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Microstructure, phase composition and mechanical properties of plasma sprayed Al_2O_3, Cr_2O_3 and Cr_2O_3-Al_2O_3 composite coatings

P. Zamani, Z. Valefi *

Materials Engineering Research Center, Maleke Ashtar University of Technology, Tehran, Iran

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ABSTRACT

In the present work, chromia and alumina coatings were produced by atmospheric plasma spray process. Phase composition, microstructure and mechanical properties of chromia and alumina composite coatings on carbon steel substrates were studied and compared to individual Cr_2O_3 and Al_2O_3 coatings. Morphology and microstructure of coatings were characterized using scanning electron microscopy equipped by EDS. The porosity of the plasma-sprayed coatings was measured by the Archimedes water immersion technique and image analysis method. X-ray diffraction was employed to identify phase composition of coatings. Also some mechanical properties such as bonding strength, Vickers microhardness and resistance to crack propagation of coatings were measured. The results showed different phases for Al_2O_3 in different coatings while Cr_2O_3 remained in eskolaite phase in all of the coatings. Addition of 75 wt% Cr_2O_3 prevented formation of metastable and undesirable γ-Al_2O_3 phase. Alumina and rich-alumina coatings showed denser microstructure and higher flattening degree of splats as well as lower surface roughness. Bonding strength of individual Cr_2O_3 and Al_2O_3 coatings was higher than composite one. Vickers microhardness increased with addition of Cr_2O_3. Alumina improved spray ability and crack propagation resistant of chromia.

1. Introduction

Oxide ceramics show high strength, hardness and high resistance to wear, as well as good resistance to high temperatures and oxidation. Plasma spraying is developed as a surface coating technique for depositing ceramics due to their high melting point. Cr_2O_3 and Al_2O_3 coatings deposited by atmospheric plasma spray (APS) are being used for many applications that require protecting components against wear, corrosion and spallation [1–5].

Mechanical properties of plasma sprayed ceramic coatings strongly depend on their microstructure. The microstructural features such as porosity, interfacial defects, the horizontal micro crack density and vertical micro crack density as well as the lamellar or splat dimensions affect the micromechanical integrity [6,7].

It has been reported that sintered alumina contains α phase while the plasma sprayed alumina coatings compose of γ, α phases and sometimes other metastable phases such as δ. The formation of metastable phases is related to the rapid quenching (around 10^6 k/s) during solidification of liquid alumina after spraying. From the fully molten particles, nucleation of metastable γ-Al_2O_3 occurs, due to lower interfacial energy than α phase. The larger particles or semi-molten particles sometimes retain an unmolten cores and α phase tends to grow from this cores. However, Al_2O_3 coating properties are still acceptable for wide variety of applications. It has also been reported that retention of α phase and preventing metastable phase formation improve the mechanical and other properties of this coating [8].The above mentioned phenomenon and the related phase transformation mechanism were firstly studied by Ault and McPherson [10,11]. Both Cr_2O_3 (eskolaite) and α-Al_2O_3 (corundum) possess same crystal structure (rhombohedral lattice) and solid solution formation is possible. So Cr_2O_3 can be an alternative for adding to Al_2O_3 coatings. Marple et al. [12] noted that minimum 27 wt% Cr_2O_3 feedstock powders is required to stabilize α phase. Yang et al. [14] investigated mechanically blended Al_2O_3-C_2O_3 coating systems with a wide range of compositions and showed that the addition of Cr_2O_3 is beneficial to the stabilization of α-Al_2O_3. Some other methods for stabilizing α-Al_2O_3 like heat treatment and changing plasma spray parameters, are summarized in [8,12].

Wear and corrosion resistance of chromium oxide coatings are better than alumina, but they are more expensive. Chromium oxide has excellent hardness and does not react with most acids and alkalis. Contrary to alumina plasma sprayed coatings, chromia doesn't show any phase transformation. However, their application has been limited owing to low toughness and process ability [14,15].

This paper aims to investigate the stabilizing effects of Cr_2O_3 on α-Al_2O_3 and effect of Al_2O_3 on improving Cr_2O_3 properties. Moreover,

* Corresponding author.
E-mail address: ziavalefi@ut.ac.ir (Z. Valefi).

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correlations between microstructure and mechanical properties of Cr_2O_3-25, 50, 75 wt% Al_2O_3 binary system coatings were analyzed and compared to pure Cr_2O_3 and Al_2O_3.

