

MECHANICAL PROPERTIES AND EROSION-OXIDATION RESISTANCE OF THERMALLY SPRAYED NANOSTRUCTURED Cr₃C₂-25(Ni-20Cr) COATINGS

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Abstract

As-received (AR) and nanostructured (NS) (crystallite size 50-70 nm) Cr₃C₂-25(Ni20Cr) powders were used to deposit ~200 µm thick coatings by HVOF thermal spraying on AISI 310 samples. The Vickers microhardness, the elastic modulus and the fracture toughness of the coatings were determined. The erosion-oxidation (E-O) resistance of the coatings was determined as wastage at room temperature, 450, 700 and 800 °C. The hardness and Young modulus of the coatings prepared with NS powders were approximately 26% higher than that of the coatings prepared with AR powders. The fracture toughness of the NS coating was 36% higher. The E-O resistance of the NS coating was around 52% higher than that of the coating prepared with AR powders at 800 °C. The E-O wastage of both types of coatings increased consistently with temperature beyond 450 °C.

Keywords: Nanostructured coating, chromium carbide, mechanical properties, erosion-oxidation.

1.0 Introduction

Increase in demand for materials with enhanced physical properties has been steady in a number of engineering fields. Coatings have met many of these demands. Chromium carbide based coatings are widely used to protect components exposed to severe conditions in many industries.¹⁻⁴ Since degradation of chromium carbide coatings has been a concern the mechanical properties and erosion behavior of Cr₃C₂-25(Ni20Cr) coatings has been the subject of other studies.^{5,6} Aware that the degradation caused by the conjoint action of erosion and oxidation is significantly higher than that caused by erosion and oxidation acting separately, the mechanical properties and erosion-oxidation resistance of Cr₃C₂-25(Ni20Cr) coatings were determined. Nanocrystalline powders of Cr₃C₂-25(Ni20Cr) were prepared by high energy milling of as-received (AR) powders. The milled and AR powders were used to prepare coatings on AISI 310 stainless steel sheets by the HVOF thermal spray process under conditions described elsewhere.¹ The Vickers microhardness, the elastic modulus and the fracture toughness of the coatings were determined. The high temperature erosion-oxidation (E-O) resistance of both coatings was evaluated as wastage of the coating and this was done in a rig where coated samples were rotated through a fluidized bed of erodent (alumina) particles inside a furnace.

2.0 Materials and methods

The Cr₃C₂-25(Ni20Cr) powder was high energy milled for 8 hours to obtain nanocrystalline powder with average particle and crystallite sizes of 20µm and 60 nm respectively. The powders in the as-received (AR) and milled condition were used to produce coatings on AISI 310 stainless steel sheet samples using a Diamond Jet HVOF thermal spray equipment. The microstructure of the coatings was examined in a scanning electron microscope coupled to an energy dispersive spectrometer system. Vickers microhardness of the coatings was determined in a test device using loads of 300g or 500g and in an instrumented microhardness test device with 500 mN load. The fracture toughness of the coatings was determined from the lengths of the cracks emanating from the hardness indents.^{8,9} The erosion-oxidation (E-O) tests were performed in a rig where coated samples were rotated through a fluidized bed of alumina particles (210 µm) inside of a furnace. The E-O tests were carried out at for 5

hours at room temperature, 450, 700 and 800 °C. Most of the E-O tests were carried out with erodent impact velocity of 19 m/s and some tests at 800 °C were also carried out with erodent impact velocity of 10 m/s. The samples were weighed before and after the tests to determine E-O as wastage. The surface roughness of the samples was also measured.

3.0 Results

The HVOF sprayed coatings with the two types of powders were 100-250 µm thick. Figure 1 shows the cross sectional micrograph of a nanostructured coating that was used to determine the Vickers hardness, as well as the Young modulus. Data from these measurements, the lengths of the cracks emanating from the hardness indents and equation (1) were used to determine the fracture toughness of the coatings.⁹

$$FT = K_{IC} = 0,0123 E^{2/5} H^{1/10} (P/l)^{1/2} \quad (1)$$

Where, FT is fracture toughness, K_{IC} - stress intensity factor, E - Young modulus, H - hardness, P – load, l - crack length.

The microhardness, Young modulus and fracture toughness of the coatings are given in Table 1. The surface roughness of all the samples was determined before and after the E-O test and the average values are shown in Table 2. The weight loss of the different samples that were E-O tested at the different temperatures and with two different erodent impact velocities was determined and averaged. These results are summarized in Figure 2. This data, or wastage, of the coating clearly indicates the higher E-O resistance of the nanostructured coatings, compared to coatings prepared with AR powders at the same test temperature and exposed to the same erodent impact velocity. The surface of nanostructured coatings after E-O tests at 450 °C and 800 °C is shown in figure 3. The surface of the specimen tested at 450 °C shows evidence of erosion. Figure 4 (a) it shows the cross section of a sample E-O tested at 800 °C. This gives indication of ‘micromachining’ as a probable mechanism of wastage, more so at regions where the oxide scale was removed and the coating was exposed again to the erodent. Figure 4 (b) shows another region of the same sample where the Cr₂O₃ oxide scale was not

removed. This oxide scale, approximately 20 μm in thickness has the aspect of being compact and adherent.

