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Effect of inorganic electrolytes on the rheological properties of the aqueous yttrium oxide/colloidal zirconia binder sols system

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Multivalent ions such as La^{3+}, Mg^{2+} function as surface-active counter ions for Y_2O_3 particles in aqueous solution. Due to the addition of these electrolytes, the solid content of Y_2O_3/ZrO_2 binder sols slurry was increased and the stability of the slurry was improved. Both ion valence and ion size of electrolytes added into the slurry are expected to influence the slurry rheological flow behaviour.

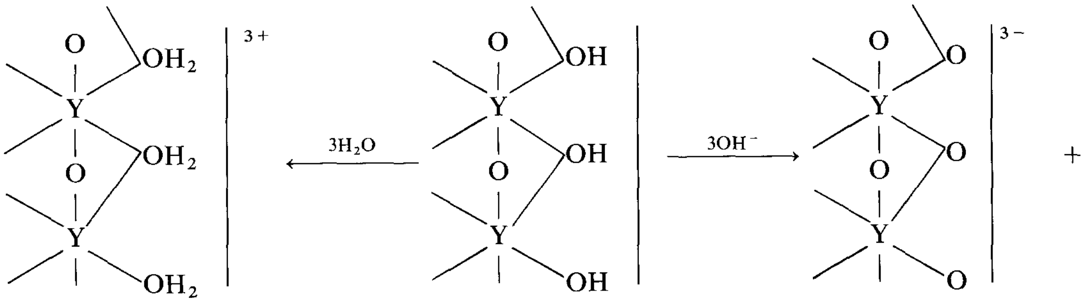
1. Introduction

Dip-coating is one of the most common methods in ceramic processing. This method has been used to prepare the ceramic shell mould for precision casting [1]. The development of a suitable slip for successful dip-coating is necessary to understand the rheological properties of the slip. The slips should satisfy the following requirements [2, 3]: (1) high solid content, (2) one should be able to redisperse slip sediment easily by shaking of stirring, and (3) the slip should have highly shear-thinning flow behaviour. In addition, the slip, should be stable (kept near constant viscosity) during a long period of ageing, this is also an important requirement for obtaining suitable dip-coating slurry. The main purpose of this paper is to present the effect of inorganic electrolytes on the stability of yttrium oxide/zirconia sols slurry.

Zirconia and yttrium oxide was adopted for the ceramic shell mould to obtain a thinner reactive layer between the shell mould surface and casting metal compared to that between other refractory shell moulds and casting metal [4]. But some difficulties exists in making stable yttrium oxide slurry in preparation of the ceramic shell mould. The major one is caking (i.e., serious flocculation) of slurry.

There are two reasons which cause caking of the Y_2O_3–ZrO_2 sols slurry. The first is the significant pH difference between Y_2O_3(pH $\simeq$ 11.10) and ZrO_2 particles (pH $\simeq$ 0.65) in aqueous solution. The second is that the surface charge of Y_2O_3 particles in water is opposite to that of ZrO_2 particles suspended in the sols. Because of this the surface of Y_2O_3 which has the corundum structure undergoes a charge transfer reaction due to the double layer. The H^+ or OH^- ion plays a potential-determining role, as suggested below [5, 6]:

$$O^-(\text{surface}) + H_2O \rightleftharpoons 2OH^-(\text{solution}) \quad (1)$$



(2)

However, the Y_2O_3 particles in water are so alkaline [7–9] and the surface charge of Y_2O_3 particles is negative. But the ZrO_2 sols have pH value of less than 2 and a positive charge of surface [10]. The mixture of Y_2O_3 powders and ZrO_2 sols will undergo a exothermic reaction, and both particles will attract each other to cake the slurry. Hence, the stable Y_2O_3–ZrO_2 sols slurry applied to dip-coating can't be easily prepared due to these reasons.

In the present study, the ZrO_2 sols were binding media. Some inorganic electrolytes were used in the present work to change the sign of the zeta potential of Y_2O_3 particles in aqueous Y_2O_3–ZrO_2 sols system such that the caking problem can be overcome.

