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Alumina coating on quartz glass and nickel substrates using aqueous sol derived from $AlCl_3 \cdot 6H_2O$

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The thick alumina films (0.2–0.5 μm) were prepared on quartz glass and nickel substrates by a dipping method using an alumina sol derived from an aqueous $AlCl_3$ solution. The hardness of this coating was compared to those of similarly coated substrates that had been heat-treated at various temperatures. The hardness of the alumina coating increased with increasing heat-treatment temperature. This sol gave crack-free and well-coated substrates that could be heat-treated to temperatures up to 800°C. This may have been due to the formation of an amorphous mixed oxide interface layer between the alumina films and the substrates. At temperatures higher than 900°C, problems with the coating started to appear because the oxide layer formed into α-alumina accompanying evolution of stress in the interface.

1. Introduction

The sol-gel method is a suitable technique for coating a substrate. Coatings made by the sol-gel method can protect against oxidation or corrosion to acids, act as insulators, or enhance the scratch resistance of the substrate. Because of these and other applications, the sol-gel method has been extensively investigated [1]. For example, the SiO_2 coating of substrates has been well studied and applied [2, 3]. The primary limitation on the use of the sol-gel coating is its thickness, which cannot exceed, in general, 100 nm per layer. Certain practical applications may occasionally require thicker and crack-free films. Cracks are due to stresses that develop as a result of the drying and the thermal expansion mismatch between the film and its substrate. In previous papers the authors prepared the alumina film using aqueous sol derived from an $AlCl_3$ solution and examined the optical properties of doped alumina films [4–7]. In practical use, it is necessary for the doped films to be prepared on substrates. There have been numerous studies on thin alumina coatings created using sol derived from alkoxide [8–10], but only a few studies have been reported on the thick alumina film coating that is sometimes used on substrates [11]. In this paper, we investigated a thick alumina coating on quartz glass and nickel substrates created by a dipping method using an aqueous sol derived from an $AlCl_3$ solution.

2. Experimental

The reagent-grade pure chemicals used in this study are all available commercially. Alumina sol derived from an inorganic salt was prepared in a manner similar to that described previously [4–7]. Hydrous aluminum oxide was prepared by dropping aqueous 6 M NH_3 solution into aqueous $AlCl_3$ solution. Precipitated hydrous oxide was aged for 12 h, filtered and washed with pure water, then transferred to a flask and made into a clear sol by peptizing with acetic acid under reflux at 80°C for 8 h. The molar ratio of acetic acid/Al was 0.15 and the concentration of Al_2O_3 in the sol was 0.4 mol/l. The sol remained stable for a few years.

In addition, a sol derived from aluminum isopropoxide was prepared using the Yoldas method [12]. The alkoxide solution molar ratio of water to alkoxide, 100:1 was agitated at 80°C for 1 h. Acetic acid was then added to the suspension of hydrolyzed aluminum oxide at the ratio of 0.15 mole of acetic acid per mole of the original alkoxide.

The substrates used for coating with alumina sol included quartz glass (20 × 20 × 1 mm; GL Science Inc., Tokyo, Japan) and nickel (20 × 20 × 1 mm; Kojundo Chemical Laboratory Co., Saitama, Japan). Before coating, the quartz glass substrate was soaked in a sulfuric-dichromate acid solution for one day. It was then washed in pure water under ultrasonic waves, rinsed with ethanol and dried in an oven. The nickel substrate was heat-treated under an N_2 atmosphere at 500°C for 1 h. Substrates were coated with alumina sol by dipping them in the sol for 3 min, then pulling them out at a rate of 3 cm/min. These samples (one time dipping) were dried in a clean box for 12 h, then heat-treated at temperatures ranging from 200–900°C for 0–10 h. Afterwards, X-ray diffraction

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(XRD) patterns were measured using a Cu Kα with a Ni filter (40 kV, 30 mA) and a JEOL JXD-8SD XRL meter. In addition, secondary ion mass spectrometry (SIMS) profiles were measured using a PHI6600 SIMS system (Perkin Elmer, Norwalk, CT), and sputtering was performed using a Cs^+ ion beam. The rate of etching, which varied slightly among samples, was approximately 0.05–0.15 μm/h. Finally, the Vickers hardness was measured by a Fischerscope H100, which uses a penetrator (a square-based diamond pyramid having an included point angle of 136 degrees between opposite faces). The indentation for applied load was measured continuously. According to our tests, the Vickers hardness (HV) value was 0.59 (GPa) for Ni and 7.4 (GPa) for quartz glass.

