Erosion-Oxidation Behavior of Thermal Sprayed Ni20Cr Alloy and WC and Cr$_3$C$_2$

Cermet Coatings

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Abstract

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 as well as physical properties of the target material. An apparatus to conduct high temperature erosion-oxidation studies up to 850°C and with particle impact velocities of up to 15 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$_3$C$_2$-Ni20Cr on a steel substrate has been studied. Details of this apparatus and the erosion-oxidation behavior of these coatings are presented and discussed.

Keywords: Erosion, oxidation, high temperature, composite coatings, HVOF
Introduction

The erosion behavior of metallic materials and ceramics at room temperature has been extensively studied\textsuperscript{1-4}. 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 temperatures\textsuperscript{5}. 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 separately\textsuperscript{6-10}. It has also been mentioned that in some cases the formation of a corrosion product can inhibit erosion\textsuperscript{11}; i.e. the wastage rate under erosion-oxidation conditions can be less than in the absence of oxidation. These contrary observations have generated, in recent years, much attention about erosion-oxidation processes.

Erosion-oxidation interactions were first described in terms of regimes by Hogmark et al. in 1983\textsuperscript{12}. Kang et.al.\textsuperscript{13} in 1985 argued that four regimes existed, based on erosion-oxidation studies of pure metals. These regimes were termed:

1. Erosion of metal
2. Oxidation affected erosion
3. Erosion-enhanced oxidation
4. Oxide erosion.

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

Procedures to combat 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, such coatings do not usually possess adequate corrosion resistance. The use of ceramic coatings may be a means to obtain both, erosion and oxidation resistance. Recently, the ‘high velocity oxy fuel’ (HVOF) process has sparked a considerable amount of commercial interest as it can produce smooth, low porosity, dense and adherent coatings. This coating process can be used to apply metal matrix composite coatings, Ni, Cr, Co or other alloy matrices reinforced with carbides like WC or Cr$_3$C$_2$, which impart increased wear resistance, especially at high temperatures to the substrates. 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 the cooling stages. Transformations such as, interactions between the carbide reinforcement and the matrix$^{16-18}$; decarburizing of WC followed by formation of undesirable W$_2$C (due to the high flame temperature and oxidizing atmosphere) and transformation of Cr$_3$C$_2$, as shown, due to the reactive atmosphere within the flame$^{19}$.

\[
\text{Cr}_3\text{C}_2 \rightarrow \text{Cr}_7\text{C}_3 \rightarrow \text{Cr}_{24}\text{C}_6
\]

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 alloy Ni20Cr, and two cermets, WC-20Cr7Ni and Cr3C2-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 at impact velocity of 3.5 m.s$^{-1}$. 
Materials and Methods

The erosion-oxidation apparatus

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

Insert 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 the particle impact velocity is controlled by a motor that rotates the specimen assembly. 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 alloy selection 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 (344-740 MPa), compression strength (2758 MPa). After granulometric separation, the alumina particle size range was defined, being 212-150 µm (Fig.2).

Insert figure 2

Coatings obtained by the HVOF process

The HVOF equipment at the firm Cascadura S/A, in Sorocaba, was used. Three different Tafa powders with compositions corresponding to Ni20Cr, Cr\(_3\)C\(_2\) 25(Ni20Cr), WC 20Cr7Ni, were
deposited on to AISI 310L sheet surfaces. A scanning electron microscope was used to examine the powders and the coatings and their micrographs are shown in Figs 3-11. Coated AISI 310 sheets (20x50 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 (500-850ºC), alumina particle impact velocity 3m.s\(^{-1}\)) and impact angle (90º). Tests were also carried out at 100ºC 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.

Results and Discussion

The erosion-oxidation behavior of the three HVOF coatings is shown as wastage as a function of temperature in fig. 12. The wastage, in mg.mm\(^{-2}\), was determined at particle impact velocity of 3.5 m.s\(^{-1}\). The three coatings did not exhibit any change in erosion-oxidation behavior at temperatures up to 500-600ºC, compared to at 100ºC. However at higher temperatures, wastage increases with temperature, reaching a maximum at 700ºC and then decreasing with further increase in temperature up to 800ºC. Above 800ºC, wastage increases again. This erosion-oxidation behavior is considered to be due to the formation of a NiCr\(_2\)O\(_4\) 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 alloy coating and that of the cermet, Cr\(_2\)C\(_2\) 25(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.\textsuperscript{13}, those of erosion enhanced oxidation and erosion of the oxide, which in our case of the two coatings, is adherent to the substrate. The formation of, and the high adhesion of the spinel type oxide was observed in the complementary oxidation tests carried out as part of this investigation. (Not reported in this paper)

X-ray diffraction analysis carried out by Toma et al. on HVOF coatings of 75Cr3C2-25NiCr revealed the presence of NiCr$_2$O$_4$, formed during the HVOF process\textsuperscript{20}. 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.

Insert figure 12.

The marked increase in wastage of the WC containing coating at temperatures beyond 650ºC is due in part to the formation of NiO and NiWO$_4$. However, the oxidation reaction leading to the formation of W$_3$O 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$_3$O layers was observed.

Above 800ºC, the wastage of all three types of coatings increases 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 alloy NiCr and the Cr$_3$C$_2$ containing coating, where chromium or spinel oxide could form.

Scanning electron microscopic examination of the surfaces and cross sections of the various 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.
Conclusions

1. It was possible to construct an apparatus to conduct high temperature erosion-oxidation studies up to 850°C and varying the process parameters.

2. The erosion-oxidation experimental results for HVOF coatings show in a comparative analysis that Cr$_2$C$_2$ 25(Ni20Cr) coating have better behavior with the process parameters used.

3. The HVOF WC 20Cr7Ni coating have better erosion-oxidation behavior than oxidation without erosion and this fact indicates the erosion-oxidation mechanism is affected by the erosion process.

4. It was possible identify the erosion-oxidation regimes of HVOF coatings at impact velocity of 3.5 m.s$^{-1}$, impact angle of 90° and temperatures from 500 to 850°C.

References


**Figure Captions**

Figure 1. Schematic diagram of the experimental apparatus that was designed and constructed in IPEN to conduct erosion-oxidation measurements: 1- compressor; 2- pre-heating 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.

Figure 3. Micrograph of Ni20Cr powder.

Figure 4. Micrograph of Ni20Cr coating surface.

Figure 5. Micrograph across Ni20Cr coating.

Figure 6. Micrograph of Cr$_3$C$_2$ 25(Ni20Cr) powder.

Figure 7. Micrograph of Cr$_3$C$_2$ 25(Ni20Cr) coating surface.

Figure 8. Micrograph across Cr$_3$C$_2$ 25(Ni20Cr) coating.

Figure 9. Micrograph of WC 20Cr7Ni powder.

Figure 10. Micrograph of WC 20Cr7Ni coating surface.

Figure 11. Micrograph across WC 20Cr7Ni coating.

Figure 12. Erosion-oxidation wastage of Ni20Cr, Cr$_3$C$_2$ 25(Ni20Cr) and WC 20Cr7Ni coatings obtained by the HVOF process.
Figures

Figure 1.

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Figure 2.

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Figure 3.
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Figures 4 and 5.
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Figure 6.
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Figures 7 and 8.

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Figure 9.

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Figures 10 and 11.

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Figure 12.

C. T. Kunioshi, O. V. Correa, L. V. Ramanathan