# The microstructure and hardness properties of plasma sprayed Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> coatings

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In this study, the surface of aluminum alloy was coated with and without bond coat with  $Cr_2O_3/Al_2O_3$  powders by using plasma spray technique. The coating layers were examined with optical microscopy, SEM, EDS and XRD analysis. The microhardness of specimens was measured. In XRD studies, such compounds as  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> have been identified on coating layers. The maximum hardness value has been determined in the sample coated with Cr<sub>2</sub>O<sub>3</sub>.

(Received November 26, 2015: accepted November 25, 2016)

Keywords: Plasma Spray Coating, Al alloy, Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>

# 1. Introduction

Thermal barrier coatings (TBCs) is a process used commonly for coating gas turbines' inner parts of gas turbines exposed to high temperature to reduce the damages caused by combustion and make them last longer [1, 2, 3]. A plasma spray coating is one of the thermal barrier coating methods. For the last 30 years, plasma spraying coating has gained high importance for the industrial and technical technologies. Plasma sprayed coatings exhibit highly anisotropic microstructure with a large content of amorphous phase and small content of recrystalled phase. Generally the deposits are composed of crystallographic phases different from the original feedstock materials. They have high thermal conductivity rates which make them unique for applications at higher temperatures. They have been employed to deposit various materials for different performance requirements.

Atmospheric plasma spraying (APS) is one of the methods provides protective coating layer for wide range of application. Various types of wear and corrosion are the severe condition for facilities that surface coatings have to deal with [4-7]. There are several ceramic coatings especially metal oxides such as Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, etc. Such coatings have complex phase composition and microstructure. Therefore, they exhibit distinctive and unusual properties. Those are highly effective coatings to improve wear, cavitation, fretting and corrosion resistance especially where high temperature is required [4, 6, 8]. Bond coatings have specific properties. the bond coatings are used to bind layers that have different thermal coefficent and provide a good thermal expansion match between the layers.

Bond coating layers are thinner with respect to main coatings [9, 10]. For the last few decades, as chromium oxide coatings ( $Cr_2O_3$ ) exhibit excellent wear resistant and friction characteristics, they have increasing potential for the usage of aerospace and automobile applications. Atmospheric plasma spray (APS) widely used to deposit

 $Cr_2O_3$  coatings as it has high deposition efficiency, lowcost and high flexibility values. APS coating has porous structures which might show favorable tribological behavior. Ease of lubrication owing to the oil storage of the pores in the coating could improve the service life of  $Cr_2O_3$  coating. Porous structures might also have unfavorable effects for the structure and properties of the deposits. For a better protection porosity of the coating should be well controlled [11, 12].

In this study, the surface of aluminum alloy was coated with and without bond coat using  $Cr_2O_3$  and  $Al_2O_3$  powder mixed into  $Cr_2O_3$  at different rates (25%, 50, 75) by using plasma spray technique. Optical microscopy, Scanning Electron Microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD) analysis of samples, microhardness test and the effect of added  $Al_2O_3$  have been examined after the coating process.

#### 2. Materials and method

The coatings were carried out on aluminum alloy plate by using plasma spray technique. The chemical composition of aluminum alloy used as substrate material was given in Table 1. The surface procedure was realized with NiCr bond coat and without bond coat using Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> powder mixed into Cr<sub>2</sub>O<sub>3</sub> at different rates (25 %, 50 %, 75 %) powders. Powders have been mixed for 45 minutes at 45 rpm in the mechanical powder mixing apparatus. The SEM images of Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> powders are given in Fig. 1. The plasma spray technique is schematically shown in Fig. 2. The Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> powders were sprayed by plasma spray technique with a 3 MB torch from Sulzer Metco, using plasma composed of argon and hydrogen. In order to produce a rough surface for good bonding, the aluminum alloy plate substrate of 100 mm x 20 mm x 5 mm in dimension were grid-blasted with alumina grits prior to the coating technique. The parameters of the plasma spray condition are summarized in Table 2.





b

Fig. 1. The SEM photo of a) Cr<sub>2</sub>O<sub>3</sub> and b) Al<sub>2</sub>O<sub>3</sub> powders.



