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The Preparation of Al_2O_3–ZrO_2 Sol-Gels from Inorganic Precursors

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Abstract

Al_2O_3–ZrO_2 sol-gel processing was achieved using basic metal salts as precursors. The sol-gel transformation occurs by polymerization of Zr^{4+} precursor at pH between 2 and 3. The concentration of precursor reagents, temperature of the mixture and addition of catalysts affect the gelation time markedly. The gel has some rudimentary structure, which is discussed.

Ausgehend von basischen Metallsalzen als Prekursoren wurden Al_2O_3–ZrO_2 Sol-Gele hergestellt. Die Sol-Gel-Umwandlung erfolgt durch die Polymerisierung des Zr^{4+}-Prekursors bei pH-Werten zwischen 2 und 3. Die Gelierdauer wird deutlich von der Stoffkonzentration der Prekursoren, der Temperatur des Gemisches und der Zugabe von Katalysatoren beeinflußt. Die etwas rudimentäre Struktur des Gels wird diskutiert.

La préparation de sol-gel Al_2O_3–ZrO_2 a été réalisée en utilisant des sels métalliques basiques comme précurseurs. La transformation du sol-gel se produit par polymérisation du précurseur Zr^{4+} à pH situé entre 2 et 3. La concentration du réactif, la température du mélange et l'addition de catalyseurs influencent remarquablement le temps de gélification. Le gel possède une structure rudimentaire qui est discutée dans cet article.

1 Introduction

Zirconia-toughened alumina ceramics have been widely studied in recent years. The dispersed ZrO_2 plays a dual role in strengthening the ceramic. First, the ZrO_2 dispersion prevents abnormal growth of large plate-like Al_2O_3 grains, the size of which constitute the strength-limiting factor in single-phase Al_2O_3. Secondly, the materials can be transformation-toughened when tetragonal (t) ZrO_2 is retained.[1–3] Yet the question is how to ensure the homogeneity of the dispersion down almost to the molecular level? Sol-gel methods offer the possibility of making initially ultra-homogeneous Al_2O_3–ZrO_2 composite materials.[4,5] Many papers have been published on sol-gel preparative routes,[6–8] but most routes require organometallic precursors, such as the alkoxides of Al and Zr. However, it is not economic to use such expensive reactants and, moreover, often not convenient because it is difficult to get rid of carbon residues from the organic ligands in the course of firing.[4] The main objective of the present investigation was to apply sol-gel methods to the Al_2O_3–ZrO_2 system using readily available inorganic precursors.

The precursors used are commercially available metal salts. These are extensively hydrolyzed in aqueous solution. It is well known that most transition elements hydrolyze spontaneously and, moreover, that the hydrolysis products can be polymerized by controlling the solution pH.[9] Zr^{4+} ions are only soluble in strongly acidic aqueous solutions[9,10] because they are readily joined by —OH— bridges to form polymeric ions or chains in which the Zr^{4+} ions are coordinated by seven or eight oxygen atoms. As the acidity decreases, slow irreversible hydrolysis occurs accompanied by an increase in the degree of polymerization and perhaps a change in polymer structure. This structure changes from one with predominantly OH^- bridges to one which is more extensively O^{2-} bridged. The polymer thus formed can contain a large number of metal ions ranging between ~10 and at least 100. Al^{3+} ions also can be hydrolyzed extensively to form solutions containing polynuclear hydroxide complexes, especially above pH ~3.[9] Al^{3+} normally has a solution hydration number of 6 although exceptions occur. For example, a large polynuclear species, which seems to dominate supersaturated solutions between pH 3·5 and 4·5, is postulated to be

$Al_{13}O_4(OH)_{24}^{7+}$;[4,11] it contains tetrahedral and octahedral Al in the ratio 1:12.

Al^{3+} solutions, because of their general lower acidity, can also be used to accelerate polymerization of Zr^{4+} ions and gelatinization of mixed Al–Zr products can occur under proper conditions. Therefore, homogeneous mixed solutions can be used as the precursors for inorganic sol-gel processes. In the present investigation, the formation of inorganic sol-gels is explored and the structure and processing properties of the resulting gels have been studied.

2 Experimental

Different solutions containing basic Al^{3+} and Zr^{4+} salts were prepared. The main precursors were zirconia sol, which, upon analysis, was found to correspond to $Zr(OH)_{2·95}(NO_3)_{1·05}$[12] and $Al_2(OH)_5Cl$ (from Albright & Wilson Ltd, West Oldbury, Warley, England) or reagent-grade hydrated aluminium nitrate. The solutions were 3·65 and 6·17M in Zr and Al, respectively, and are referred to as ZrO_2 and Al_2O_3 sols.

