Erosion-Oxidation Behavior of Thermal Sprayed Ni20Cr Alloy and WC and Cr₃C₂ Cermet Coatings

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An apparatus to conduct high temperature erosion-oxidation studies up to 850 °C and with particle impact velocities up to $15 \, \text{m.s}^{-1}$ was designed and constructed in the Corrosion Laboratories of IPEN. The erosion-oxidation behavior of high velocity oxy fuel (HVOF) sprayed alloy and cermet coatings of Ni20Cr, WC 20Cr7Ni and Cr_3C_2 Ni20Cr on a steel substrate has been studied. Details of this apparatus and the erosion-oxidation behavior of these coatings are presented and discussed.

The erosion-oxidation behavior of HVOF coated Cr_3C_2 25(Ni20Cr) was better than that of WC 20Cr7Ni, and the erosion-oxidation regimes have been identified for these coatings at particle impact velocity of 3.5 m.s⁻¹, impact angle of 90° and temperatures in the range 500 to 850 °C.

Keywords: erosion, oxidation, high temperature, composite coatings, HVOF

1. Introduction

Industrial components in gas turbine engines, fluidized bed combustors and catalytic converters are often subject to the conjoint effect of erosion and high temperature oxidation processes. Adequate characterization of high temperature erosion-oxidation behavior of materials involves the reproduction of process conditions such as temperature, impacting particle parameters such as size, shape, hardness, velocity, impact angle and mechanical properties as well as physical properties of the target material. The erosion behavior of metallic materials and ceramics at room temperature has been extensively studied1-4. Nevertheless, a number of questions regarding correlations between erosion properties and physical parameters of the material remain unanswered. A vast amount of information is available about the oxidation behavior of various metals and alloys at high temperatures⁵. However, only limited information is available about the conjoint effect of erosion and oxidation at high temperatures. The results of some of the erosion-oxidation studies demonstrate that synergy is observed between erosion and oxidation. This indicates that the degradation caused by erosion-oxidation can be greater than the sum of the processes operating separately⁶⁻¹⁰. It has also been mentioned that in some cases the formation of a corrosion product can inhibit erosion¹¹; or the wastage rate under erosion-oxidation conditions can be less than in the absence of oxidation. These contrary observations have generated much attention about erosion-oxidation processes in recent years.

Hogmark et al. first described erosion-oxidation interactions in terms of regimes in 1983¹². Kang et al.¹³ in 1985 argued that four regimes existed, based on erosion-oxidation studies of pure metals. These regimes were termed: a) erosion of metal; b) oxidation affected erosion; c) erosion-enhanced oxidation; and d) oxide erosion.

Modifications in these regimes and other interpretations about the existence of a variety of sub erosion-oxidation regimes have been proposed^{14,15}.

Procedures to control erosion-oxidation induced degradation are not readily available. At low temperatures, where oxidation is not a

problem, hard coatings are often used. At higher temperatures, these coatings do not usually exhibit adequate corrosion resistance. The use of ceramic coatings may help achieve both, erosion and oxidation resistance. Recently, the 'high velocity oxy fuel' (HVOF) process, a thermal spray deposition process, has generated a considerable amount of commercial interest as it can produce smooth, low porosity, dense and adherent coatings. In the HVOF process, metallic powders at high temperatures are sprayed at supersonic speed onto a substrate. This coating process can be used to apply Ni, Cr, Co or other alloy based metal matrix composite coatings reinforced with carbides, like WC or Cr₂C₂, to impart increased wear resistance to the substrates, especially at high temperatures. The HVOF process, as compared to plasma spraying, has the advantage of not altering the integrity of the carbide particles. In most high temperature coating processes, complex chemical transformations take place during the coating and cooling stages. Transformations such as, interactions between the carbide reinforcement and the matrix 16-18; decarburization of WC followed by formation of undesirable W2C (due to the high flame temperature and oxidizing atmosphere) and transformation of Cr₂C₂, as shown, due to the reactive atmosphere within the flame¹⁹.

$$\operatorname{Cr}_{3}\operatorname{C}_{2} \to \operatorname{Cr}_{7}\operatorname{C}_{3} \to \operatorname{Cr}_{24}\operatorname{C}_{6}$$
 (1)

Fewer transformations take place in coatings applied by the HVOF process. The lower flame temperature (3000 °C), and higher particle velocity (~1700 m.s⁻¹) in this process, produces dense and relatively pore free coatings.

