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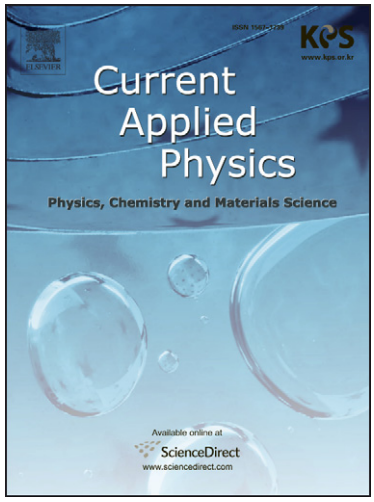

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Optically transparent, dense α-Al_2O_3 thick films deposited on glass at room temperature

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Abstract

Alumina films up to 5 μm thick have been deposited on fused silica and stainless steel substrates by a novel aerosol-jet deposition process at room temperature. The films are dense, uniform and adherent. Moreover, Al_2O_3 film deposited on fused silica substrate is transparent for visible light. Transmittance of 1.5 μm thick alumina film is 83% measured at 800nm, and that of 5.5 μm thick film is 68%. Scanning electron microscopy images and XRD analysis have revealed that the films have α-Al_2O_3 crystallite structure however crystallite size is order of magnitude smaller than that raw material powder. Vickers micro hardness of the films deposited on stainless steel has been measured. Aerosol jet deposition becomes promising method for surface coating.

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Keywords: Aluminium oxide, Hardness; Transparent film, Aerosol-jet deposition.

1. Introduction

Optically transparent ceramic coatings are important for products such as organic light emitting devices (OLED), solar selective coatings, bar code readers, optical lenses and windows. There are few reports of fabrication of transparent alumina thin films. The main issue for manufacturing transparent protective coatings on glass and polymers is the low processing temperature required. Amorphous alumina films can be deposited by electron beam deposition [1] or electrophoretic deposition at low temperatures [2], some of these films are transparent, however their mechanical properties are not suitable for some applications. Crystalline alumina film can be deposited by conventional methods such as magnetron sputtering [3, 4], sol gel [5-7], pulsed laser deposition [8] and chemical vapour deposition [9], however thermal stress and high thermal expansion mismatch between film and substrate are additional problems for higher temperature deposition methods.

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Aerosol Jet Deposition (AJD) [10-11] is a novel room temperature deposition technique which uses kinetic energy rather than thermal energy to form thin films from bulk powder. Ceramic powder is entrained in a carrier gas, accelerated through a converging nozzle and is impacted on the substrate. The resulting high energy impact deposition results in dense layers with nanocrystallite microstructure. The selection of primary powder and control of the jet particle speed and substrate positioning are essential for film formation and properties. In this paper, we demonstrate an optically transparent alumina (Al_2O_3) thick film deposited at room temperature onto fused silica substrate by AJD. Alumina films were also deposited on stainless steel and the mechanical properties investigated by indentation hardness testing.

2. Experimental

The deposition of alumina was carried out using AJD equipment fabricated in-house. Twenty grams of the primary ceramic powder (purity 99.5%, average particle size 0.4 µm) (AL160-SG-3 courtesy supplied by Showa Denko K.K) was dried at room temperature under vacuum. The powder was dispersed by agitation into nitrogen carrier gas, forming an aerosol of solid particles in gas. A converging nozzle (rectangular orifice 2 mm x 0.2 mm, see Fig. 1a) exits into a vacuum chamber and is targeted on the substrate 5mm from the nozzle on the manipulator. The nozzle exit velocity is calculated to be in the range of 300 m/s. Others parameters are shown in the Table I.

Table I. Aerosol Jet Deposition experimental parameters

Volume of deposition chamber	0.8 L
Nozzle orifice	0.2mm x 2mm
Carrier gas	N_2
Distance between nozzle and substrate	5 mm
Gas flow rate	1.8 L/min
Vacuum system pumping rate	167 L/min
Pressure incise deposition chamber	5 Torr (650 Pa)
Substrate's temperature	300 K

The ceramic particles hit the substrate and form a dense layer. The substrate was continuously scanned perpendicular to the aerosol jet by a rotating stage. The deposition rate reaches 2 µm/min in the deposited area of 2 mm by 3 mm. During deposition, the substrate temperature does not change and remains 25°C. No post-deposition procedure for densification was performed. Field-emission SEM (JEOL JSM-7000F) was utilized for morphological inspection of the deposited film and measurement of powder size and film thickness. The microstructure was analyzed using X-ray Diffraction (XRD) (PW1729, Philips). Transmittance in the visible wavelength range was observed by using spectrophotometer (Cary 50 UV-Vis, Varian Co., Australia). Hardness of the coatings was measured at 10 - 300 g loads using a LECO M400-H1 microhardness tester with a Vickers indenter, and dimensions of the indentation marks were measured by SEM.