Polymerization is initiated by mixing the two solutions in appropriate ratios. Viscosity changes occurring during the sol-gel transformation were examined using a Brookfield-Lvt (Neslab Instruments, Newington, NH, USA) micro-viscometer and the pH changes were followed with a PT1-6 universal digital pH meter. X-Ray diffraction (XRD) data were obtained with a Philips automated powder diffractometer system PW 1710, using CuK_α radiation, 40 kV and 40 mA. Weight loss and thermal characteristics were examined by thermogravimetry (TGA) and differential thermal (DTA) analysis. For both TGA and DTA, the samples were heated at 10°C/min in a free-flowing oxygen atmosphere in a Stanton (London, UK) STA 781 simultaneous DTA/TGA instrument.

3 Results and Discussion

3.1 Gelation and composition of sol-gel

The gelation times at constant temperature depend strongly on the concentration of the solution or sol, due to the key parameters of reaction kinetics: $V = k[Zr^{4+}]^m[Al^{3+}]^n$, where [ ] refers to molar concentrations of the designated species and V is a reaction rate parameter. The gelation time, t_g, is the inverse of the rate parameter, V. In general, the lower the concentration of reactants in the system, the longer will be its gelation time.

The variables which affect gelation times can be described as follows. At constant molarities of the two components increasing the content of Al_2O_3 sol in the mixture shortens the gel time; Fig. 1 shows data on gel time as a function of volume ratio of the two sols at 20°C. The greater the content of Al_2O_3 sol or H_2O, or both, in the initial mixture the more difficult it becomes to densify the resulting gel during subsequent processing. The Al salt increases the solution pH and consequently more Zr appears as hydroxide, which inhibits the polymerization of Zr^{4+} and thereby impedes formation of a gel network. When the content of Al_2O_3 or H_2O exceeds a critical point, gels can no longer be obtained. The solubility product constant of $Zr(OH)_4$ is about 10^{-56}, so it is easy to precipitate zirconium hydroxide even at the low pH (2–3) at which polymerization and gel formation occur. However, hydroxide precipitation is undesirable.

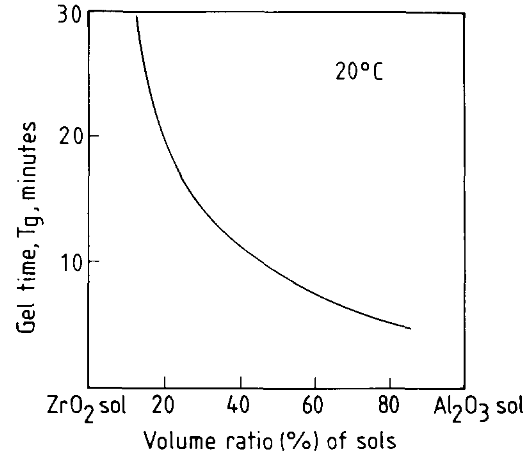

Fig. 1. Gelation time and the composition of sol-gel.

Gelation time also strongly depends on basicity, which is partly a function of the different precursors used, such as chlorides or nitrates, e.g. $Al(OH)_x(NO_3)_{3-x}$ or $Zr(OH)_x(NO_3)_{4-x}$. Thus, the nature of the anion also affects gel formation. This can be controlled; for example, the ratio of OH^- to NO_3^- was regulated by partial denitration of the precursor without affecting the stability of the sol.

Tables 1 and 2 show that the higher the pH of the precursors, the shorter the gelation time is. Undoubtedly, gelation is initiated by OH^- activation

Table 1. Gelation time of ZrO_2 sol with $Al(OH)_x(NO_3)_{3-x}$[a]

x	0·914	0·942	1·084	1·599	2·116	2·223
pH	1·985	2·128	2·150	2·740	3·133	3·570
t_g	More than one month			160[b]	39[b]	31[b]

[a] ZrO_2 sol:$Al(OH)_x(NO_3)_{3-x}$ (2·11M) = 3:1 (by volume).
[b] In minutes.

Table 2. Gelation time of $Zr(OH)_x(NO_3)_{3-x}$ with $Al_2(OH)_5Cl$[a]

x	2·605	1·929	1·338
pH	0·980	0·390	<0
t_g(min)	12·5	24·7	33·8

[a] $Zr(OH)_x(NO_3)_{3-x}$ (2·02M):$Al_2(OH)_5Cl$ = 3:1 (by volume).