3. Results and discussion

Thermal transformations of aluminum hydroxides have been extensively studied [13]. As dehydration proceeds, the structure evolves through a series of disordered states. Because of their amorphous nature the intermediate states are still poorly understood. Yoldas reported that a transparent monolithic alumina could be obtained via the sol-gel method using alumina sol derived from alkoxide [12]. Inorganic salts can also be used to derive the alumina sol, though they are used less frequently than alkoxide.

The alumina films prepared from both sols demonstrated a high transmittance for light ranging from visible to near infrared. However, when the films heat-treated at low temperatures, the film prepared using an $AlCl_3 \cdot 6H_2O$-derived sol was more transparent than that prepared using the sol from aluminum iso-propoxide [7]. Both films (10 μm) were transparent up to 800°C. But at temperatures above 900°C they gradually became opaque with increasing treatment temperature, accompanying the formation of α-alumina. XRD patterns of the pulverized gels are shown in Fig. 1. The dehydration of the hydroxide generally leads to α-Al_2O_3 via the various transition forms. The alumina made from the inorganic salt, when treated at 300–800°C, appeared to be more or less structureless, although it seemed to partially contain γ-alumina. The alumina created from the alkoxide showed broad and diffuse bands. In the alkoxide gel, boehmite formed at temperatures lower than 300°C, and was transformed into γ-alumina at 400°C to 700°C. For the alumina coating on substrate, the sol derived from inorganic salt provided better wettability and uniformity than the sol derived from the alkoxide. It has been reported that stainless steel plates coated by the alumina film remained uncorroded after 1000 h in the Ringer's solution [14]. On the other hand, in similar experiments, corrosion was not effectively prevented in coated steel treated at temperatures lower than 700°C [15]. A protective coating could be obtained, however, by repeated coating at the highest possible treatment temperature, which causes the films to be mostly amorphous [15]. The growth of γ-Al_2O_3 and the transformation into α-Al_2O_3 at higher temperatures resulted in the formation of an island-like coating and hence was detrimental for use as a protective coating.

