

STRUCTURE AND PROPERTIES OF THERMAL SPRAYED NANOSTRUCTURED Cr₃C₂-25(Ni20Cr) COATINGS

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ABSTRACT

Chromium carbide based coatings have been used for corrosion and wear resistant applications. One of the shortcomings of these coatings is its lower hardness and wear resistance compared to tungsten carbide based coatings for long term high temperature applications. Coatings prepared with nanocrystalline materials have in general exhibited higher hardness and strength. This paper presents the microstructure of coatings prepared by thermal spraying (HVOF) using as-received and nanocrystalline Cr₃C₂-25(Ni20Cr) powders. Hardness measurements across sections of the two types of coatings revealed a marked increase in hardness and fracture toughness of the nanostructured coating. The erosion-oxidation behavior of the two types of coatings was evaluated in a test rig and a marked improvement in the wastage behavior of the nanostructured coating was observed.

Keywords: Chromium carbide, nanostructured coating, mechanical milling, thermal spraying.

INTRODUCTION

Coatings of chromium carbide particles distributed in a nickel-chromium alloy matrix, (also referred to as $\text{Cr}_3\text{C}_2\text{-NiCr}$ system) have been used for corrosion and wear resistant applications. These coatings can be used in corrosive environments at temperatures up to 900°C , much higher than that at which the harder WC-Co coating systems can be used. However, one of the shortcomings of $\text{Cr}_3\text{C}_2\text{-NiCr}$ system coatings is its low hardness, and consequent lower wear resistance, compared to WC-Co system coatings. In the last decade, thermal sprayed coatings produced using nanostructured feed stock have exhibited higher hardness, strength and corrosion resistance. [1-3] Hence, it is anticipated that nanostructured $\text{Cr}_3\text{C}_2\text{-NiCr}$ coatings will have higher hardness, strength and corrosion resistance and therefore possess improved performance characteristics. Preparation of nanostructured feed stock powders is the first step for synthesis of nanostructured coatings. Among the various techniques available to produce nanostructured materials, mechanical milling is an effective process to synthesize nanostructured powders because the powder grains are continuously refined by cold welding and fracturing. [4-7] This process also enables large quantities of nanostructured materials to be produced. Nanostructured composites consisting of hard particles and a metal binder, such as $\text{Cr}_3\text{C}_2\text{-NiCr}$ and WC-Co systems have been successfully synthesized using mechanical milling.[8,9]

This paper presents the microstructure and mechanical properties of nanostructured $\text{Cr}_3\text{C}_2\text{-25%Ni20Cr}$ coatings formed by high velocity oxygen fuel thermal spraying. (HVOF).

MATERIALS AND METHODS

The $\text{Cr}_3\text{C}_2\text{-25% Ni20Cr}$ powder in the as-received condition and that milled for 4 hours in nitrogen were used as feed stock for thermal spraying using the high velocity oxygen fuel (HVOF) process to coat specimens $50 \times 20 \times 2$ mm of AISI 310. The powders milled for 4 hours had average particle size of $11\ \mu\text{m}$, which was close to the lower limit of acceptable particle sizes for the HVOF spray gun. Coatings of varying thicknesses in the range $50 - 200\ \mu\text{m}$ were prepared. The spraying conditions and gun to specimen distance were identical in all cases. The microstructure and phase composition of the coating surfaces and cross-sections were determined with a SEM/EDS. The micro-hardness of the coatings on cross-sections was determined using loads of 500 g and 1000 g. The erosion-oxidation (E-O) behavior of the coatings was evaluated in a test rig in which a specimen assembly was rotated through a fluidized bed of erodent particles. Alumina powder in the size range $212\text{-}150\ \mu\text{m}$ was used as the erodent. The fluidized bed of particles was obtained by pumping pre-heated air through a porous plate supporting a bed of erodent particles. Fluidization of the erodent particles was done within a furnace and the particle impact velocity (PIV) on the test specimens was controlled by a motor that rotated the specimen assembly. The E-O behavior was tested at 500°C for 5h with erodent impact velocity of 20 m/s. Wastage of the specimens was determined as weight loss after the test.