3. Results and Discussion

Figure 1shows a schematic of the AJD process incorporating an actual optical reflection image of a 4-µm-thick alumina film on a fused silica substrate. The smooth surface and interference fringes can be clearly recognized.

Figure 2 shows scanning electron microscopy (SEM) images of the primary source powder particles and the deposited alumina film surface. In Figure 2(a) the primary powder has particles with a size range from 0.1 to 0.5 µm. Figure 2(b) shows that the grain size evident on the film surface is in range of 10 nm. Comparing the surface image with that of ceramic

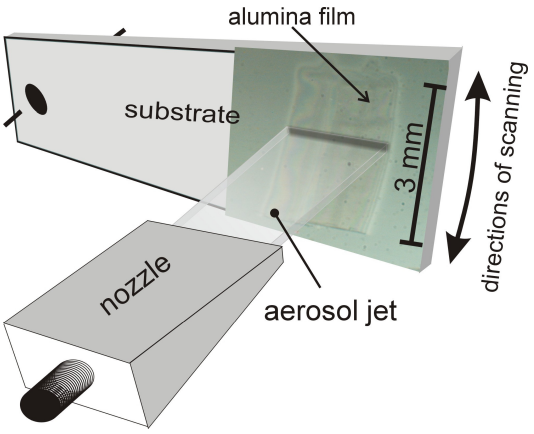
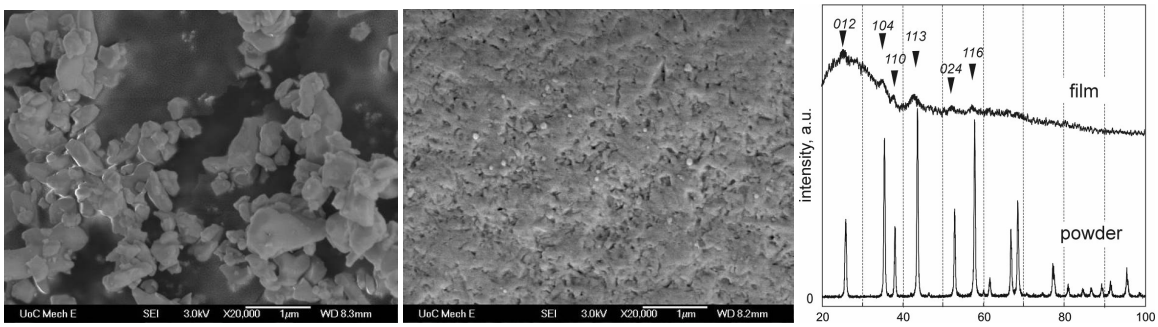


Fig. 1. Schematic of AJD process and image of actual film on glass



(a) **(b)** **(c)** 2θ/θ

Fig. 2. SEM images: a) alumina powder before deposition. b) as deposited (not polished) surface of 5-μm-thick alumina film deposited on fused silica substrate (same magnification for both SEM images). c) XRD of powder and as deposited film. (Cu K-α at 50kV/40mA).

powder we can see that large source particles are not incorporated into or on the surface of the film. The ten-fold decrease in crystallite size as compared to the primary particles was also confirmed for lead zirconate titanate (PZT) by XRD and TEM analysis in previous studies [10]. The proposed deposition mechanism is that during film formation by AJD the fracture of ceramic particles is caused by impact [11], however, this model has not yet been verified.

Figure 2(c) shows the XRD pattern of the as deposited film and powder. The powder showed the XRD pattern of α –alumina and the films exhibited the same XRD patterns. However, the XRD pattern of the as-deposited film became broader, the intensity of all X-ray peaks in the films were lower than those of host powder and all peaks were shifted to the low angle degree. The film XRD pattern is typical of very small grain size and introduced stress. Estimation of the average crystallite size using the Debye-Scherrer equation from the XRD patterns for the film gives value crystallite size from 5 to 40 nm.

Figure 3 shows the visible transmittance spectrum of deposited films in the wavelength range 200-800 nm. High transmittance (up to 83% at 800 nm for 1.5 μm film) and a clear absorption edge of the alumina film were observed.

