

Nanoporosity of Al₂O₃ coatings obtained by impulse plasma deposition

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Investigations of the size distribution of nanopores were carried out for alumina coatings deposited by the impulse plasma method. The single-phase (metastable and stable correspondingly) alumina coatings were deposited under different conditions of impulse plasma processes. The investigation of nanopore distribution was carried out using small-angle X-ray scattering. Despite the different phase composition of the coatings obtained, the most probable value of nanopores for both alumina coating materials were practically the same and equal to 5 nm. It appears that a coating porosity of the order of nanometres is characteristic for all coatings deposited by the impulse plasma method, because previously similar dimensions of nanopores were found for diamond, TiN and BN. It seems that during the impulse plasma deposition the coating grows on the substrate surface by condensation of ultra-small particles nucleated in the impulse plasma.

1. Introduction

Aluminium oxide is an electrical insulator, which is hard and exceptionally resistant to chemical agents, and shows a good heat conductivity [1, 2]. As a coating material, it seems to be a prospective candidate for many engineering applications and is especially suitable wherever the surfaces involved should show an increased mechanical strength and chemical resistance, in particular at elevated temperatures, and where heat should be quickly removed. Aluminium oxide is also used as an electrically insulating layer in multi-layer semiconductor devices [3–10]. Al₂O₃ coatings may be produced using either the physical (PVD) or chemical (CVD) vapour deposition method [11–13].

Recently, the impulse plasma deposition (IPD or IPPVD) method has been used for obtaining aluminium oxide coatings [14]. This method uses a strongly non-isothermal impulse plasma which is almost fully ionized (lifetime of 10⁻⁴ s). The plasma is generated in a coaxial accelerator which operates in a quasi-stationary mode [15, 16]. A characteristic feature of IPD coatings is their ultrafine-grained structure [17–19]. They adhere well to the substrate even though no external source heats it during the plasma process (the substrate surface is heated only by the impulse plasma [19]). So far we have accumulated a thorough knowledge of the fundamental and practical problems associated with coatings made of diamond [18], titanium nitride [17] and multicomponent metallic alloys [19]. We have also studied some aspects of the mechanism of Al₂O₃ synthesis [14]. We found that the Al₂O₃

coatings were built up from ultra-small particles of metastable alumina phases, which were crystallized in the very plasma. According to the IPD process parameters, we are able to produce alumina coatings with different numbers of macrodefects; in some cases it is possible to obtain very dense coatings even without characteristic grain boundaries [14, 20] (this corresponds to the “freezing zone” concept proposed by Zdunek [19]).

The aim of the present study was to find a more precise answer to the problem of the condensation mechanism of alumina coatings obtained by the IPD method. In our opinion the condensation mechanism can be best studied by the small angle X-ray scattering (SAXS) method. This is because this method makes it possible to determine the distribution of nanopores existing in the material.

2. Experimental procedure

2.1. Condensation of Al₂O₃ coatings

The synthesis of Al₂O₃ coatings took place in the apparatus described in detail elsewhere (e.g. [16, 21]). In this apparatus the source of the vapours is the front face of the end of an internal electrode of the plasma accelerator [16]; the gaseous source of the vapours could be the plasma gas, which is supplied to the plasma accelerator in a continuous way. Taking this into account we have chosen the following vapour sources.

(A) An internal metal–ceramic (diameter 14 mm) electrode, i.e. an aluminium electrode with an Al_2O_3 insert pressed into the front face of its free end; an additional source of Al_2O_3 vapour was a thin (8 mm) alumina ring with an internal diameter smaller by 4 mm than the diameter of the external electrode of the plasma accelerator; this ring was placed directly at the outlet of the plasma accelerator.

(B) The same electrode as in (A) but with an additional massive (ring thickness 22 mm) alumina ring; using the large mass, the ceramic ring heated only by the impulse plasma was an internal heater with respect to the substrate surface and stabilized the stationary temperature of the substrate surface at higher values.

The energy driving the plasma process was supplied by a 100 μF capacitor battery which, prior to each plasma impulse, was charged to 3 kV. The pressure of the plasma gas (oxygen) was 20 Pa. The coatings were deposited on iron and nickel substrates using 3000–5000 plasma impulses generated at intervals of 4 s (condition A) and 2 s (condition B).