RESULTS AND DISCUSSION

The average particle and crystallite sizes of $\text{Cr}_3\text{C}_2\text{-25%Ni20Cr}$ powders milled for 8 hours in gaseous nitrogen were $10\ \mu\text{m}$ and $75\ \text{nm}$ respectively. [10] Scanning electron

microscopic (SEM) examination of the milled powders revealed Cr_3C_2 particles embedded in the Ni-Cr alloy phase. The energy dispersive spectrum of different regions of milled powder particles indicated formation of alloy-ceramic composites. [10]

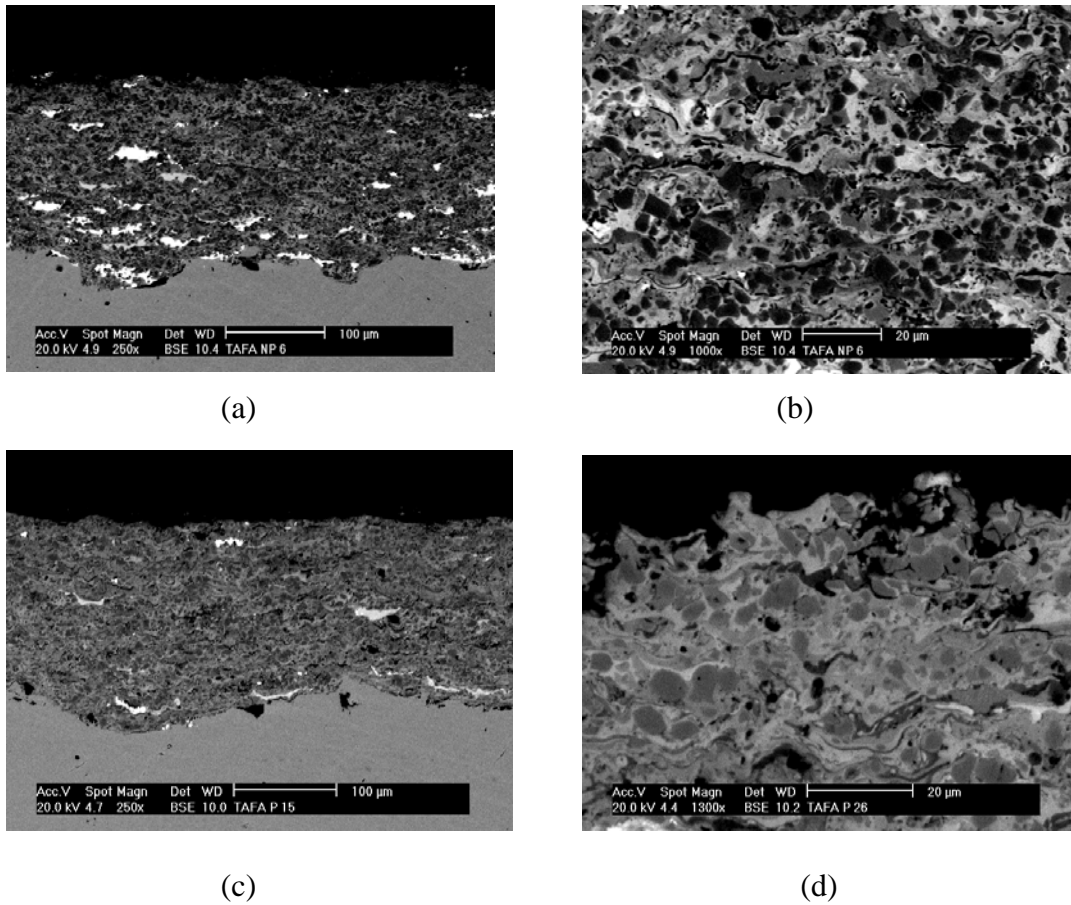


Figure 1. Cross-sections of HVOF coatings: (a) and (b) with as-received Cr_3C_2 -25%Ni20Cr; (c) and (d) nanostructured Cr_3C_2 -25%Ni20Cr.

The microstructure of cross-sections of coatings prepared with as-received and milled Cr_3C_2 -25%Ni20Cr powders is shown in figure 1. The latter, nanostructured coating is uniform and dense compared to the coating with as-received powder. The coating with the as-received powder revealed an inhomogeneous microstructure. The very bright regions in the micrographs are contaminants. The light, light grey and dark grey regions were analyzed using EDS in the SEM. This analysis revealed as shown in figure 2 large Ni peaks and very small Cr peaks on the light regions indicating it to be the Ni-Cr alloy phase. The dark grey regions rendered large Cr peaks indicating it to be the Cr_3C_2 phase. The light grey regions contained the two phases indicating a composite phase. Quantitative evaluation of the peaks from coatings obtained with the as-received and the nanostructured coating indicated that more composites formed in the latter. Similar observations have been reported. [11]

