶ mm³m⁻¹N⁻¹. This is much less than a specific wear rate of steel (Table 3). The wear resistance value of the composite layers was much better than that of the uncoated steel and there exist many types of carbide in the dense layer coatings. For wear testing were performed according to ASTM G99 standard on ground and polished coating surfaces (Ra ≈10μm). Micro hardness at low loads (5N) is affected by technical deposition and by intralamellar properties and depends of the carbide dissolution observed in the HVOF and EDS microstructures. The coatings contained significant amount of W₂C, which has a higher density (W₂C =17.2g/cm³) and the specifically of the density of each hard metal coating is based on its volume fraction of pores and carbide grain (WC =15.7g/cm³). At room temperature wear of cermets HVOF and ESD layers are characterized by two mechanisms: ductile low, wich causes the formation of traces-wavy and the brittle fracture, which cause direct detachment of small portion of cermet layer from deposition [8].

3.4. Corrosion resistance characterization
To asses structural changes due to thermal corrosion, the addition of Na₂SO₄+10%NaCl mixture on coatings, can easily cause the degradation of protective layers on the steel at 655°C. After hot corrosion in 10 cycles, salts penetrated in the protective layers and contacted with the matrix, causing significant corrosion/sulfidation (Figure 9).

During initial oxidation, the SS 304 samples exhibited oxidation owing to the reaction of oxide scale and NaCl/Na₂SO₄ coating. A large amount of corrosion products spelled from specimens during the tests and obvious mass loss was observed. At the melting point of NaCl/Na₂SO₄ eutectic, the salt penetrates the oxide scale via the capillary effect, through pores and voids and in the end reacts with the steel substrate to cause corrosion/oxidation. From the external surface, all samples exhibit a first
zone that lost its initial carbides. In Figure 10 show the scale morphologies predominantly are Cr-rich that were developed on surface cermets.

When the scale was predominantly Cr₂O₃ the sulfur component increased the rate of oxidation. In the case when only a cermet layer deposition is used as coated steel, NaCl would interact with Cr to form metal chlorides, which would migrate outward to the salt/scale surface. Due to high vapor pressure, the O₂ interaction occurs, causing Cr-oxide to form. The formation of mixed oxide layer in the intermediate corrosion product region (cermet and SS304 steel), results from the continuous oxidation of the steel substrate. To prevent this, a multilayer or hybrid supplementary composite deposition is necessary, because the properties such as: hardness, abrasion resistance and strength are affected by the porosity of WC cemented carbides. The content percentages of the carbide phase and the Co binder matrix are very important since Co has poor corrosion resistance.

4. Conclusions
HVOF spray and ESD cermet depositions are currently investigated due to their promising results in obtaining gradual structures. HVOF and ESD are capable techniques of depositing wear and corrosion resistance coating to repair, to improve and extend the service life of the important components of geothermal turbines.

The HVOF spray process and ESD deposition used in this study are capable of producing dense WC-Co-Cr cermets coatings. In the generally context, the cermets exhibited superior erosion-corrosion resistance over all comparative materials. The results of this WC deposition HVOF and EDS
techniques produced denser and harder coatings, with higher indentation fracture toughness and higher elastic modulus.

At room temperature, under abrasive and slider and were condition, the 85WC9Co5Cr1Ni coating layers obtaining by ESD deposition, are more resistant then reference 86WC10Co4Cr cermet coatings obtaining by HVOF deposition; this is attributed to the exceptionally fine grain size and homogeneity of the deposits.

In this experimentally simulated corrosive conditions, used as a substitute for the geothermal high enthalpy steam environment system at more than 300°C (in the corrosion and tensile stresses conditions), a complete failure of the WC-coatings by brittle creaking is possible, due to thermal expansion and the inter-face corrosion. The SS 304 displayed greater pure corrosion resistance compared to the cermets, indicating that structural properties are of greater importance than corrosion resistance in aggressive environments.

5. References

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