The coating materials were tested using the X-ray diffraction method, as well as TEM and SEM observation. The nanoporosity of the coating material was determined by the SAXS method (see below).

2.2. SAXS method

The principles of the SAXS method were described previously [18, 22, 23]. The method makes use of the X-ray diffraction on whole particles which have interphase boundaries and a mean electron density, ρ , different from that of the medium, ρ_0 . Such particles can be pores or regions with structure or chemical composition different from those of the medium. The intensity of radiation, J , scattered by the particles is proportional [24] to

$$J(K) \sim (\rho - \rho_0)^2 (\Sigma K) \quad (1)$$

where K is a wave vector, $K = 4\pi \sin \theta / \lambda$ and λ is the radiation wavelength. The total intensity, scattered in the small-angle region, can be expressed by the formula [25]

$$J(K) = \int D(R) m^2(R) \phi(KR) dR$$

where $D(R)$ is the size distribution function of particles depending on the linear parameter R . In the case of spherical particles, R is the radius of the sphere, $m^2(R)$ is an integral over excess density in the medium surrounding the particle, $\Phi(KR)$ is the factor of the particle shape.

Research samples were made from layers removed from the substrate and then powdered. The sample thicknesses were optimum for the radiation CuK_α applied. The measurements of the intensity of scattered X-rays were performed in a compact small-angle camera vacuum chamber, coupled with a Siemens diffractometer. The function $D(R)$ was calculated, taking into account corrections for the collimation effect and the wavelength effect, by the method of inverse Fourier transform, proposed by Glatter, by applying his computer program MPT-79 [25]. As a result of the

studies, functions of particle size distribution $D(R)$ were obtained.

3. Results

Fig. 1 shows fracture of a coating deposited under condition A. Characteristically, as in the case with the metallic coatings produced from an impulse plasma [19], no typical grain boundaries could be observed in the oxide coatings material. The boundaries usually occur in coatings produced by other PVD techniques, such as can be described using the Movchan–Demchishi–Thornton model [26–28]. In our opinion, the morphology of the oxide coatings resulted directly from the fact that the aluminium oxide coatings were built up by clusters and very small but critical nuclei which were nucleated in plasma. According to Rusanov [29], the nucleation that proceeds “on ions” leads to the formation of ultrafine critical nuclei.

Fig. 2 shows an image of products of impulse plasma synthesis. We can see that some of the particles formed within the plasma undergo partial agglomeration. After direct measurements we found that the average value of the diameter of alumina particles was of the order of tens of nanometres formed within the plasma undergoing partial agglomeration. The

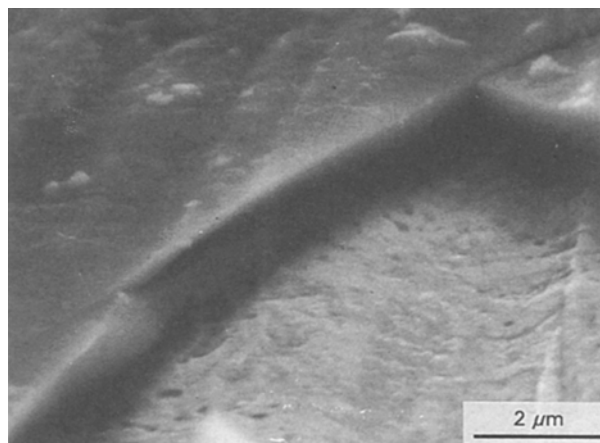


Figure 1 Fracture of an Al_2O_3 coating deposited under the conditions A.