2. Experimental procedure

2.1. Materials and preparation

The A-3000S atmospheric plasma spraying system equipped with a F4-MB plasma gun (Sulzer Metco AG, Switzerland) was applied to deposit coatings onto cylindrical carbon steel specimens (10 mm in height; 25 mm in diameter). Commercially available Metco 101NS (fused and crushed) and Metco 106NS (sintered and crushed) powders were used as feedstock. Size distribution of powders was −45 + 11 and −90 + 11, respectively. Chemical composition of powders is presented in Table 1. Three different weight fractions of Al_2O_3 and Cr_2O_3 powders were used for the preparation of composite coatings. Al_2O_3-Cr_2O_3 composite coatings were defined as 3C1A, CA and 1C3A. More details are presented in Table 2. To inject the powders to the plasma plume a twin powder feeder was used. The feeder no. 1 was allocated to Cr_2O_3 and the feeder no. 2 was allocated to Al_2O_3-TiO_2. In these powder feeders the feed rates and also the powder carrier gas flow rates for two powders can be adjusted and established separately. Two injectors with internal diameter of 1.8 mm for Cr_2O_3 and 1.5 mm for Al_2O_3-TiO_2, perpendicular to the plasma plume were mounted at the torch head one connected to feeder no. 1 and the other connected to feeder no. 2. The injector distance to the centerline of plasma plume was 6 mm for two injectors. At first the powder disk speeds were adjusted for each powder so that the desired feed rate of the two powders according to proportions shown in Table 2 can be achieved. The overall feed rate for composite coatings was regarded as 21 g/min. At the second step the carrier gas feed rate for each powder was adjusted separately so that the stream of powder be at the centerline of the plasma plume. The plasma was established according to the parameters of Table 3. Pure Al_2O_3 and Cr_2O_3 coatings were also prepared for performance comparison. Prior to spraying, the substrates were degreased by acetone and grit blasted with alumina grits. Listed in Table 3 is the plasma spraying parameters. Regarding higher melting temperature, lower thermal conductivity and larger size distribution of Cr_2O_3 starting powders, stronger plasma spray parameters was selected for pure chromia. Due to good effect of alumina on process ability of chromia [15], spray parameters for other coatings were the same. The thickness of coatings was around 300 ± 10 μm.

2.2. Microstructural analysis and phase composition

Microstructure of coatings was analyzed with a scanning electron microscope (SEM) equipped with energy-dispersive spectrometer (EDS) (Tescan, VEGA3 XMU) and optical microscope (union 8799). To produce images from cross-section, mounted coatings ground by SiC paper and then polished by alumina powder suspension. To produce images from top surface of the coatings, as-sprayed coatings without any preparation were used. Porosity of coatings was determined by the image analysis (IA) method [16] and Archimedes water immersion technique [17]. Also stylus profilometer (Mitutoyo, SJ-201) was used to measure the roughness of as-sprayed coatings.

The phase composition of as-sprayed coatings was identified by X-ray diffraction (XRD) using Phillips X-ray diffractometer (PW3710) with nickel-filtered Cu Kα radiation (λ = 0.15406 nm). The XRD measurements were performed in the 2θ range from 10.1° to 89.99° at a scanning speed of 0.04° min^{-1}. The X-ray generator has been operated at 30 kV and 40 mA.

Table 1
Chemical composition of powders.

Product	Al_2O_3	Cr_2O_3	TiO_2	SiO_2(max)	Fe_2O_3 (max)
Metco 101NS	94.00	0	2.5	2.0	1.0
Metco 106NS	0	99.00	0	0.25	1.0

Table 2
Definition of composite coatings.

Sample	Corresponding powder
C	100% Cr_2O_3
3C1A	75% Cr_2O_3-25% (Al_2O_3-3%$TiO_{۲}$)
A	50% Cr_2O_3-50% (Al_2O_3-3%$TiO_{۲}$)
IC3A	25% Cr_2O_3-75% (Al_2O_3-3%$TiO_{۲}$)
A	100% (Al_2O_3-3%$TiO_{۲}$)

2.3. Mechanical properties measurements

The bonding strength of coatings, was determined by pull-off test based on ASTM C633. Grit blasted and as-sprayed specimens adhered by high strength adhesive Scotch Weld 2214 with adhesion strength of at least 60 MPa and cured in furnace for 2 h at 130 °C. Pull-off testing machine was Zwick (Z050, Germany)with stretching rate of 1 mm/min and 5 N preload. Since the bonding strength measurement is very sensitive to operational parameters like coaxiality of the tensile specimen with grip and degree of penetration of adhesive in coating, bonding strength obtained from performing four different pull-off tests on each specimen.

Vickers microhardness measurements were done using an OSK 14218-1 microhardness tester (OGAWA SEIKI CO., LTD). The indentations were applied near the centerline on the cross-section of coatings with 300 g load and a dwell time of 15 s. To reduce the effects of the stress field of nearby indentations, indentation distances were kept at least three times greater than the diameter of indentation. The microhardness value ($HV_{0.3}$) of each coating resulted from average of 10 indentations.

Crack propagation resistant (CPR) as expression of toughness (MPa·√mm) was measured using indentor method. Vickers indentor was applied on polished coatings surface. During applying the load, elastic/plastic contacts may form radial cracks parallel to substrate as shown schematically in Fig. 1. As it is clear from this figure, crack propagation starts at tip of indentor and remains after unloading. Average of cracks length (a) was used to determine CPR. In this work, Vickers indentor was used under load of P = 30 kg and dwell time of 30 s and average of cracks length was measured by optical microscopy images. Resistance of coatings to cracking was calculated using equation of $CPR = P / a^{3/2}$ ($N \cdot mm^{-2/3}$) [18].

3. Discussion

3.1. Microstructure

SEM micrographs in Fig. 2 describe the microstructure of C, 3C1A, CA, 1C3A and A as-sprayed coatings surface that resembles the last solidified layer after plasma spraying. This layer contains splats, deposited with different degree of flattening causing, high surface roughness. As it can be seen in the micrographs, adding alumina to coatings composition increases the amount of splats due to lowering the melting point. Roughness of as-sprayed 3C1A, CA, 1C3A and A coatings (Ra) was 3.02, 2.85, 2.68 and 2.27 μm, respectively, which are in consistent with morphology observations. It should be remembered that C coating was prepared with stronger parameters owing to low process ability (Ra was 2.05 μm). Molten, semi-molten and unmolten particles are visible in all coatings structure. Fractions of these particles strongly depend on plasma parameters that define the heating history of particles passing through different zones in plasma plume. Generally it is accepted that the amount of porosity is inversely related to the degree of flattening [20].