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2. Experimental procedure

All experiments were performed with a high purity yttrium oxide (99.9% pure, MCI–Megon A.S., Norway). Typical mass spectrometric analysis(in p.p.m.): La < 0.1, Ce < 0.05, Pr < 0.1, Nd < 0.05, Sm < 0.05, Eu < 0.01, Gd < 14, Tb < 0.1, Dy < 0.1, Ho < 0.1, Er $\simeq$ 0, 5, Tm $\simeq$ 0.7, Yb $\simeq$ 1.4, Lu $\simeq$ 0.5). The surface area of the as-received powder was about 9 $m^2 g^{-1}$. The as-received powder was calcined at 1550 °C for 5 h before the preparation of slurry to decrease the basicity and zero point of charge of Y_2O_3-based slurry [11].

Slurries were prepared by mixing calcined yttrium oxide powders and colloidal zirconia sols($\simeq$ 20 wt % ZrO_2 nitrate stabilized, Remet Corp., U.S.A.). The pH of the as-received sols is less than 2. The particle size of the zirconia particles is about 0.002 μm. The zirconia particles have a positive charge. The sols have specific gravity of 1.32. HfO_2 is present to the extent of 0.4 wt % in the sols. Other metals such as Na, Fe, Ca and Mg are also presented and totalled less than 0.13 wt %. However, it is important that gelation of the sols will occur upon the addition of alkalis, multivalent ions such as sulphates or phosphates, or refractory materials such as MgO. The electrolytes $La(NO_3)_3 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$(> 99% pure, Merk Company, FRG) were used in this investigation.

Suspensions with 11 vol % Y_2O_3/89 vol % aqueous solution of various concentration electrolytes were mixed. After stirring for 1 h, the ZrO_2 sols were added into the suspensions to become the Y_2O_3/ZrO_2 sols slurry comprising of about 8.9 vol % Y_2O_3 and 0.88 vol % ZrO_2. The soft agglomerates were grown after stirring for about 5 min. A known amount of water was added into the suspension followed by thorough mixing of the slurry to redisperse it. The flow properties of the slurry were measured. Generally the working viscosities of slurry are no more 5000 mPa s^{-1} for dip-coating. Hence, a suitable amount of water was added into the slurry to adjust the viscosity of slurry to about 4500 mPa s^{-1} at 30 r.p.m. We use the viscosities of slurry as comparable datum. And the stability of slurries is based on comparing with the variations at 70 r.p.m.

Slurry rheological flow behaviours were determined using a Brookfield Model LV Rheoset Viscomet(Brookfield Engineering Laboratories, Inc., Massachusetts, USA.) shortly after mixing, 8 cm^3 slurry was used for each viscometry. The flow properties of the slurries were measured by changing shear rate (r.p.m.) from 30 to a maximum (< 250 r.p.m.) with a computer program which controlled the increasing rate (20 r.p.m. per 15 s). Unless otherwise noted, the viscosity results were reported at an LV4 spindle speed of 70 r.p.m. The slurries after measurement were stored in a desiccator at room temperature which was kept in about 55% relative humidity atmosphere provided by a saturated magnesium nitrate solution. After every 24 h ageing, the slurries were stirred at 60 r.p.m. for about 5 min, and the slurries' viscosities were measured again.

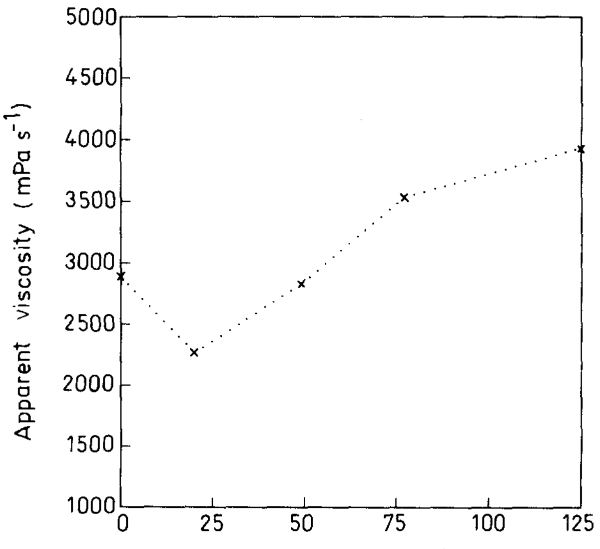

Figure 1 Plot of apparent viscosity versus ageing time for the slurry without electrolyte addition.