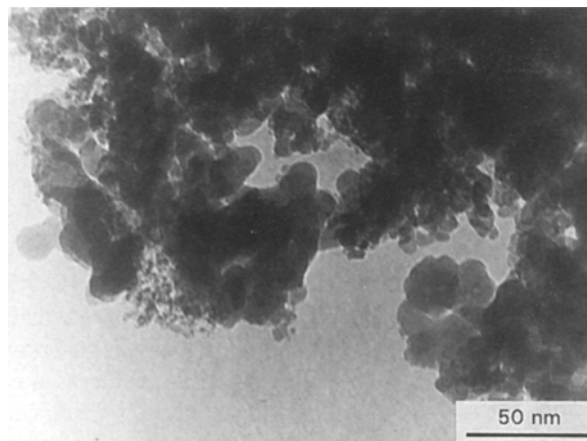


Figure 2 Products of impulse plasma synthesis of Al_2O_3 (before their condensation on the substrate).

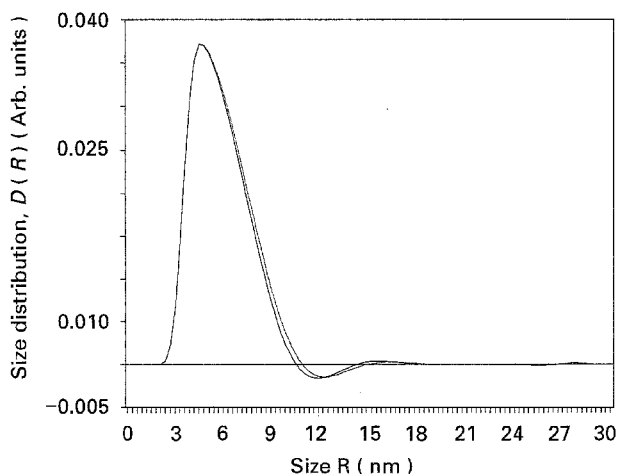


Figure 3 Size distribution of nanopores existing in Al_2O_3 coatings. (—) Condition A, (···) Condition B.

rounded shapes of the particles suggest that most probably they could be in the liquid state. After direct measurements we found that the average value of diameter of alumina particles was of the order of tens of nanometres.

Examination of the phase composition of the coatings condensed on an iron substrate has shown that they were composed of metastable Al_2O_3 – ASTM 10–425 (variant A) and of stable phase Al_2O_3 – ASTM 10–173 (variant B).

The size distribution function, $D(R)$, is illustrated at Fig. 3, where, because of the fact that the function $D(R)$ represents the relative values of the number of particles, the heights of the main peaks were equated for better comparison. Sight drops below zero on these curves, apart from the main maximum, are characteristic of the SAXS method. Taking this into account we can see from Fig. 3, that the curves obtained for coatings deposited under conditions of both deposition processes are very similar.

4. Discussion and conclusions

The most probable size value (maximum of the $D(R)$ function) is about 5 nm and is at least several times lower than that of single-phase aluminium oxide particles (diameter of the order of tens of nanometres). Therefore, the maxima in Fig. 3, must correspond to the size distribution of micropores treated as particles in the SAXS method.

Assuming that our view is correct and taking into account the results of studies reported elsewhere [14, 29], we propose the following mechanism for condensation of Al_2O_3 coatings.

1. Clusters and ultra-small critical nuclei which are formed in very plasma [14] reach the substrate surface as impulse plasma components.

2. The coating grows from the specific “aerosol” of hot particles which agglomerate on the substrate surface by the sintering mechanisms [30]; each portion of condensed particles is cooled down by the heat transfer in the metallic substrate (i.e. with velocity $\sim 10^6 \text{ K s}^{-1}$ [19]).

3. By heating the substrate surface by the ceramic ring we can raise the surface temperature to the level which is sufficient for phase transfer of Al_2O_3 but insufficient for its coagulation.

The proposed mechanism of condensation of Al_2O_3 coatings corresponds, in general, to that suggested previously for diamond [18], TiN [17] and metallic [19] coatings obtained by the IPD method. It is worth noting that in our studies we achieved practically the same size of nanopores for Al_2O_3 coatings as for diamond and TiN coatings [23]. That proves that nanoporosity of the order of nanometres is a general property of coating materials produced by IPD, independent of the type of chemical bond.

In summary, our experiments lead to the following general conclusions.

1. The most probable radius of nanopores of Al_2O_3 coatings is about 5 nm.

2. The nanoporosity of IPD coatings seems to be a general property and is an important feature of the IPD method.

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