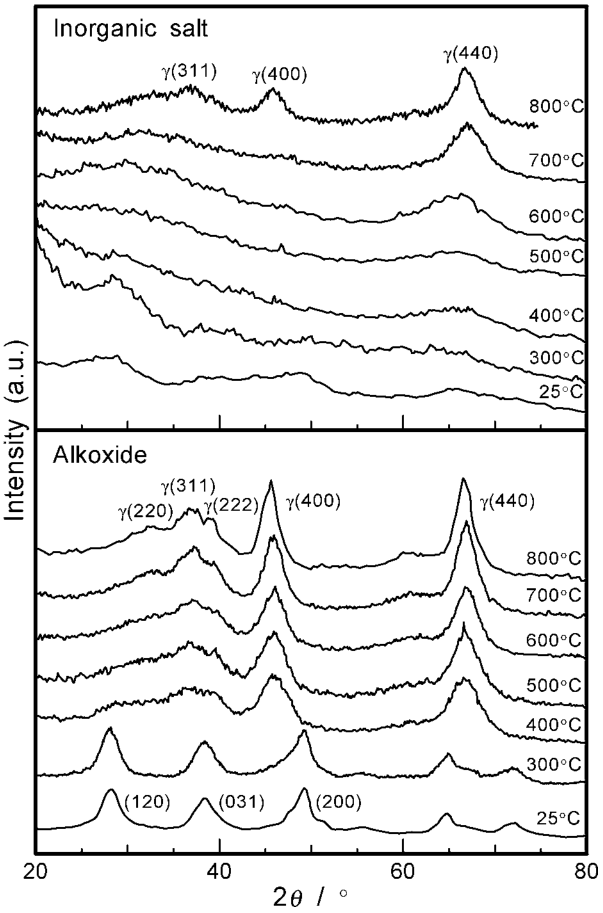

Figure 1 XRD patterns of pulverized gels derived from $AlCl_3 \cdot 6H_2O$ and aluminum iso-ropoxide. Temperature denotes treat-temperature.

Considering these facts, our alumina sol derived from an inorganic salt appears to be suitable as a coating. SIMS depth profiles for alumina-coated Ni substrates are shown in Fig. 2. The abscissa denotes the duration of Cs^+ gas-sputtering. From the figure, one can see that Ni species (perhaps hydrous Ni oxide) partially dissolved by alumina sol (weakly acidic) diffused into an alumina layer, and that this diffusion went deeper into the alumina layer with increasing heat-treatment temperature. The diffused layer was considered to have formed a mixed (Ni-Al) oxide layer.

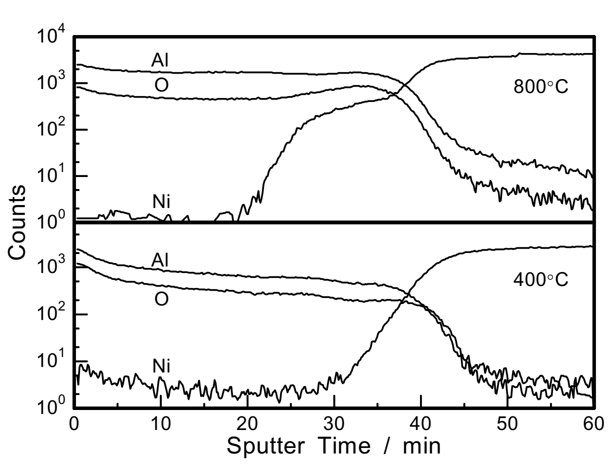

Figure 2 SIMS depth profiles for alumina coated Ni substrates treated at 400 and 800°C. Sputtering was performed using a Cs^+ ion beam. Etching rate was 0.05–0.15 μm/h.

SIMS depth profiles for alumina-coated quartz glass plates treated at various temperatures are shown in Figs 3 and 4. The abscissa denotes the duration of Cs^+ gas-sputtering. One common feature should be noted. An initial decrease of Al coincides with an increase of Si. This means that Si does not diffuse into the alumina layer, but the alumina diffuse into the pits of the uneven substrate surface. The diffusion of alumina into the surface occurs in conjunction with increasing treatment temperature and treatment times. Fig. 4 shows the SIMS profile of alumina-coated substrates annealed at 800°C and 900°C. In the case of 800°C-annealing, counts of Si began to increase the moment counts of Al decreased for sputter time. In contrary, counts of Si for the 800°C-annealed film increased gradually with the sputter time even during constant Al-counts. This indicates that Si atoms diffused into the alumina layer due to concentration gradient. Thus, the diffusion layer must have been composed of a mixed oxide. An increase in the formation of this layer induced an increase in the adhesiveness of alumina on the surface. The effect of treatment time on hardness is shown in Fig. 5. The time required to reach a steady state was longer for coated glass treated at higher temperature. The effect of treatment temperatures on hardness is shown in Fig. 6 together with the density and weight loss of alumina sol alone (non-coated sol). The increases in Vickers hardness (*HV*) value corresponded with increasing treatment temperature. In the range between 25–500°C, the temperature dependence of weight loss roughly paralleled that of the density of alumina alone. However, this was not the case at higher temperatures. This change may indicates that the hardness of the coated substrate treated at lower temperature is attributable to less sintered alumina, while the hardness of the coated substrate treated at higher temperature was due primarily to the densification of alumina with temperature and additionally to a mixed oxide sublayer, as described above. A modified Vickers hardness is called a universal hardness (*HU*). *HU* is calculated on the base of the penetrator