4.0 Discussion

It has been frequently mentioned in literature that the reduced wear rate of nanostructured materials compared to conventional materials is due to the higher hardness and fracture toughness of the nanostructured materials. These statements were corroborated by the results in this investigation which show that coatings produced with nanostructured $\text{Cr}_3\text{C}_2\text{-25(Ni20Cr)}$ powders had higher hardness and fracture toughness compared to coatings produced with 'as received' powders. The E-O test results indicate that the E-O resistance of the nanostructured coatings tested at 450 $^{\circ}\text{C}$ was higher than that tested at 800 $^{\circ}\text{C}$ and this could be attributed to the higher hardness of the nanostructured coating at 450 $^{\circ}\text{C}$, given that material retains its original hardness until around 600 $^{\circ}\text{C}$ ¹ and even though the hardness of the coating after the test at 800 $^{\circ}\text{C}$ was still as high as approximately 600 HV. It appears that at 450 $^{\circ}\text{C}$ there is competition between the erosion process and oxide scale formation, with the latter being more dominant. After prolonged exposure to high temperature, the oxide scale spalls off at discrete regions and at these exposed regions 'micromachining' of the coating appears to be the prevailing erosion mechanism. It should be noted that heterogeneities present in the microstructure (porosities, internal oxides, etc) increase wastage of the coatings. Additionally, decohesion of splats appears to influence the erosion rate of the coatings at all the test conditions. At room temperature this is presumably the dominant mechanism that controls the erosion of the coating. The weight gain observed in the E-O test carried out with lower erodent impact velocity (10 m/s) at 800 $^{\circ}\text{C}$ can be attributed to higher rate of oxide scale formation as opposed to its removal by the erodent.

5.0 Conclusions

1. The hardness and Young modulus of the coatings prepared with NS powders were approximately 26% higher than that of the coatings prepared with AR powders. The fracture toughness of the NS coating was 36% higher.

2. The E-O resistance of the NS coating was around 52% higher than that of the coating prepared with AR powders at 800 °C. The E-O wastage of both types of coatings increased consistently with temperature beyond 450 °C.

6.0 References

1. J. HE and J.M. SCHOENUNG, 'Nanostructured coatings', *Materials Science and Engineering*, A336, 2002, **A336**, 274.
2. J. HE, M. ICE, E.J. LAVERNIA, 'Synthesis of nanostructured Cr₃C₂-25(Ni20Cr) coatings', *Metallurgical. and Materials Transactions*, 2000, **31A**, 555.
3. A.PADIAL, C.A.CUNHA, A.H.A BRESSIANI, L.V.RAMANATHAN, 'Structure and properties of thermal sprayed nanostructured chromium carbide based coatings' *Proceedings of 18 Brazilian Materials Science and Engineering Conference, Porto de Galinhas, 2008.*
4. B.Q. WANG, K. LUER, in: C.C. BERNDT, S. SAMPATH (Eds.), *Thermal Spray Industrial Applications*, ASM International, Materials Park, OH-USA, Boston, Massachusetts, 1994, 115.
5. M. ROY, A. PAUSCHITZ, J. WERNISCH, F. FRANEK, 'The influence of temperature on the wear of Cr₃C₂-25(Ni20Cr) coating—comparison between nanocrystalline grains and conventional grains', *Wear*, 2004, **257**, 7-8, 799.
6. S. MATHEWS, B. JAMES, M. HYLAND, 'Erosion of oxide scales formed on Cr₃C₂-NiCr thermal sprayed coatings', *Corrosion Science*, 2008, **50**, 3087..
7. C. A. CUNHA, N.B. DE LIMA, J. R. MARTINELLI, A. H. A. BRESSIANI, A. G. F. PADIAL, L. V. RAMANATHAN, 'Microstructure and mechanical properties of thermal sprayed nanostructured Cr₃C₂-Ni20Cr coatings', *Materials Research*, 2008, **11**, (2), 137.
8. M. ROY, A.PAUSCHITZ, J. BERNARDI, T. KOCH, F.FRANEK, 'Microstructure and mechanical properties of HVOF sprayed nanocrystalline Cr₃C₂-25(Ni20Cr) coating, *Journal of Thermal Spray Technology*, 2006, **15**(3), 372.
9. K. NIHARA, R. MORENA, D.P.H. HASSELMAN, 'Evaluation of K_{IC} of brittle solids by the indentation method with low crack-to-indent ratios', *Journal of Materials Science Letters*, 1982, **1**, 13.