Table 3. The gelation time at presence of different additions

	H_2O blank	Catalyst							
		H_2SO_4[a]	HNO_3	HCl	HF	NH_4OH	KCl	H_2O_2	HAc
t_g(min)	9·2	4·0	8·5	9·5	14·7	15·2	16·5	19	29

[a] Milky precipitate appears upon addition.

because the polymerization of Zr^{4+} proceeds more quickly at high pH.[4]

Acid catalysts are often used in sol-gel processing to increase the rate of hydrolysis and polymerization, and the gelation time of this system can also be changed by the presence of acidic catalysis. Table 3 shows results for a typical precursor composition: ZrO_2 sol; Al_2O_3 sol; catalyst (each solution 2M), mixed 3:1:1 (by volume). These are contrasted with a control, which was diluted by the volume of distilled water equivalent to that which was present in the catalyst solution.

Calculations based on the partial charge model assist in checking the feasibility of proposed polynuclear structures.[14] Briefly, each constituent atom or group is assigned some charge, δ_i, which may be either positive or negative. Charge transfer will occur between constituent species when the mean electronegativity becomes equal to the effective electronegativity of the individual species. The partial charge is given by

$$\delta_i = (\bar{X} - X_i^0)/k\sqrt{X_i^0} \quad \text{and} \quad \bar{X} = \frac{\Sigma_i P_i \sqrt{X_i^0} + kZ}{\Sigma_i (P_i/\sqrt{X_i^0})}$$

where $\bar{X}$ is the mean electronegativity of all constituent atoms, P_i the stoichiometry of the ith atom in the formula, Z the total charge of ionic species, X_i^0 the electronegativity of the neutral atom, and k a constant for Pauling electronegativities (k = 1·36).[12]

Calculations based on this model, shown in Table 4, are in agreement with the observations. Zr has a high positive charge and its full coordination is not readily satisfied by neutral groups. Therefore, nucleophilic addition of anions occurs. Table 4 shows that most of the hydroxo and acidic anion groups in the postulated species remain negatively charged and hence retain some nucleophilic character, with the result that polycondensation can still occur.

3.2 Gelation time and temperature

The effect of temperature on gelation time is shown in Fig. 2. These data are typical: as the temperature decreases, the gelation time increases very markedly; the relationship is exponential. Since temperature affects the rate of reaction (i.e. polymerization) an activation energy, E, of polymerization can be calculated from the Arrhenius equation, $k = A\exp(-E/RT)$. The calculated activation energy is about 76·9 kJ/mol (18·4 kcal/mol), using a linear regression treatment of the data. This low activation energy implies that the process occurs rapidly and may also occur at all temperatures at which the aqueous phase persists.

During gelation the liquid phase pH value changes, as shown in Fig. 3. The pH increases rapidly at first but gradually slows down as reaction

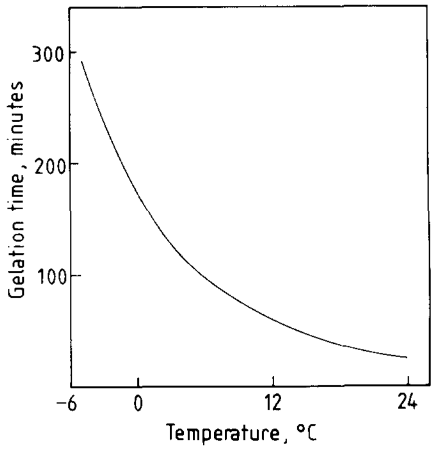

Fig. 2. Gelation time and temperature. Composition: ZrO_2 sol: Al_2O_3 sol = 3:1 (by volume).

Table 4. Partial charge calculations for different Zr salts[a]

Precursor species	M	δ(M)	δ(X)[b]	δ(OH)
$[Zr(OH)_2(NO_3)(OH_2)_2]^+$	2·791 6	0·972 1	−0·240 9	0·036 0
$[Zr(OH)_2(SO_4)(OH_2)_2]$	2·667 2	0·891 6	−0·148 3	−0·019 6
$[Zr(OH)_2Cl(OH_2)_2]^+$	2·623 2	0·863 1	−0·077 7	−0·039 2
$[Zr(OH)_2F(OH_2)_2]^+$	2·668 6	0·892 5	−0·519 8	−0·018 9
$[Zr(OH)_2CH_3COO(OH_2)_2]^+$	2·588 0	0·840 3	0·015 3	−0·054 9
$[Zr_4(OH)_8(OH_2)_{16}]^{8+}$	2·691 3	0·907 2	—	−0·008 8

[a] All atomic electronegativities on the Pauling scale are taken from Ref. 12, except $X_{Zr}^0 = 1{\cdot}29$ from Ref. 11.

[b] X is the appropriate value for the acidic anion group.