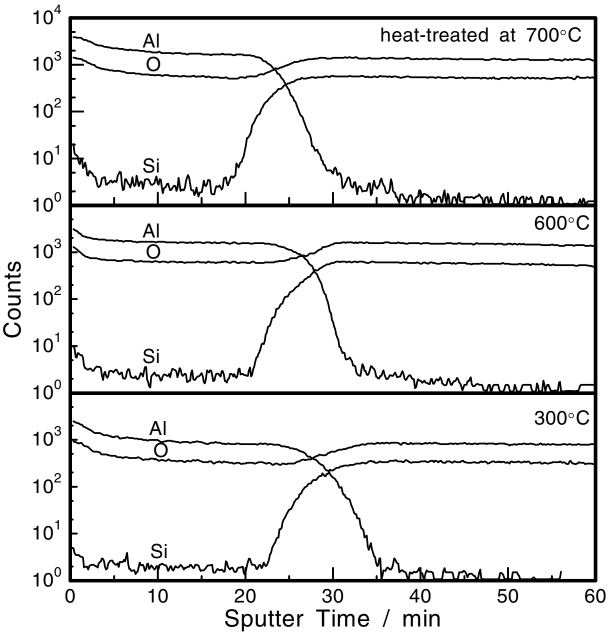

Figure 3 SIMS depth profiles for alumina coated quartz glass substrates treated at 300, 600 and 700°C. Sputtering was performed using a Cs^+ ion beam. Etching rate was 0.05–0.15 μm/h.

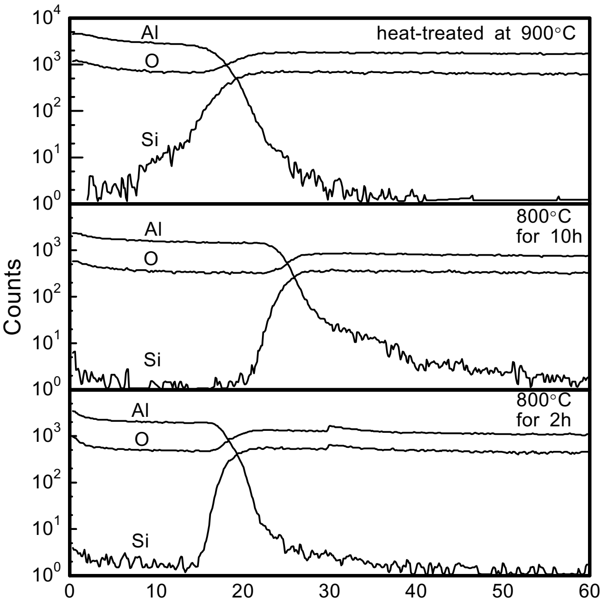

Figure 4 SIMS depth profiles for alumina coated quartz glass substrates treated at 800 (2 h), 800 (10 h) and 900°C. Sputtering was performed using a Cs^+ ion beam. Etching rate was 0.05–0.15 μm/h.

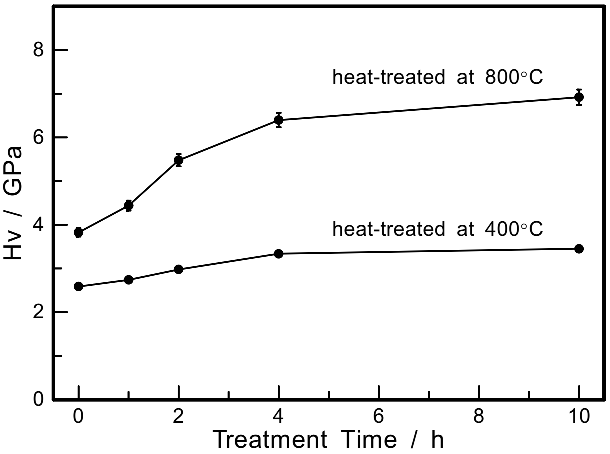

Figure 5 Effect of treatment time of alumina-coated quartz glass substrates on hardness of coating film. (treat-temperature: 400 and 800°C).

