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Influence of aqueous aging on surface properties of plasma sprayed oxide coatings

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Abstract

The influence of aging in mild aqueous conditions (pH 4, 7 and 9) on surface properties of plasma sprayed oxide was studied using electrophoretic mobility studies and measuring concentrations of dissolved species from exposure liquids. In addition, required acid/base additions to maintain constant pH, redox potentials suspension conductivities were measured. The experiment time was two weeks. The plasma sprayed materials were based on Al_2O_3, TiO_2 and Cr_2O_3. Materials based on Al_2O_3 dissolved easily at pH 4 due to presence of metastable γ-Al_2O_3 phase. In addition there was clear change in surface charging properties (zeta potential) of Al_2O_3 surfaces so that the estimated IEP value drifted from >9 at the beginning of aging and dropped down to 8.5–8.7 after 2 weeks of treatment. Plasma sprayed TiO_2 did not dissolve under the experiment conditions. Even thought the surface charging (zeta potential) changed during the exposure, the estimated IEP remained close to the values reported for pure TiO_2 materials. Plasma sprayed Cr_2O_3 based materials were also insoluble at the studied pH values. On the other hand, the estimated IEP values deviated radically from the reported PZC values of similar materials.

Keywords: Plasma spraying; Zeta-potential; Isoelectric point; IEP; Alumina; Titania; Chromia

1. Introduction

The purpose of this work was to characterize influence of aqueous exposure on surface properties of plasma sprayed oxide coatings at pH range 4–9 at normal room temperatures. The zeta potentials of sample powders were measured during the liquid exposure period. The sample materials in this study were based on Al_2O_3, Cr_2O_3 and TiO_2.

The principle of plasma spraying is simple. Raw material (oxide) powder is fed to the thermal plasma torch using carrier gas such as nitrogen or argon. Inside the torch the plasma of the working gas is formed between the anode and cathode. The working gas heats up and expands rapidly forming a jet from the plasma gun to the open atmosphere.

Powder particles melt in plasma are carried with the expanding working gas to the substrate where they solidify rapidly forming oxide splats. The final microstructure of plasma sprayed coating is composed of partly interconnected lamellae containing defects like micro cracks and pores.

Oxide materials often transform during the plasma spraying process so that the properties of plasma sprayed coating deviates from their traditionally made counterparts or raw material powders. A classical example is formation of γ-Al_2O_3 when plasma spraying pure α-Al_2O_3 [1–3]. Another example is formation of oxygen deficient phases to Cr_2O_3 [4] and TiO_2 [5,6] based materials. It is assumed that the formation of metastable phases and material defects decrease the chemical stability of plasma sprayed materials.

The current knowledge of surface properties and chemical stability of plasma sprayed oxide coatings is very limited. There is only one published study available concerning surface acidity of plasma sprayed oxides [7]. Since the plasma sprayed coating is always more or less porous, most of the corrosion studies performed for these coatings have concentrated on characterizing dissolution behaviour of under laying metal layer [8–12]. The only corrosion study [13], which considers the dissolution

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Table 1
Studied coating materials and their composition. All listed coating properties represent the properties of crushed coating materials [7]

Spraying powder properties					Plasma sprayed coating properties	
Spraying powder trade name	Nominal composition (mass%)	EDS composition (mass%)	Type	Crystallographic structure	Crystallographic structure	EDS composition (mass%)
Amperit 740.1	Al_2O_3	Pure Al_2O_3	Fused	α-Al_2O_3 (corundum)	γ-Al_2O_3 (main phase) α-Al_2O_3	Pure Al_2O_3
Amperit 782.1	TiO_2	Pure TiO_2	Fused	TiO_2 (rutile) Magneli phases (Ti_nO_{2n-1} ($4 \leqslant n$))	TiO_2 (rutile) Magneli phases Ti_nO_{2n-1} ($4 \leqslant n$)	Pure TiO_2
Amperit 704.1	Cr_2O_3	Pure Cr_2O_3	Fused	α-Cr_2O_3 (eskolaite)	α-Cr_2O_3 (eskolaite)	Pure Cr_2O_3
Amperit 744.1	$87Al_2O_3$–$13TiO_2$	$80Al_2O_3$–$20TiO_2$	Blended	α-Al_2O_3 (corundum) TiO_2 (rutile)	γ-Al_2O_3 (main phase) α-Al_2O_3 Magneli phases Ti_nO_{2n-1} ($4 \leqslant n$)	$70Al_2O_3$–$30TiO_2$
Amperit 712.066	$75Cr_2O_3$–$25TiO_2$	$76Cr_2O_3$–$24TiO_2$	Fused	α-Cr_2O_3 with dissolved Ti (eskolaite)	α-Cr_2O_3 with dissolved Ti (eskolaite) Magneli phases Ti_nO_{2n-1} ($4 \leqslant n$)	$72Cr_2O_3$–$28TiO_2$