This paper presents the results of an investigation carried out to determine the high temperature erosion-oxidation behavior of HVOF coatings of Ni20Cr alloy, and two cermets, WC 20Cr7Ni and $\rm Cr_3C_2$ 25(Ni20Cr). The erosion-oxidation measurements were made in the apparatus constructed in the Corrosion Laboratories of IPEN/CNEN-SP. The measurements were made in the temperature range 500-850 °C, using alumina particles at an impact angle of 90° and impact velocity of 3.5 m.s⁻¹.

2. Materials and Methods

2.1. The erosion-oxidation apparatus

A schematic diagram of the erosion-oxidation apparatus is shown in Figure 1.

This apparatus consists of a fluidized bed of erodent particles through which a specimen assembly enters and leaves at periodic intervals. The fluidized bed is within a furnace and a motor that rotates the specimen assembly controls the particle impact velocity. The fluidized bed of particles is obtained by pumping pre-heated air or oxygen through a porous plate supporting a bed of erodent particles. This porous plate was also designed in IPEN and prepared using conventional powder metallurgical techniques. The plate was made of AISI 310L, and selection of this alloy was dictated by high temperature oxidation resistance.

Alumina powder (AL-R grade 80, supplied by Elfusa Geral de Eletrofusão Ltd.) was used as the erodent, mainly because of its chemical inertness and stability below its melting point (2050 °C). Other desirable properties of alumina for use as an erodent are its high hardness (1710 HV), Young's modulus (400 GN.m⁻²), fracture

toughness (3.44-7.40 MPa) and compression strength (2758 MPa). After granulometric separation, the alumina particle size range used was 212-150 μ m (Figure 2).

2.2. Coatings obtained by the HVOF process

A HVOF equipment at the Cascadura S/A, company in Sorocaba, was used. Three different powders with compositions corresponding to Ni20Cr, Cr₃C₂25(Ni20Cr), WC 20Cr7Ni, were deposited on AISI 310L sheet surfaces. Scanning electron micrographs of the powders and the as-deposited coatings are shown in Figure 3-11.

Coated AISI 310 sheets (20 x 50 mm) were used as erosion-oxidation test specimens. These specimens were cleaned, degreased ultrasonically in acetone and fixed to the support rods with AISI 310 screws. The erosion-oxidation tests were carried out in the apparatus and the following conditions were used: temperature (500-850 °C), alumina particle impact velocity (3.5 m.s⁻¹) and impact angle (90°). Tests were also carried out at 100 °C to evaluate erosion behavior in the absence of oxidation. After the tests, the specimens were again examined in a scanning electron microscope and the surface reaction products were analyzed by both energy dispersive spectroscopy and X-ray diffraction analysis.

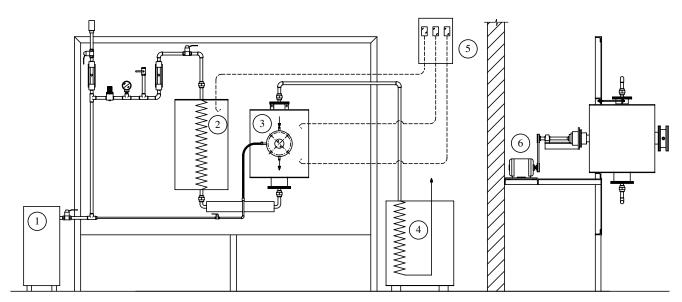


Figure 1. Schematic diagram of the apparatus that was designed and constructed in IPEN to conduct erosion-oxidation measurements: 1) compressor; 2) preheating furnace; 3) erosion-oxidation furnace; 4) system for retaining particles and for cooling; 5) control panel for controlling the motor and the furnaces; 6) motor to rotate the specimens through the bed of particles in the furnace.

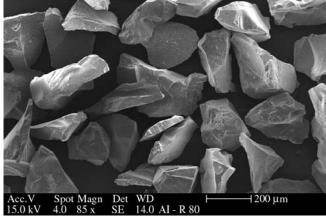


Figure 2. Micrograph of AL-R 80 alumina powder used as the erodent.

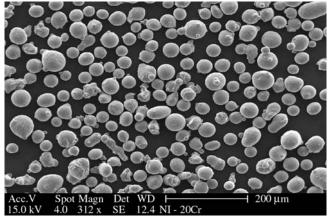


Figure 3. Micrograph of Ni20Cr powder revealing spherical particles.