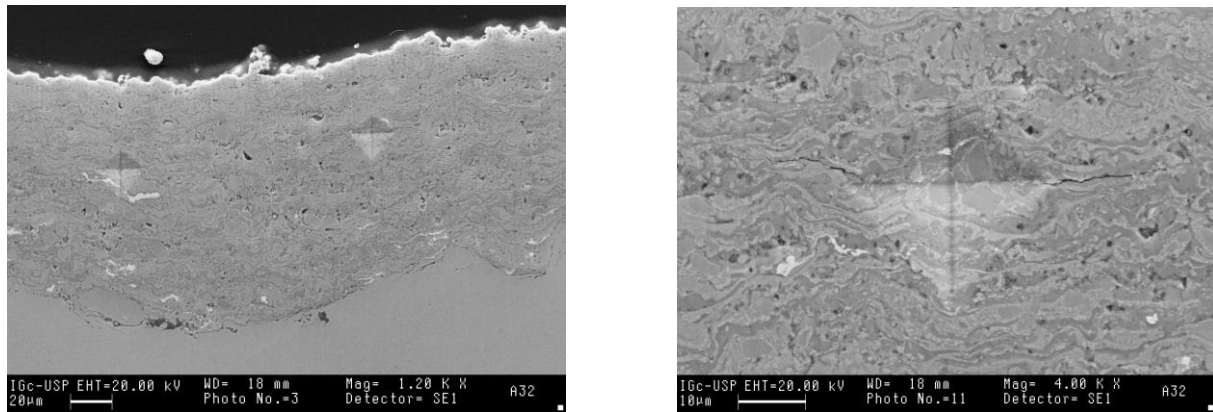


Figure. 1: (a) Secondary electrons image of the nanostructured coating layer showing a region with two Vickers microhardness indents ; (b) another region of the same sample showing cracks emanating from the indent formed with a higher load. Note the typical lamellae microstructure of a HVOF thermal spray coating.

Table. 1. Hardness, Young modulus and fracture toughness of the coatings prepared with Cr_3C_2 -25(Ni20Cr) powders.

Coating condition	HV (GPa)	E (GPa)	K_{IC} ($\text{MPa m}^{1/2}$)
AR	7.97 +/- 0.83	172.29 +/- 12.85	1.77
NS (AS)	10.37 +/- 1.21	223.40 +/- 12.23	2.23
NS (oxidized)	10.79 +/- 0.74	232.35 +/- 10.07	2.41

AS – as sprayed.

Table 2 . Average surface roughness (Ra) of the coatings produced with the Cr₃C₂-25(Ni20Cr) powders, before and after the E-O tests.

Coating condition	Before (μm)	After (μm)
AR	6.02 +/- 0.44	5.05 +/- 0.18
NS (AS)	3.00 +/- 0.50	2.09 +/- 0.58