Table 2
The used plasma spray parameters for each powder

Plasma spray powder	Gas flow parameters	Spraying distance (mm)	Current (A), voltage (V), plasma power (kW)
Al_2O_3	Ar: 41 l/min H: 14 l/min	110	610, 68.8, 41.7
$87Al_2O_3$–$13TiO_2$	Ar: 41 l/min H: 13 l/min	110	600, 66.9, 40
Cr_2O_3	Ar: 38 l/min H: 13 l/min	110	630, 73.0, 45.5
$75Cr_2O_3$–$25TiO_2$	Ar: 38 l/min H: 13 l/min	110	630, 64.5, 40.5
TiO_2	Ar: 47 l/min H: 13 l/min	120	600, 73.6, 44.2

of the oxide coating material is performed for plasma sprayed Al_2O_3 coating.

Fortunately, the surface properties and dissolution behaviour of common oxides have been studied intensively during past decades giving a good background to compare results obtained for plasma sprayed oxide counterparts. For example, there are numerous comprehensive reviews about surface acidity of a wide selection of different oxides [14–16]. In addition, dissolution behaviour of traditional oxides relevant in this study, γ-Al_2O_3, Cr_2O_3 and TiO_2 are well characterized [17–25].

2. Materials and methods

All spray powders were provided by H.C. Starck GmbH (Laufenburg, Germany). Sample materials were based on pure Al_2O_3, TiO_2 and Cr_2O_3 and their mixtures. The Al_2O_3–$13TiO_2$ spraying powder was a mechanical mixture of pure Al_2O_3 and TiO_2 powders. The Cr_2O_3–$25TiO_2$ powder was composed of homogeneous particles containing both chromium and titanium. Properties of the spraying powders and the final coatings are listed in Table 1. The raw material powders were plasma sprayed using optimised spraying parameters for each material. The sample materials were identical with samples used in a previous study [7]. Most important spraying parameters are presented in Table 2. Plasma spraying was performed to the relatively smooth stainless steel rods, which were rotating during spraying. Since the rods were only slightly sand blasted before plasma spraying, the coating material spalled easily from the substrate steel. Spalled shavings were collected and crushed using ball mill using alumina chamber and alumina balls. Formed powders were used as sample materials in all experiments.

Three suspensions of pH 4, 7 and 9 with a dry content 0.02% were made for each powder and the ionic strength was adjusted to 10^{-3} M using NaCl. The used water was purified using a Millipore Milli-Q system. The suspensions were stirred constantly using magnetic stirrers and the pH of suspensions were maintained constant using 0.1 M HCl or 0.1 M NaOH. The pH was checked daily and before each measurement. Exposures were performed in polyethylene beakers to minimize possible influence of glassware dissolution. No attempts, for example N_2 bubbling, were performed to remove dissolved gases present in suspensions.

The suspensions were aged for two weeks. The conductivity, the redox potential and the zeta potential were measured 7 times during the experiment, and the liquid samples for ICP-MS analyses were collected 5 times during the first 10 days. The sample suspensions were centrifuged and a small amount of exposure liquid was collected from the top of the centrifuged test tubes. After that the ICP-MS analysis were performed for collected exposure solutions using an ELAN 6000 equipment. A high number of elements was included in liquid composition analyses representing the elements present in electrolyte (Na), main elements present in sample oxides (Al, Ti, Cr), possible residuals from the coating substrates (Fe, Cr, Ni) and possible contaminants from plasma spraying equipment (Cu), filling so-