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Mullite-rich plasma electrolytic oxide coatings for thermal barrier applications

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Abstract

A study has been undertaken of the characteristics exhibited by mullite-rich plasma electrolytic oxide coatings grown on aluminium alloys by using silicate-rich electrolytes. It is found that they can be grown at a higher rate, and to a greater thickness, than alumina PEO coatings on aluminium. The thermal conductivity of these coatings has been measured using a steady-state method. It is shown to be of the order of 0.5 W m^{-1} K^{-1}, which may be compared with ~1.5 W m^{-1} K^{-1} for pure alumina PEO coatings and ~10–15 W m^{-1} K^{-1} for dense polycrystalline mullite. Coupled with excellent substrate adhesion and good mechanical properties, this relatively low conductivity makes these coatings attractive for thermal barrier applications. Furthermore, they are shown to exhibit a relatively low global stiffness (~40 GPa), which will reduce the magnitude of thermally-induced stresses and improve the resistance to spallation during temperature changes.

Keywords: PEO coatings; Mullite; Thermal conductivity; Thermal barrier; Alumina

1. Introduction

Plasma electrolytic oxide (PEO) coatings [1–4], which are sometimes referred to as micro-arc oxide coatings or spark/discharge anodic coatings, are formed by the oxidation of metal substrates in an aqueous electrolyte, via a series of localized electrical discharge events. These discharges allow oxide growth to proceed so as to produce films with thicknesses of the order of 100 μm on aluminium. They have been explored and developed for various applications, particularly those in which wear resistance [5–10] and corrosion resistance [7,9,11] are required. Among the attractions of the process are that it involves very few health or safety hazards, and that coatings of uniform thickness can quickly and easily be produced on components with complex surface geometry, over a wide range of sizes. Because substrate conversion is involved, rather than simple deposition, the interfacial adhesion is usually excellent.

Thermal protection [12–14] has received less attention, having been dismissed in a major review paper [1] on the basis of there being a large thermal expansion mismatch with the substrate. However, the recent work by Curran and Clyne [4] has demonstrated that PEO coatings tend to have relatively low stiffness, which will limit the magnitude of thermally-induced stresses. Furthermore, the thermal conductivity of PEO coatings has been shown to be an order of magnitude lower than those of corresponding bulk crystalline oxides [14], making them potentially attractive for thermal barrier applications.

The present paper focuses on mullite-based coatings grown on aluminium alloys, using alkaline electrolytes rich in silicates. There have been some previous indications that these can be grown to greater thicknesses and at a greater rate than most other PEO coatings on aluminium, although there is little information about this in the open literature. In the present work, the structure and composition of these coatings are studied. Their stiffness and thermal expansivity are also measured. Finally their thermal conductivity is evaluated, using a steady-state method.

2. Experimental techniques

2.1. Sample preparation

Coatings were produced on a 6082 aluminium alloy, in the form of a 3 mm thick sheet, with in-plane dimensions of

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100 mm × 50 mm, and on cylinders of a 2011 aluminium alloy 33 mm in diameter, and 20 mm in length. Coatings were prepared using a 10 kW Keronite™ processing rig and an electrolyte consisting primarily of a dilute aqueous solution of KOH and Na_2SiO_4. The electrolyte was maintained at a temperature of approximately 25 °C by re-circulation through a heat exchanger, with a whistle pump agitating and aerating the electrolyte. A constant capacitance condition was set, so as to achieve a current density of approximately 15 A dm^{-2} after the initial transitory regime. Coatings were grown to a thickness of between 100 μm and 200 μm. Thicknesses were measured using an Eban 2000 eddy current thickness gauge, the accuracy of which was confirmed by occasional microscopy of cross-sections. Free-standing coatings were obtained by immersion of coated substrates in a saturated solution of NaOH for several minutes, leading to dissolution of the substrate. These samples were then rinsed in water and dried.