During the film formation the surface is impacted by the high speed particle jet, with velocity previously reported in the range of 200-500 m/s as measured by a modified time-of-flight method proposed by Lebedev *et al.*[12]. The high velocity impact phenomenon produces the small particles, supplies the energy for incorporation of nanoparticles into a film, and results in surface craters and hills, thus introducing surface defects. However, the size of these surface defects is less than the wavelength of visible light, so they have minimal effect on the optical properties of the deposited film. Film transparency is usually associated with very thin films, amorphous materials and glasses, or high crystallinity with a low number of defects. In the case of the thick film deposited by AJD, the high transmittance is attributed to the small particle size, which has minimal light scattering [13]. AJD deposition energetics and film growth mechanisms are the subject of on-going research and modelling.

Nanocrystallite structure materials may exhibit unique mechanical properties. At low concentrated loads, or higher distributed loads, coating of ductile materials by brittle ceramics can drastically increase the surface hardness and wear resistance. Microhardness testing was used to investigate mechanical properties, and to get and indication of

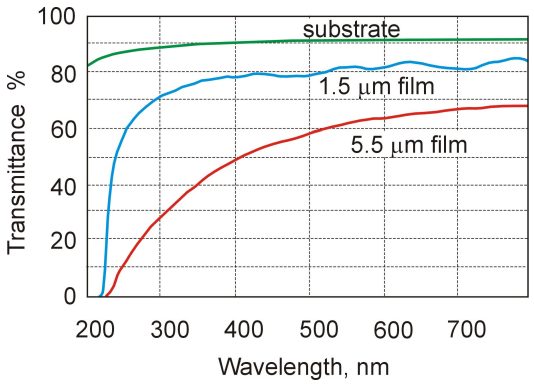


Fig. 3. Transmittance of alumina film deposited on fused silica.

the as-deposited density. A 5.5 μm thick alumina film was deposited on stainless steel (S30400) substrate at room temperature. The film and a bare substrate sample were hardness tested over a range of loads. The results are shown in Figure 4. The indentation marks are clearly visible by optical microscope and the sizes were confirmed by SEM. Under a load of 25 g, the as-deposited film exhibited hardness of 1600 HV which is close to that of bulk alumina (~2000 HV.) Microhardness values obtained at a low loading best represent the film material hardness, but the small size of the indention mark limits the accuracy of the measurement and, under low loading conditions the influence of substrate is still significant. Under high load the indenter penetration depth is comparable with film thickness. As a result the influence of the substrate is seen at high loads with the effective hardness being close to but slightly higher than that of the steel substrate. The high hardness value at low penetration indicates that the alumina material is near full density.

The value of hardness of the deposited film depends on particle jet speed, i.e. at low jet speed the film is less dense than at high jet speed. This phenomenon will be studied in the future.

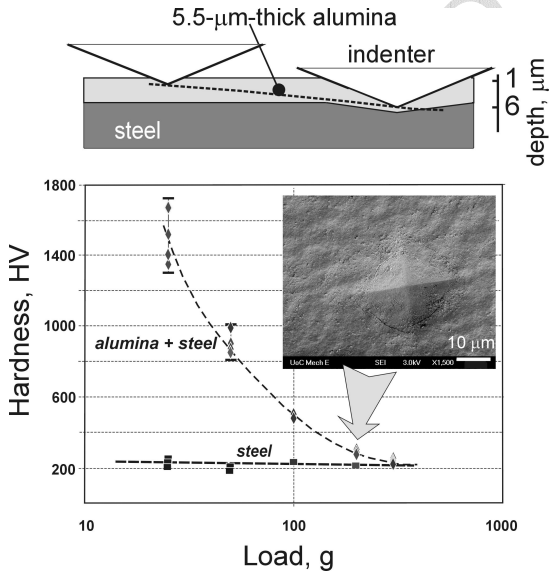


Fig. 4. Vickers hardness over a range of load for a 5.5-μm-thick alumina film deposited on stainless steel substrate, and for the bare substrate. Inset- SEM image of an indentation mark in the film.

4. Conclusion

Optically transparent alumina film with thickness of several microns was deposited on a fused silica substrate by aerosol jet deposition (AJD) at room temperature. The films produced from 0.4 micron alumina powders were observed through surface SEM imaging to have a structure with order of magnitude smaller features than the parent material and very small void fraction. Transmittance of 1.5 μm thick alumina film is 83% measured at 800nm, and that of 5.5 μm thick film is 68%. The hardness of 1600 HV AJD alumina film at low point loads indicates that the film is dense, although thin film results cannot be compared directly to results for bulk materials. Future improvement of the technique and engineering research on process control and equipment scaling is continuing for deposition of transparent films on glass devices and polymer substrates.

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