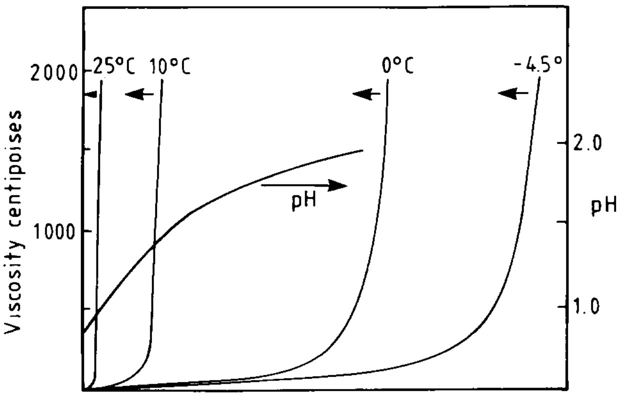

Fig. 3. Viscosity, pH and time at different temperatures (same composition with the sample in Fig. 2).

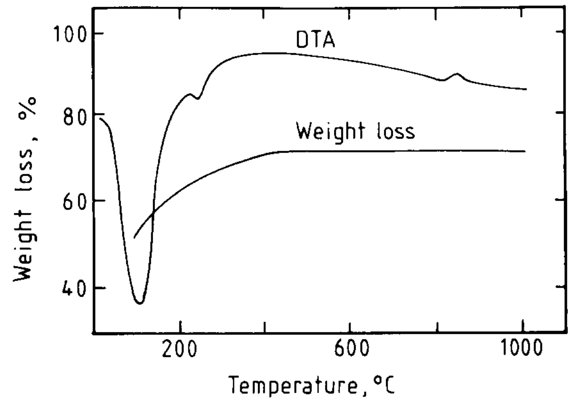

Fig. 5. Thermal analysis of gel. Gel composition and ageing time are the same as for sample in Fig. 4.

proceeds. This change occurs because OH^- ions are released during the course of the polymerization reaction.

3.3 Change in the sol-gel transformation of viscosity, XRD spectra and the thermal behaviour of the gel

During gelation the sample viscosity increased progressively at early stages. The rate of initial increase was low, but beyond some critical value of it, it increased sharply. Figure 3 shows typical curves obtained by isothermal ageing at various temperatures between −4·5 and 25°C. Temperature will, of course, significantly affect the time taken to reach the gel point. The rate at which Zr is transformed to high polymers is mainly responsible for the changes to viscosity.

XRD patterns, shown in Fig. 4, disclose that the X-ray diffraction pattern has several features: three broad regions of diffraction effects characteristic of very poorly ordered materials are observed between 15° and 60° 2θ (CuK_α radiation). Although the gel is disordered, it has a rudimentary structure which is preserved essentially unchanged during drying at temperatures up to ~300°C. Above 300°C the pattern increasingly resembles that of ZrO_2, although the eventual transformation to crystalline ZrO_2, between 700 and 800°C, is sharp and apparently discontinuous. Nucleation is perceived to be a discrete step in the gel to crystal transition.

Thermal analysis, shown in Fig. 5, disclosed that the gel loses most of its water at temperatures less than 120°C. This is regarded as 'free water', loss of which does not significantly affect the gel network, although it results in an increase in porosity. The remaining water is lost in the range 200–300°C, and is probably partly structural and partly gel network water. Above 500°C the gel is essentially completely desiccated; further weight loss between 500 and ~1000°C is only about 1%. A small but characteristic endotherm at ~900°C arises from crystallization.

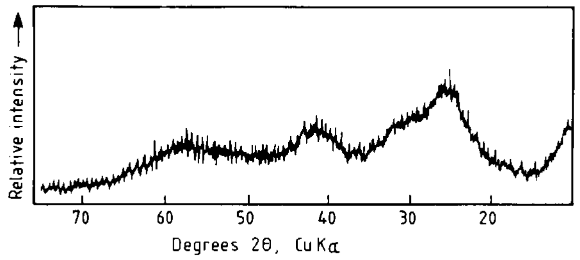

Fig. 4. XRD spectra of gel. ZrO_2 sol:Al_2O_3 sol = 3:1 (by volume), ageing for one day at 20°C.

4 Conclusions

Inorganic Al_2O_3–ZrO_2 sol-gels are easily made using basic metal salts as precursors. The mechanism of sol-gel transformation is the polymerization of Zr^{4+} at a pH conditioned by the Al^{3+} solution and can thus be controlled by the concentration of Al, the solution volume and, for nitrate precursors, the OH^-/NO_3^- ratio. Additionally, solution temperature strongly affects the gel time. The lower the basicity of the precursors, or the lower the temperature, the longer the gelation time will be. Application of the partial charge model, together with solution speciation concepts, has been used to predict conditions favourable to gelation. The gel is basically amorphous, but has some rudimentary structure with respect to nearest-neighbour arrangement.

Acknowledgement

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