3. Results and Discussion

The stability of the slurry without electrolyte addition is shown in Fig. 1. It depicts that the variation of viscosities with ageing time, which is quite obvious when no electrolyte exist. Suitable electrolyte solutions were adopted to improve the stability of the slurry. On the basis of the double layer theory, the oxide particles suspensed in water will carry a surface charge. The surface charges of the particles of ZrO_2 and Y_2O_3 in aqueous solution are opposite to each other. When the sols and powders were mixed together, the exothermic reaction would happen and caking(i.e., serious flocculation) would occur. The report of Modi and Fuerstenau [13] indicated that multivalent ions would change the sign of zeta potential of particles. Therefore, the electrolytes such as $La(NO_3)_3$, $Mg(NO_3)_2$ were used in the present study to try to change the sign of zeta potential of Y_2O_3 powder in aqueous solution. The water addition was expected to decrease the thickness of double layer of ZrO_2 particles in sols and lower the difference of pH value between Y_2O_3 and ZrO_2 particles in aqueous solution. Hence, a known amount of water was added into the flocculated slurry to redisperse the particles in our slurry preparation. The effect of water addition on the concentration of electrolytes and solid content of the slurry have also been taken into account.

Figs 2a and b show the influence of electrolyte concentration on the solid content of slurry. These illustrations indicated that the solid content of the slurries were increased with the increment of the concentration of electrolytes until the maximums were reached. The maximums were at 0.18M and 0.07M for electrolytes $La(NO_3)_3$ and $Mg(NO_3)_2$, respectively. The difference between maximum points is believed to be due to the smaller radius of the Mg^{2+} ion in comparison with that of La^{3+} ion. The smaller one expects to pass across Y_2O_3 particles' double layer [13], so the concentration of $Mg(NO_3)_2$ at maximum is lower than that of $La(NO_3)_3$. Indeed, the trends shown in Fig. 2a and b are consistent with the results

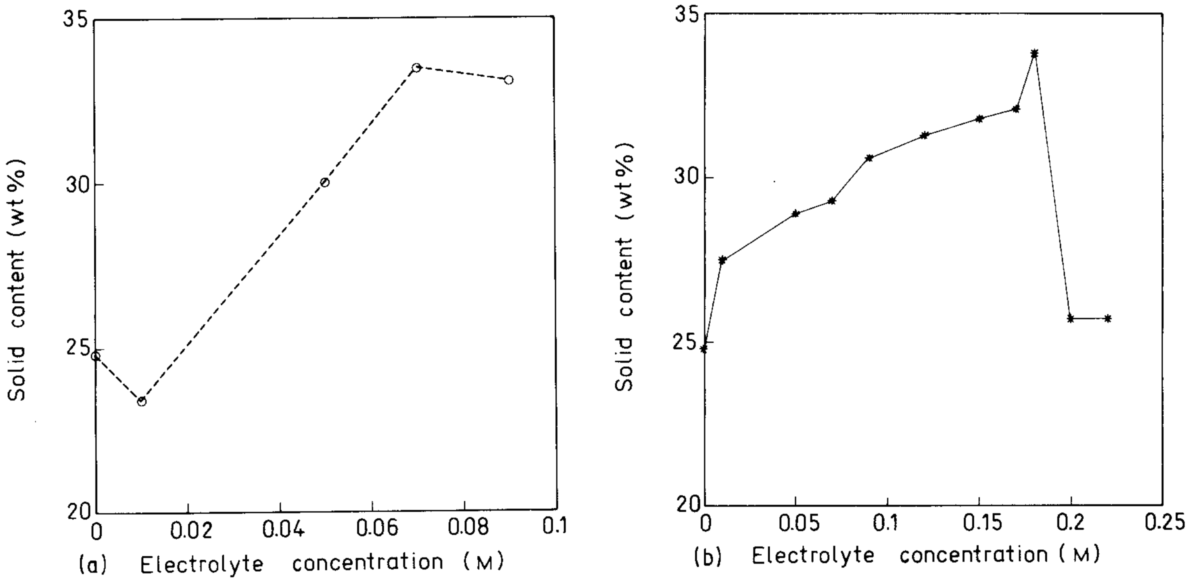

Figure 2 Plots of the solid content of the slurry versus different concentration of electrolytes, (a) $Mg(NO_3)_2$, (b) $La(NO_3)_3$.