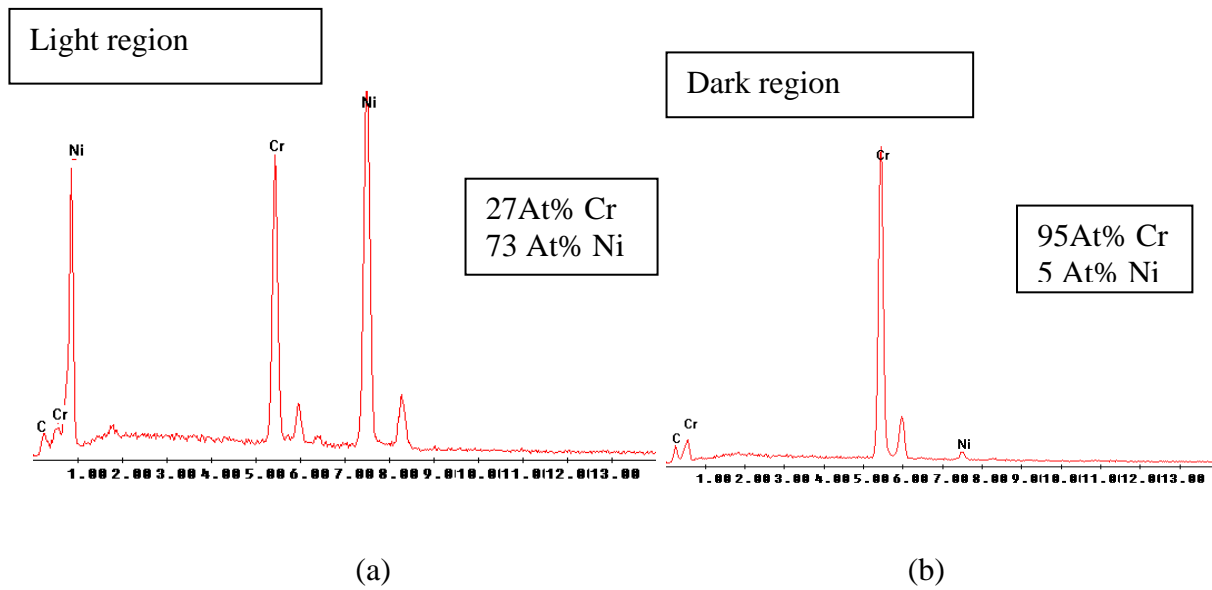


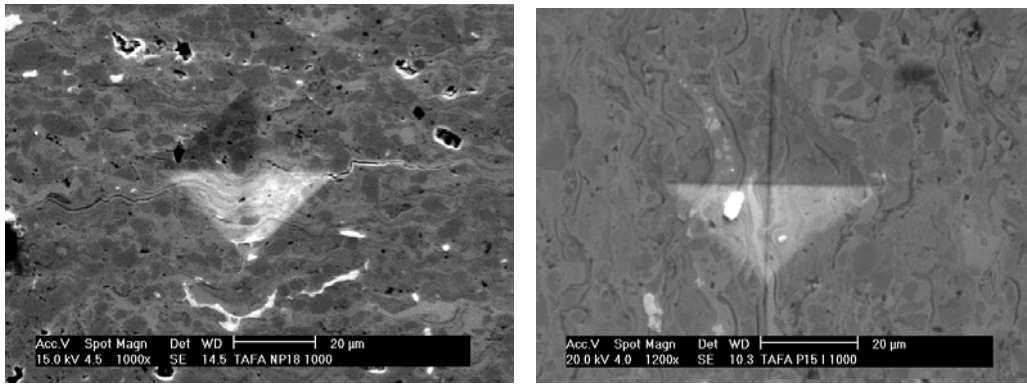
Figure 2. EDS of light and dark regions in figure 1d indicating these to be the Ni-Cr alloy and Cr_3C_2 respectively.

Diamond pyramid microhardness tests carried out on sections of the coatings revealed that the hardness of the nanostructured coatings were higher compared with those obtained with as-received powders as shown in Table I. Cracks emanating from the edges of the indents were observed in the two types of coatings. However, the cracks seen in the coatings obtained with the as-received powders were longer and wider. The cracks in all cases were mainly parallel to the substrate as shown in figure 3. This indicated the higher relative fracture toughness of the nanostructured coating. Some of the cracks were along the phase interface in the coating. There were fewer such cracks in the nanostructured coating as a result of composite formation, increased hardness and relative fracture toughness.