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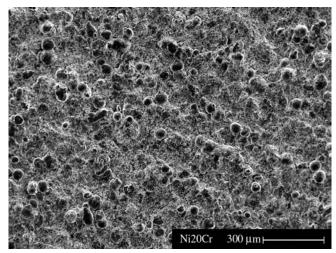


Figure 4. Micrograph of the surface of Ni20Cr coat revealing slight undulations.

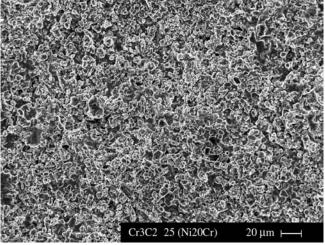


Figure 7. Micrograph of the surface of ${\rm Cr_3C_2}$ 25(Ni20Cr) coat revealing uniform features.

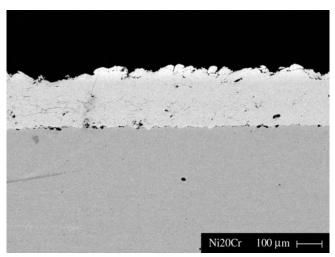


Figure 5. Micrograph of Ni20Cr coat revealing uniform thickness.

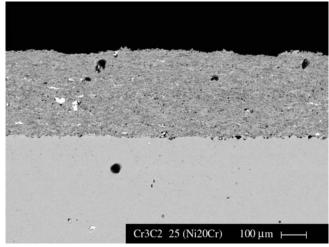


Figure 8. Micrograph across Cr_3C_2 25(Ni20Cr) coat revealing uniform thickness.

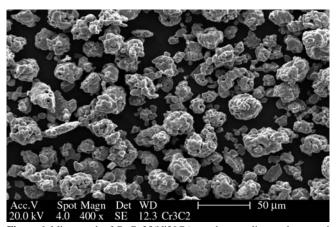


Figure 6. Micrograph of Cr_3C_2 25(Ni20Cr) powder revealing agglomerated particles.

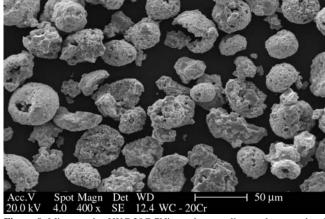


Figure 9. Micrograph of WC 20Cr7Ni powder revealing agglomerated and spherical particles.

3. Results and Discussion

The erosion-oxidation behavior of the three HVOF coatings is shown as wastage, in mg.mm⁻², as a function of temperature in Figure 12. The three coatings did not exhibit any change in erosion-

oxidation behavior at temperatures up to 500-600 °C, compared to at 100 °C. However at higher temperatures, wastage increased with temperature, reaching a maximum at 700 °C and then decreased with further increase in temperature up to 800 °C. Above 800 °C, wastage increased again. This erosion-oxidation behavior is considered to

be due to the formation of a NiCr₂O₄²¹ type spinel layer. This layer increases the ductility of the matrix (NiCr) and consequently, increases the erosion-oxidation resistance. At particle impact velocity of 3.5 m.s⁻¹, no significant differences in wastage between the Ni20Cr

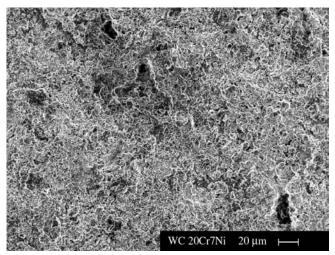


Figure 10. Micrograph of the surface of WC 20Cr7Ni coat revealing roughened features.

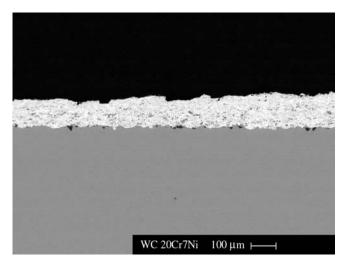


Figure 11. Micrograph across WC 20Cr7Ni coat revealing uniform thickness.