AS – as-sprayed

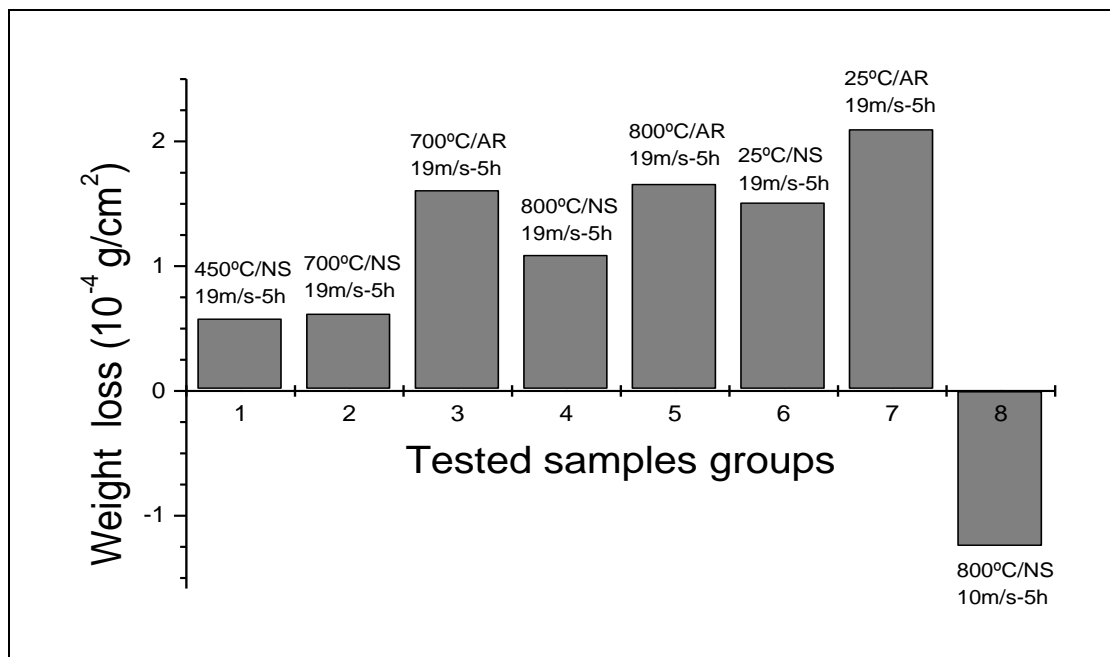


Figure 2. Erosion-oxidation test results of samples coated with AR and NS $\text{Cr}_3\text{C}_2\text{-25(Ni20Cr)}$ powders. Tests were carried out for 5 hours at 25, 450, 700 and 800 C and erodent velocities of 10 and m/s. Note the improved performance of the coatings produced with nanostructured powders.

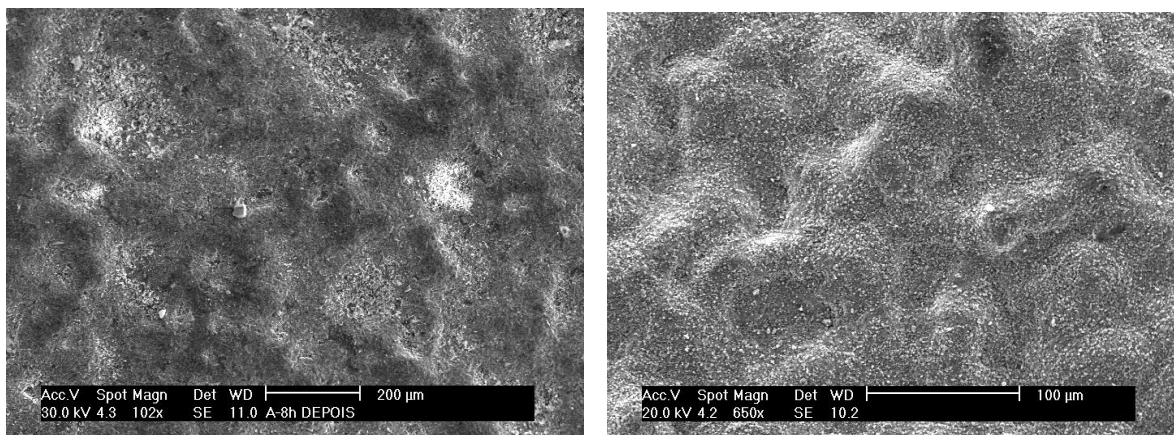


Figure 3: Secondary electrons image of the surface of a nanostructured coatings that was E-O tested for 5 h at 19 m/s and (a) 450°C and (b) 800°C. Note the clear evidence of erosion on the surface of sample tested at 450°C.

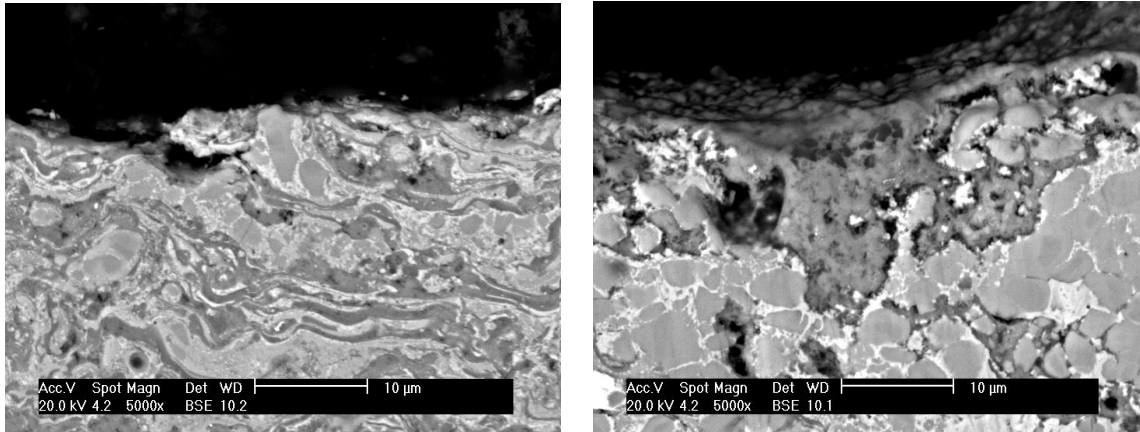


Figure 4: (a) Backscattered electrons image showing surface of sample E-O tested at 800°C, 19 m/s and 5 h. indicating ‘micromaching’ as probable erosion mechanism. (a) Region where the oxide scale was removed and (b) another region of the same sample showing Cr₂O₃ oxide scale.