

## SYNTHESIS OF AN ALUMINA COATING FROM CHELATED ALUMINIUM ALKOXIDES

Rüdiger NASS<sup>1</sup> and Helmut SCHMIDT

Fraunhofer-Institut für Silicatforschung, Neunerplatz 2, D-8700 Würzburg, FRG

Chelating agents, such as acetylacetone (AcAcH) and ethylacetoacetate (EAA) are used to avoid the undesirable precipitation of gelatinous aluminum hydroxides during hydrolysis of aluminum-sec-butoxides,  $\text{Al}(\text{O}i\text{Bu})^s$ . This procedure leads to alumina sols with particle size distributions in the range of 1 to 15 nm which depend on the type of chelating agent as well as on the molar  $\text{Al}(\text{O}i\text{Bu})^s_3$ /chelating agent ratio. Generally, EAA leads to particles smaller than AcAcH. Because of the small particle size, gel powders are X-ray amorphous and do not crystallize at temperatures  $< 750^\circ\text{C}$ . Crystallization of  $\alpha$ -alumina starts between 950 and  $1000^\circ\text{C}$ . Complete transformation to  $\alpha$ -alumina is achieved between 1050 and  $1100^\circ\text{C}$ . Coating experiments with different sols on silica glass lead to nearly crack-free dried gel films with AcAcH system. An ultrafine, dense microstructure is obtained.

### 1. Introduction

Chemical modification of metal alkoxides with chelating agents has gained an increasing interest in sol-gel processing, since the processing properties of metal alkoxides can be improved drastically by this method [1-11]. It has already been shown that aluminum alkoxides react with chelating agents, such as acetylacetone or ethylacetoacetate, giving rise to new molecular precursors [12,13]. Hydrolysis and condensation of these compounds have been studied [13]. Depending on the nature of the chelating agent precipitation of gelatinous alumina during hydrolysis can be completely avoided. In addition, condensation as well as agglomeration can be controlled, leading to a pentameric chelated aluminum hydroxide with new properties.

This paper reports on further investigations of chelated aluminum hydroxides. The main interest was the influence of preparation condition on the particle size distribution in solution as well as on the crystallization behavior of gel powders. In addition, coating experiments on silica glass were performed to obtain transparent alumina coatings.

### 2. Experimental

To a solution of aluminum-sec-butoxide,  $\text{Al}(\text{O}i\text{Bu})^s_3$ , (2 mol/l) of iso-propanol acetylacetone (AcAcH) or ethylacetoacetate (EAA) in different molar ratios was added, giving clear solutions. Hydrolysis of the modified precursors was performed with stoichiometric quantities of water in relation to the number of hydrolyzable ( $\text{O}i\text{Bu}^s$ )-groups. In the case of precipitation (AcAcH), the pH was adjusted to 4.5 with concentrated nitric acid, leading to clear solutions. The experimental procedure is shown in detail in fig. 1 and the reaction conditions along with the experimental

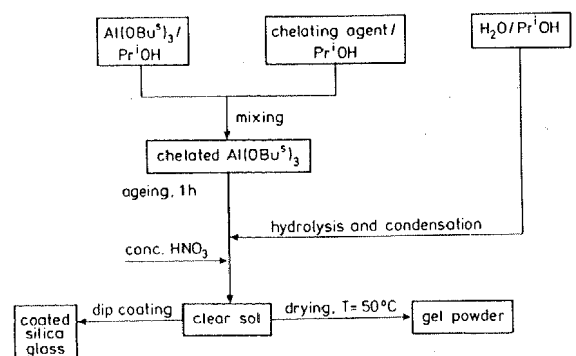


Fig. 1. Flow chart for the preparation of chelated aluminum hydroxide sols.

<sup>1</sup> Present address: INM gem. GmbH, Universität des Saarlandes, Gebäude 43, D-6600 Saarbrücken, FRG.

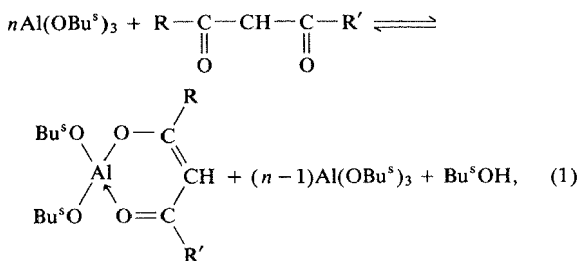
observation during hydrolysis are summarized in table 1.

Particle size distributions were measured by dynamic light scattering (Malvern 4700). The generation of crystalline alumina phases was investigated between 100 and 1100 °C, using bulk materials and X-ray diffraction. The coating properties of different sols were tested on fused silica which were annealed up to 1100 °C after drying at 25 °C for 2 h. The development of microstructure during heat treatment was followed by SEM.