2.2. Microstructural studies

SEM observations were made using a JEOL 5800 LV and a JEOL 6340F FEGSEM. Both secondary electron (SE) and back-scattered electron (BSE) modes were used. The elemental composition of the coating was ascertained using *Oxford Instruments INCA* energy dispersive X-ray spectroscopy (EDS) in the JEOL 5800 SEM. A Phillips PW 1710 X-ray diffractometer was used to perform θ–2θ scans (in Bragg–Brentano geometry) from 10° to 120°, with a 0.02 step size. A CuK_α radiation source was used, with a 40 kV accelerating voltage and a 40 mA filament current. Data were obtained from the as-deposited free surfaces. The Hanawalt search method was used for phase identification. *Phillips X'Pert ProFit* software was then used to fit the diffraction pattern and to determine the relative integrated area under peaks corresponding to amorphous material and crystalline material. Finally, topographic studies were carried out, using a Wyko RS-2 interferometric profilometer, in order to measure the surface roughness.

2.3. Thermo-physical property measurement

The thermal expansion of detached coatings was investigated using a Netszch 402L push-rod dilatometer, over the temperature range 20 to 700 °C. This allowed evaluation of the (in-plane) thermal expansivity, which was found to be approximately constant over this temperature range. Samples with a U-shaped section were used to reduce the danger of buckling, and a gauge length of ~20 mm was used.

The global in-plane Young's modulus of coatings was measured by a four-point bending of thick (~200 μm) detached coatings. Load was applied via a counter-balanced platen, using small pre-weighed masses. A brief period was allowed for the beam to settle after each addition, but both this and the timing of additions was defined, in order to standardise the effect of any small amount of creep that could have been taking place. The response to unloading was also measured, so as to ensure that the beam was still in the elastic regime.

For accurate measurement of the deflection under applied loads, a scanning laser extensometer was used, intersecting the beam at its centre (the point of maximum deflection). This allows measurement of deflections with a resolution of about 5 μm. Together with each measurement of the nominal beam deflection (as measured up to the bottom of the beam intercept), the apparent thickness of the specimen was recorded, in order to monitor any twisting of the specimen. This could be used to correct the nominal deflection for the centreline of the specimen, but any large values suggest unevenly distributed loading and data from any such cases were discarded.

With the deflection (δ) measured at the centre, the bending modulus can be obtained from

$$E = \frac{Pa}{48I\delta}\left(3L^2 - 4a^2\right) \tag{1}$$

where L is the distance between the outer loading points, a is half the difference between the spans of the outer and inner loading points, P is the applied load, and I is the second moment of area of the beam section. The main factor limiting the accuracy of results obtained with this method is the precision to which specimen thickness can be measured and the effect of any non-uniformity in thickness.

2.4. Nanoindentation

Depth-sensitive nanoindentation was performed on polished cross-sections and in-plane sections, using a *Micromaterials Nanotest 600* indenter and an *MTS Nanoindenter XP*. In each case, a Berkovitch indenter was used, with a maximum load of 50 mN. Hardness was calculated from load and indentation depth data, while the local stiffness was determined from the unloading response, using the standard Oliver and Pharr technique [15]. It may be noted that this stiffness differs from that measured by beam bending measurements in that: (a) it is local, and hence influenced by defects such as porosity and microcracks only if the indenter happens to probe a region containing such a defect, and (b) it is obtained under predominantly compressive loading.

2.5. Thermal conductivity measurements

The thermal conductivity was measured using a steady-state method. Full details are given elsewhere [16]. Three or four small (1 mm diameter) radial holes were drilled as far as the centreline in each of the two cylinders with coated ends, which were located coaxially with the coatings in contact. Thermocouples were then inserted to measure the temperature at these known points along the cylinder axis. The assembly was placed between the heating and cooling blocks of the apparatus. A small amount (~0.1 ml) of high conductivity paste was smeared at the interfaces, and a fixed torque of 2 N m was applied to the securing screw, bringing the two coated ends into good thermal contact.

Electrical resistance heating coils were then switched on (at a fixed power setting), and a steady flow of water was passed through the cooling block. Data-logging of the thermocouple output was used to determine when a steady state had been reached. Once the temperatures had been stable to within 0.5 °C for about 30 min, average thermal gradients through the