Fig. 2. Schematic cross-section of a typical plasma spray [13].

Table 1. The chemical composition of the substrate
material to the aluminum alloy

Weight (%) Composition					
Al	Si	Ni	Cu	Mg	Fe
Balance	12,6	1,96	0,88	0,60	0,5

Table 2. Plasma spray coating parameters of the NiCr bond coat and the Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> coatings

Parameters	NiCr Bond Coat	Cr <sub>2</sub> O <sub>3</sub> and Cr <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>
		Coatings
Plasma Gun	3 MB	3 MB
Current (A)	500	500
Voltage (V)	64	70
Primary Gas-Ar (l/min)	150	80
Secondary Gas-H <sub>2</sub>	5	15
(l/min)		
Spray Distance (mm)	100-150	64-90
Nozule Diameter (mm)	7,6	7,6

The cross-sectional surface for metallographic examination of the coated surface were wet-ground with 400, 600, 800 and 1200 grit SiC paper and polished with diamond paste. The microstructures of the specimens were investigated by optical microscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD) analysis. Microstructure measurements were carried out by Qness-10M microhardness tester.

# 3. Results and discussion

# 3.1. Microstructure and XRD analysis

The optical microstructure images of the  $Cr_2O_3$  and  $Cr_2O_3/Al_2O_3$  coating produced by the plasma spray technique is shown in the Fig. 3 and 4. The thickness of the oxide coating layers without bond coat is approximately 300 µm, and that of the oxide coating layers with bond coat is approximately 250 µm at a thickness of the bond coat 70 µm. A lamellar structure can be seen in the coating layer of specimens. The porosity in generally present in the thermal sprayed coating and ranged between 6 and 9 %. [14, 15] The porosity amount was generally increased with increased of  $Al_2O_3$ .

The SEM image, EDS and XRD analysis taken from  $Cr_2O_3$  coating specimen are shown in Fig. 5. The composition of the region 1 marked with circle consisted of 65wt.% Cr and 35wt.% O. The region 2 marked with circle consisted of 66.19 wt.% Cr and 33.81 wt.% O. Fig. 5d shows the XRD pattern of the coating layer.  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> compounds were formed in the coating layer. The porosity is very low in Cr<sub>2</sub>O<sub>3</sub> coated specimen.



Fig. 3. Optical microstructure of  $Cr_2O_3/Al_2O_3$  coatings without bond coat, a)  $Cr_2O_3$  coated, b) 25 wt. %  $Al_2O_3$  added, c) 50 wt. %  $Al_2O_3$  added, d) 75 wt. %  $Al_2O_3$  added.



Fig. 4. Optical microstructure of  $Cr_2O_3/Al_2O_3$  coatings with bond coat, a)  $Cr_2O_3$  coated, b) 25 wt. %  $Al_2O_3$  added, c) 50 wt. %  $Al_2O_3$  added, d) 75 wt. %  $Al_2O_3$  added.





Fig. 5. SEM photo, EDS and XRD analyses of specimen coated with Cr<sub>2</sub>O<sub>3</sub> powder.

2-Theta(°)



cps/eV 25-El Series norm. C Atom. C [wt.%] [at.%] 20 O K-series Al K-series Cr K-series 34.73 62.30 3.25 3.46 34.24 Total: 100.00 100.00 15-10-5 0 keV 2 4 6 b cps/eV 25 El Series norm. C Atom. [wt.%] [at.% С [at.%] 20 57.78 70.25 29.02 0 K-series Al K-series 40.26 Cr K-series 1.95 0.73 Cr Total: 100.00 100.00 15 10-5-0 2 keV 4 с

Fig. 6. SEM photo, EDS and XRD analyses of specimen coated with Cr<sub>2</sub>O<sub>3</sub>+75 wt. %Al<sub>2</sub>O<sub>3</sub> powder.