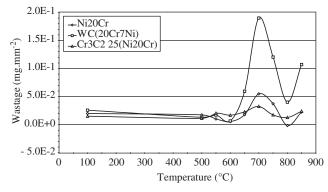


Figure 12. Erosion-oxidation wastage of Ni20Cr, Cr_3C_2 25(Ni20Cr) and WC 20Cr7Ni coatings obtained by the HVOF process.

alloy coating and that of the cermet, $\operatorname{Cr}_3\operatorname{C}_2 25(\operatorname{Ni20Cr})$, were observed. This indicates that the mechanism of erosion-oxidation of these two coatings is quite similar. The formation of the protective spinel type surface oxide prevents erosion of the coating. This erosion-oxidation mechanism corresponds to a combination of regimes defined by Kang et al.¹³, those of erosion enhanced oxidation and erosion of the oxide. The formation and the high adhesion of the spinel type oxide were observed in the complementary oxidation tests carried out as part of this investigation. (Not reported in this paper²⁰).

X-ray diffraction analysis carried out by Toma et al. on HVOF coatings of $75\text{Cr}_3\text{C}_2$ 25NiCr revealed the presence of NiCr $_2\text{O}_4$, formed during the HVOF process 21 . They also reported grain size reduction and formation of a nanocrystalline structure. All these factors seem to improve the erosion-oxidation behavior of this coating.

The marked increase in wastage of the WC containing coating at temperatures beyond 650 °C is due in part to the formation of NiO and NiWO $_4$. However, the oxidation reaction leading to the formation of W_3O from WC, which should have started at this temperature, seems to have been affected by the erosion process. Further proof of this observation, is the total absence of scaling (spalling) of the coating. In the oxidation tests, formation of flaky, non-protective W_3O layers was observed.

Above 800 °C, the wastage of all three types of coatings increased again and this is due to oxide erosion. Thus, the oxide erosion regime operates at these temperatures. The higher oxide growth rate, because of the higher temperature, makes it brittle and non-protective, even on the NiCr alloy and the Cr_3C_2 containing coating, where chromium or spinel oxide could form.

Scanning electron microscopic examination of the surfaces and cross sections of the coatings following the erosion-oxidation tests are in progress to corroborate the regimes of erosion-oxidation of the coatings as a function of the test conditions. The morphology of the WC 20Cr7Ni coated specimens that were erosion-oxidation tested at 100, 700 and 800 °C are shown in Figures 13-15, respectively. Presence of surface oxides is considered to inhibit coating wastage at temperatures up to 700 °C.

4. Conclusions

 An apparatus to conduct high temperature erosion-oxidation studies was constructed, and this enabled the erosion-oxidation behavior of three different coatings to be characterized.

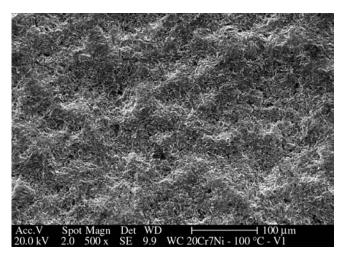


Figure 13. Micrograph of WC 20Cr7Ni coating surface after erosion-oxidation test at 100 °C.

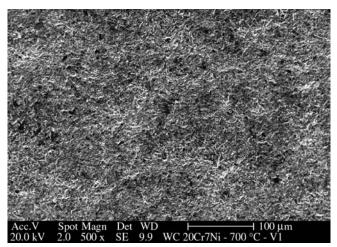


Figure 14. Micrograph of WC 20Cr7Ni coating surface after erosion-oxidation test at 700 °C.

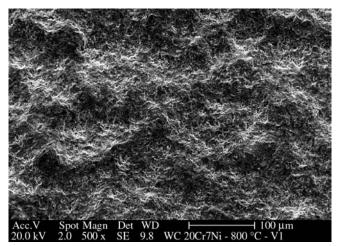


Figure 15. Micrograph of WC 20Cr7Ni coating surface after erosion-oxidation test at 800 °C.

- 2. The erosion-oxidation behavior of HVOF coated Cr₃C₂ 25 (Ni20Cr) was better than that of WC 20Cr7Ni.
- The erosion-oxidation resistance of WC 20Cr7Ni coating was higher than its oxidation resistance without erosion. This indicated that the erosion process affects the erosion-oxidation mechanism.
- 4. Erosion-oxidation regimes have been identified for HVOF coatings at particle impact velocity of 3.5 m.s⁻¹, impact angle of 90° and temperatures in the range 500 to 850 °C. The erosion-oxidation regime at temperatures up to 600 °C is 'erosion of substrate (coating)'. The regime 'oxidation affected erosion' has been observed in the temperature range of 600-700 °C. The behavior of the coatings at temperatures up to 700 °C corresponds to the 'erosion-enhanced oxidation' regime.

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