Table I. Microhardness of as-received and nanostructured Cr_3C_2 -25%Ni20Cr coatings.

	Hardness of HVOF coating with					
	As-received Cr_3C_2 -25%Ni20Cr			Nanostructured Cr_3C_2 -25%Ni20Cr		
Coating thickness (μm)	56	190	234	73	175	214
500 g load	697.5	810.0	958.0	977.0	1025.5	1124.5
1 Kg load	425.5	795.0	668.5	828.0	696.0	1062.5

The E-O wastage or weight loss of the coatings prepared with as-received and milled powders at 500°C for 5 h were $9.2 \times 10^{-3} \text{ g/cm}^2$ and $6.0 \times 10^{-3} \text{ g/cm}^2$ respectively. This indicated clearly the higher resistance of the nanostructured coating. The surfaces of both types of coatings following the E-O tests revealed marked reductions.



(a)

(b)

Figure 3. Typical microhardness indents with 1000g load and cracks emanating from edges of indents on cross-sections of HVOF Cr_3C_2 -25%Ni20Cr coatings. (a) with as-received powder; (b) nanostructured.

GENERAL DISCUSSION

The hardness of coatings is affected by the thermal spray technique as well as parameters of the feed stock. [12-15] The HVOF technique is characterized by high particle velocity and low thermal energy, and this leads to high hardness. [16] It has been reported that nanostructured materials often exhibit a marked increase in hardness compared to corresponding conventional materials, although it is lower than that predicted using the classical Hall-Petch equation. [17-19] In this investigation the hardness of nanostructured Cr_3C_2 -NiCr coatings was significantly higher than that of coatings prepared with as-received powders of the same material. The higher hardness of the nanostructured Cr_3C_2 -NiCr coatings is considered to be due to the uniform microstructure caused by the mechanical milling process to obtain feed stock and the intrinsically high hardness of nanostructured materials.

The indentation fracture method has been used to characterize the relative fracture toughness of coatings. ⁽¹¹⁾ In this investigation at the higher hardness test load of 1000g, indentation cracks were observed in both types of coatings. These cracks usually appeared in the direction parallel to the coating surface and were not present directly on the extended line of the diagonal of the indentation. Many indentation cracks were also observed along the carbide phase - metal binder interface in coatings prepared with the as-received powder. (figure 2) However, only few such cracks were observed in the nanostructured coatings at the same hardness test load. These results indicated that crack propagation within the coating had a preferred direction and there was high resistance to indentation fracture in the direction perpendicular to the coating surface. The preferred direction for crack propagation could be attributed to the thermal spray process. A complete coating is produced by passing the spray torch many times across the substrate and this could result in contamination of a deposited layer prior to deposition of the next layer. Also differences in the thermal expansion coefficient between the carbide and alloy phases could contribute to crack propagation along the phase interface. Discontinuity in heat and mass transfer has also been cited to result in discontinuity in the coating along which cracks propagate. ⁽¹¹⁾ Indents associated with the lower hardness test load of 500 g revealed few cracks in the coating prepared with as-received powders, and none in the nanostructured coating. These observations

suggest that the nanostructured coating possesses a higher apparent fracture toughness relative to that of the coating prepared with as-received powders. Since abrasion resistance of a coating is related to the apparent fracture toughness, it is evident that the nanostructured Cr₃C₂-25 Ni20Cr coatings have higher abrasion resistance. [20] This was corroborated by the E-O results which revealed the higher erosion-oxidation resistance of the nanostructured coating.

CONCLUSIONS

1. The milled Cr₃C₂-25%Ni20Cr powders contained the ceramic, the alloy and the Cr₃C₂- Ni20Cr composite phases.
2. The microstructure of thermal sprayed coatings prepared by the HVOF process using Cr₃C₂-25% Ni20Cr powders milled for 4hours in nitrogen was uniform compared with coatings prepared with as-received powders.
3. The nanostructured Cr₃C₂-25%Ni20Cr coatings were significantly harder and had higher relative fracture toughness compared with coatings prepared with the as-received powder.
4. The erosion-oxidation resistance of the nanostructured Cr₃C₂-25%Ni20Cr coating at 500° C was higher than that of the coating prepared with the as-received Cr₃C₂-25%Ni20Cr powder.

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