of Modi and Fuerstenau's work. These would be indirect proof of the change of zeta potential of Y_2O_3 particles. The multivalent ions can decrease the zeta potential of the particles, consequently, the attractive force between Y_2O_3 and ZrO_2 particles is expected to decrease. When the sign of zeta potential is changed, the solid content of the slurry which exhibits a given viscosity value, 4500 mPa s^{-1}, reach the maximum. Adding higher concentration electrolytes did not increase the solid content at the given viscosity value. The possible explanation for this maximum is that owing to hydrolysis of the multivalent salts, polymeric hydroxides are formed in the solution. Since the hydrolysed solution will be slight acidic, the polymeric hydroxides will be positively charged. The positive units are adsorbed by the negative particle, and mutual flocculation occurs. Hence, the small amount of multivalent ion salts added into the slurry will flocculate the slurry. When an excess of salt is added, an excess of positive hydroxide units were adsorbed by the Y_2O_3 particles, and a stable slurry is obtained. Finally this stable slurry flocculates with a large excess of salt solution [14]. The abrupt decrease in solid content cannot be found at lower concentrations of $La(NO_3)_3$ electrolytes added into the slurry as shown in Fig. 2b. But the solid content at the given viscosity value indicated an abrupt decrease due to a small amount (< 0.01M) of $Mg(NO_3)_2$ being added into the slurry as shown in Fig. 2a. Therefore, the ion size is expected to be another important factor in addition to the valency of the ion, for changing the sign of zeta potential of particles.

Figs 3a and b show the viscosities of slurry versus different concentration of electrolytes, for different amounts of H_2O added into slurries. For each water addition, the viscosity increases with the initial increase of electrolyte concentration as shown in Fig. 3a. This increase is directly related to the flocculation, caused by hydrolysis of $Mg(NO_3)_2$ electrolyte. At $Mg(NO_3)_2$ electrolyte concentrations of $\geq$ 0.01M and