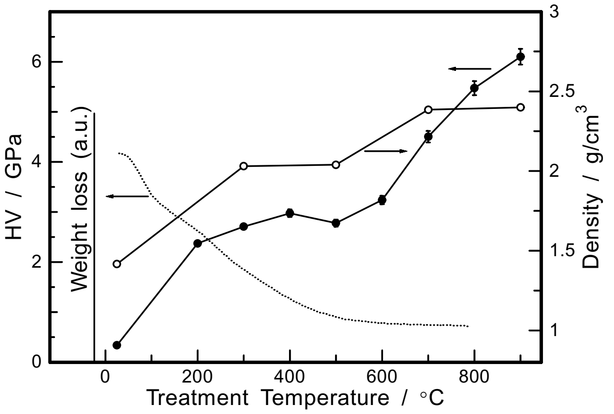

Figure 6 Effects of treat-temperature on Vickers hardness of alumina coated quartz glass, and the density and weight loss of alumina gel.

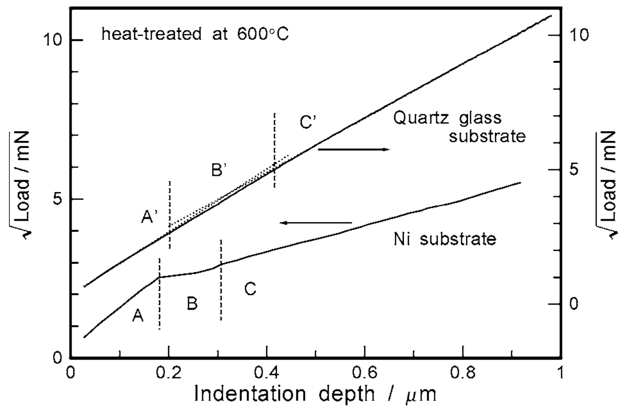

Figure 7 Indentation depth dependence of load for alumina coated substrate treated at 600°C. Dotted lines are fitting lines at regions of indentation depth from 0 to 0.15 and 0.6 to 1 μm.

indentation depth h (mm) under the test force F (N) using the equation [16]:

$$HU = \frac{F}{26.43h^2} \qquad (1)$$

HU represents the strength characteristics of the material with including both plastic and elastic deformation of the test part though HV represents without including elastic deformation. Therefore, if materials have a uniform HU, the square root of F will be in proportion to h. Typical relationships between the square root of F and h are shown in Fig. 7 for Ni and quartz glass substrates treated at 600°C. The dotted lines are the extrapolation of linear fitting lines at h ranges of from 0.05 to 0.15 μm and 0.7 to 0.95 μm, respectively, for the alumina coated on quartz glass substrate. As for the alumina coating on a Ni substrate, linear relations were clearly shown at each region of A, B and C. As for the alumina coating on a quartz glass substrate, regions A′, B′ and C′ were identifiable, although not clearly. Regions A and A′ correspond to alumina, regions B and B′ correspond to a layer of mixed oxide, and regions C and C′ correspond to a substrate. The thickness of the mixed oxide layer (as estimated from figure) is ca. 0.1 μm for the alumina coated on Ni substrate and ca. 0.2 μm for that coated on quartz glass substrate. Alumina coating on a permalloy (Fe-Ni alloy) substrate was also obtained by this method. And thick alumina film (1–3 μm) coatings on quartz glass substrate were attained by repeating the dipping process.

4. Conclusion

Alumina was well-coated on Ni and quartz glass substrates by using aqueous alumina sol derived from $AlCl_3 \cdot 6H_2O$. It appears that the creation of a sufficient coating was due to formation of an amorphous mixed oxide layer between the alumina and the substrate. The existence of an inter-oxide layer was suggested both from the hardness and the SIMS measurements.

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