The SEM images, EDS and XRD analysis taken from  $Cr_2O_3+75\%$  Al<sub>2</sub>O<sub>3</sub> coating specimen applied NiCr bond coat are shown in Fig. 6. The composition of the region 3 marked with circle consisted of 62.02 wt.% Cr, 34.73 wt.% O and 3.25 wt.% Al. The marked spot 4 consisted of 40.26 wt.% Al, 57.78 wt.% O and 1.95 wt.% Cr. The dark grey lamella regions in the coating are attributed to Al<sub>2</sub>O<sub>3</sub>,

while the grey ones are  $Cr_2O_3$ . Fig. 6d shows the XRD pattern of the coating layer.  $\alpha$ - $Cr_2O_3$ ,  $Cr_2O_3$  and  $Al_2O_3$  compounds were formed in the coating layer. The porosity is increased in specimen coated with  $Al_2O_3$  powder mixed into  $Cr_2O_3$ .

#### 3.2. Microhardness

The microhardness measurement of the coatings layer and bond coats are shown in Fig. 7. It can be seen that the microhardness of the Cr<sub>2</sub>O<sub>3</sub> coating without bond coat is 969 HV and with bond coat is 867 HV. The microhardness of the Cr<sub>2</sub>O<sub>3</sub>+25 wt.% Al<sub>2</sub>O<sub>3</sub> coating without bond coat is 857 HV and with bond coat is 790 HV. The microhardness of the Cr<sub>2</sub>O<sub>3</sub>+50 wt.% Al<sub>2</sub>O<sub>3</sub> coating without bond coat is 775 HV and with bond coat is 702 HV. Also, the microhardness of the Cr2O3+75 wt.% Al2O3 coating without bond coat is 664 HV and with bond coat is 528 HV. The hardness of the bond coat for the Cr<sub>2</sub>O<sub>3</sub>,  $Cr_2O_3+25$  wt.%  $Al_2O_3$ ,  $Cr_2O_3+50$  wt.%  $Al_2O_3$  and Cr<sub>2</sub>O<sub>3</sub>+75 wt.% Al<sub>2</sub>O<sub>3</sub> coatings are 266 HV, 244 HV, 258 HV and 244 HV, respectively. These values are higher than that of the substrate. The maximum hardness was measured in the Cr<sub>2</sub>O<sub>3</sub> coating layer. The figure 3 and 4 showed that the porosity was increased with increasing the Al<sub>2</sub>O<sub>3</sub> content during the microstructural investigation. The minimum hardness was measured in the Cr<sub>2</sub>O<sub>3</sub>+75% Al<sub>2</sub>O<sub>3</sub> coating layers.



Fig. 7. Microhardness of plasma spray coatings

# 4. Conclusions

The surface of Al alloy has been coated with  $Cr_2O_3$ and  $Cr_2O_3/Al_2O_3$  powders by using plasma spray technique. The following results have been obtained after the microhardness tests, optical and SEM microstructure analysis, EDS and XRD analysis of the coated layers.

1- The porosity available in all coatings. The porosity is very low in  $Cr_2O_3$  coated specimen. The porosity amount was increased with increased of  $Al_2O_3$ .

2- The mainly represented phase is  $Cr_2O_3$  in all coatings. Also,  $Cr_2O_3$  and  $Al_2O_3$  phases were formed in specimen coated with  $Al_2O_3$  powder mixed into  $Cr_2O_3$ .

3- The microhardness values were decreased with increasing the  $Al_2O_3$  content in specimen coated with  $Al_2O_3$  powder mixed into  $Cr_2O_3$ . The maximum hardness was measured in the  $Cr_2O_3$  coating layer. Generally, The microhardness were decreased in the specimes coated with bond coat.

# Acknowledgements

This work was supported by Scientific Research Project Unit of Bitlis Eren University under project-No: BEBAP-2014.15. The authors would like to thanks the Bitlis Eren University Science and Technology Research and Application Center for tests of specimens.

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