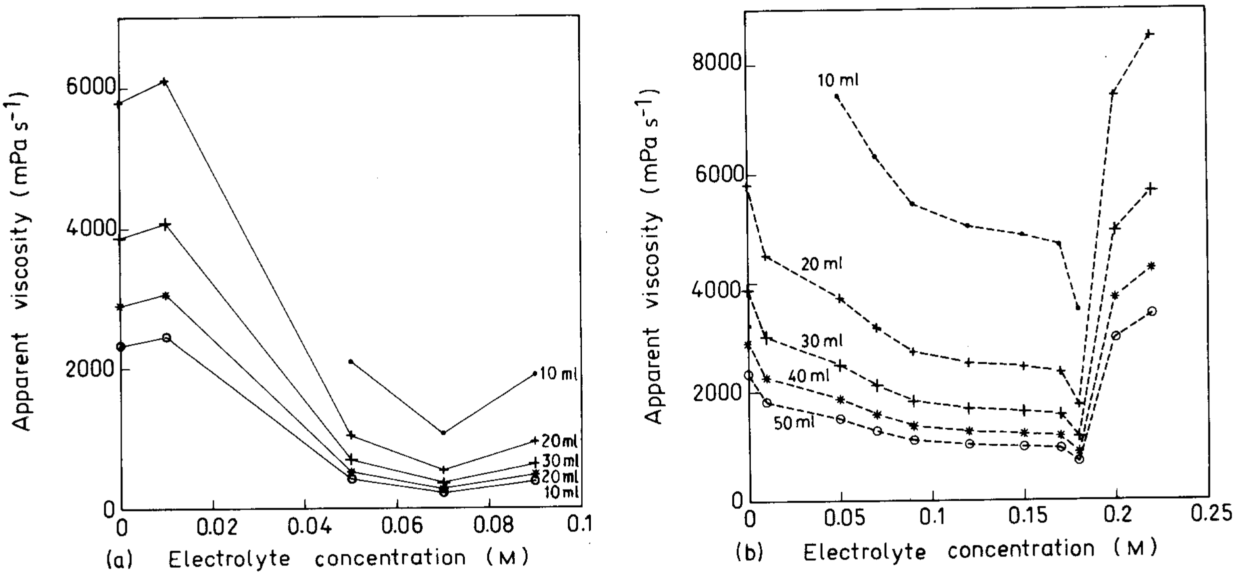

Figure 3 Plots of apparent viscosity versus different electrolytes concentrations for different amounts (as indicated) of water addition, (a) $Mg(NO_3)_2$, (b) $La(NO_3)_3$.

after the addition of $La(NO_3)_3$ electrolyte, the viscosities of the slurries gradually decrease. However, at an electrolyte concentration (0.07M and 0.18M for $Mg(NO_3)_2$ and $La(NO_3)_3$) respectively, at which minimum viscosities occur. With further increase of electrolyte concentrations, increased viscosities are believed to result from the flocculation due to large excess of electrolyte [14]. These results are consistent with the results, given in Fig. 2, and show the relationship between solid content at a given viscosity value and different concentration electrolytes added to the slurries.

The flow properties of the slurries at maximum solid contents are shown in Fig. 4a and b. The hysteresis curve of apparent viscosity against shear rate for 0.18M $La(NO_3)_3$ addition slurry is more reversible compared to that of 0.07M $Mg(NO_3)_2$ addition slurry. The rheological behaviour of $Mg(NO_3)_2$ addition slurry shows a high degree of thixotropy which is undesirable for the dip-coating process; while $La(NO_3)_3$ addition slurry shows a slightly thixotropy behaviour which is expected to produce a low viscosity during dip-coating, but a high viscosity will be achieved once the coating has been deposited so that the slurry can be solidified and allow uniform coverage of the coated surface [3].

However, it is worth noting that the electrolytes applied to the slurries should not be added into ZrO_2 sols to change the sign of zeta potential of ZrO_2 particles, because the sol particles will flocculate or agglomerate in the presence of electrolytes [15, 16]. Fig. 5 shows that 0.07M $Mg(NO_3)_2$ and 0.18M $La(NO_3)_3$ addition slurries were relatively stable (kept at near constant viscosity) during a long period of ageing compared to that without electrolyte additions as shown in Fig. 1. Obviously, the electrolytes are advantageous for the stability of slurry.

4. Conclusion

Multivalent ions such as La^{3+}, Mg^{2+} changed the sign of zeta potential of Y_2O_3 particles as observed

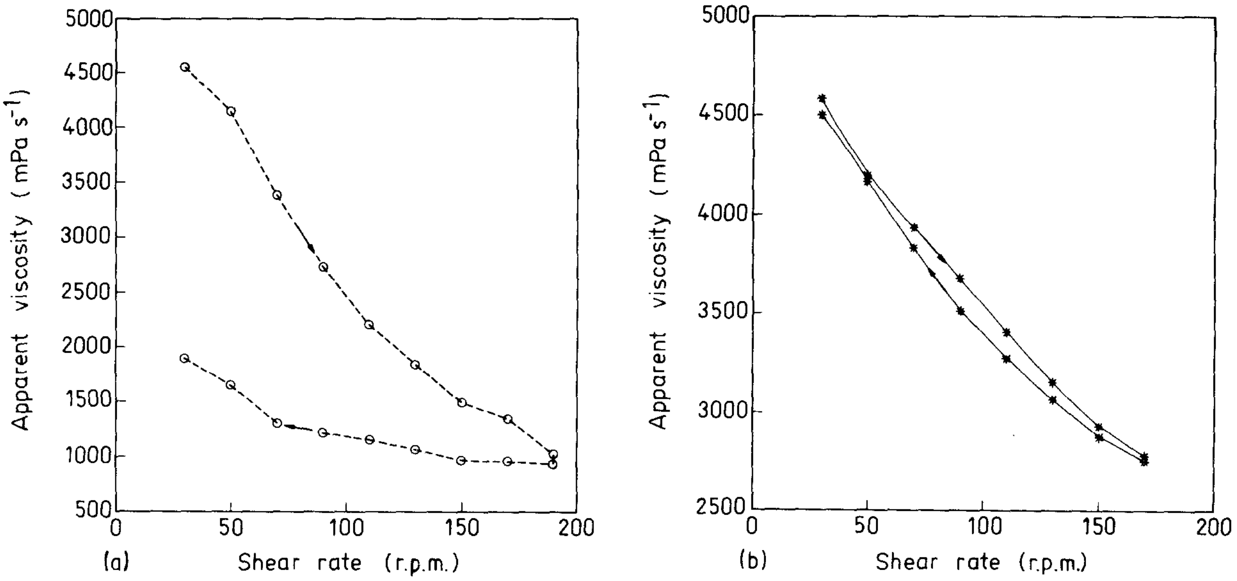

Figure 4 Plots of apparent viscosity versus shear rate for 0.07M (a) $Mg(NO_3)_2$ and (b) $La(NO_3)_3$ electrolyte addition.

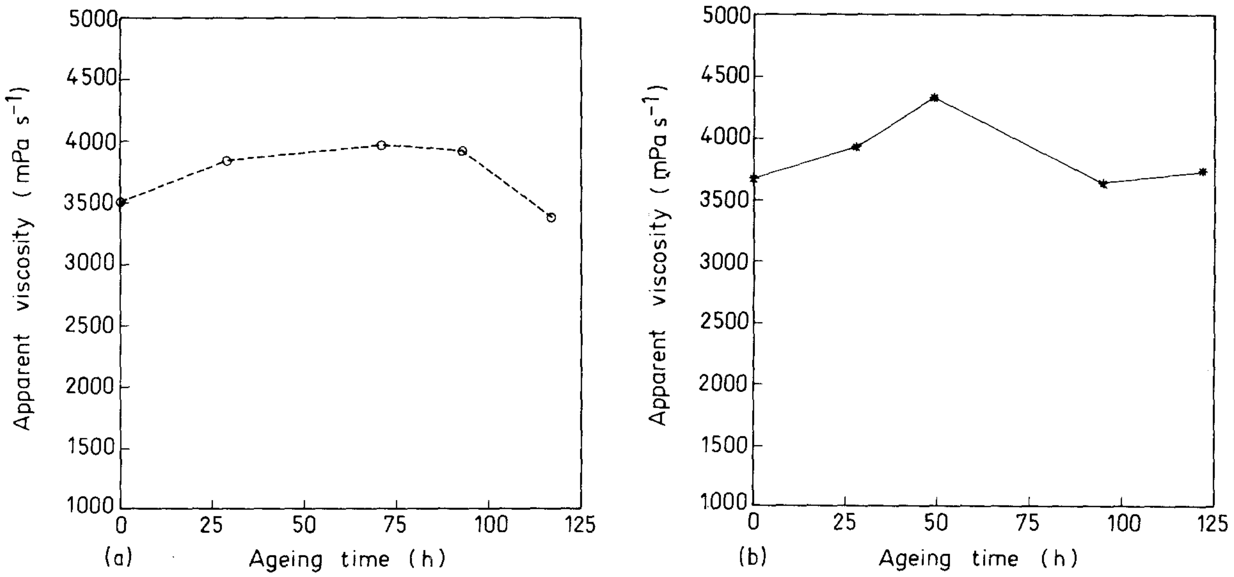

Figure 5 Plots of apparent viscosity versus ageing time for (a) 0.07M $Mg(NO_3)_2$ and (b) 0.18M $La(NO_3)_3$ electrolyte addition.

from the illustrations of experimental results. The solid content of the slurries increased with addition of electrolytes until reaching the maximum. Hence, the application of multivalent electrolytes in the ceramic processing is useful for enhancing the solid content in the slurry.

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