### 3. Results and discussion

#### 3.1. Sol preparation and characterization

The reaction of aluminum-sec-butoxide,  $\text{Al}(\text{O}i\text{Bu})_3$ , with acetylacetone (AcAcH) and ethylacetoacetate (EAA) has been described recently and leads to chelated  $\text{Al}(\text{O}i\text{Bu})_3$  [13]. Following the procedure described there, different precursors were prepared, which were hydrolyzed with stoichiometric quantities of water with regard to the number of hydrolyzable (O*Bu*<sup>s</sup>)-groups. The chelation and hydrolysis reactions can be written as follows. For chelation:



where R, R' is  $\text{CH}_3$  (AcAcH), R is  $\text{CH}_3$ , R' is  $\text{OC}_2\text{H}_5$  (EAA) and  $n = 1-4$ .

For hydrolysis:

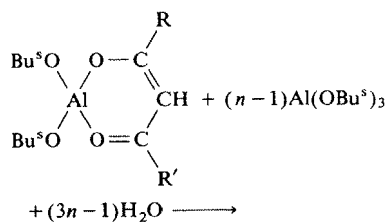
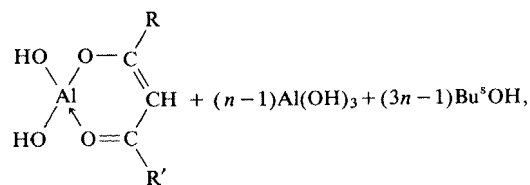


Table 1

Reaction conditions and experimental observations for the preparation of chelated aluminum hydroxides

Sample no.	Chelating agent (ligand)	Molar ratio		Product after hydrolysis
		$\text{Al}(\text{O}i\text{Bu})_3/\text{ligand}$	$(\text{O}i\text{Bu})_2/\text{H}_2\text{O}$	
A1		1	2	precipitate
A2	AcAcH	2	2.5	precipitate
A3		4	2.75	precipitate
E1		1	2	clear solution
E2	EAA	2	2.5	clear solution
E3		4	2.75	precipitate



(2)

where  $n = 1-4$ .

The different molar  $\text{Al}(\text{O}i\text{Bu})_3/\text{chelating agent}$  ratios,  $n$ , used for sol preparation give rise to different precursors. Assuming that  $\beta$ -dicarbonyl compounds act only as chelating agents and not as bridging ones, it is obvious (eq. 1) that a fully chelated  $\text{Al}(\text{O}i\text{Bu})_3$  is obtained only when  $n = 1$ . Molar ratios greater than 1 lead to mixtures of chelated and non-chelated species. From this point of view, it could be expected that the hydrolysis behavior of the precursor solutions differ from each other. Whereas hydrolysis of sample E1 and E2 results in clear sols, precipitates occur for the samples A1–A3 and E3. For either A1 or A2, precipitation could be avoided by adjusting the pH to 4.5. In contrast, samples A3 and E3 gave only translucent sols after the addition of nitric acid which is similar to the peptisation of boehmite in aqueous solution [14].

The influence of reaction conditions and of chelating agents on the sol properties was studied by dynamic light scattering. Figure 2 shows particle size distributions of the sols. Two important points can be established from fig. 2: first, chelation of  $\text{Al}(\text{O}i\text{Bu})_3$  leads to sol particles with diameters  $< 20$  nm. Second, the particle size depends on the molar  $\text{Al}(\text{O}i\text{Bu})_3/\text{chelating agent}$  ratio as well as on the reaction conditions. Using EAA as the chelating agent the particle size decreases with

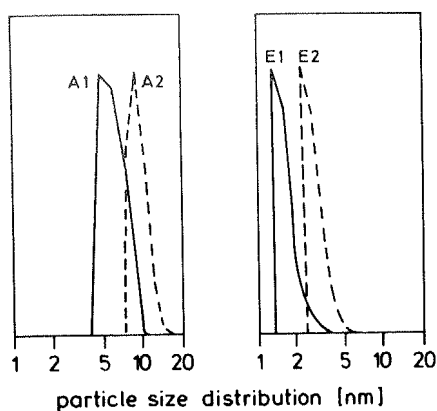


Fig. 2. Particle size distribution in different sols.

an increasing quantity of EAA and is just halved going from E2 to E1. In contrast, the influence of the molar  $\text{Al}(\text{OBU})_3/\text{chelating agent}$  ratio on the particle size for the AcAcH systems is not so pronounced compared with the EAA system. Only slight differences were found for the samples A1 (3–11 nm) and A2 (5–16 nm). In addition, EAA leads to particles smaller than AcAcH. These results clearly display the role of reaction conditions and the influence of the chelating agent on the particle size distributions and can be understood from the standpoint of colloidal chemistry.

The effect of the chelating agents is a twofold one: it modifies the alkoxide by occupying a site for condensation, thus leading to different molecular structures of the oligomers. In addition to this, the oligomers become more soluble than uncomplexed 'pure inorganic' hydroxides and higher solid contents can be obtained from complexed alkoxides. On the other hand they act as a surfactant, which prevents agglomeration. The latter assumption is in close agreement with the high stability of sols E1 and E2 which do not gel during aging for more than three months. Since these sols are prepared under neutral conditions, a mainly sterical sol stabilization can be concluded, which is caused by the bulky hydrophobic ethylacetoacetate anion. In contrast to this, the sols A1 and A2 lead to translucent gels within a few days indicating a poorer stabilization effect of AcAcH as complex former.

The addition of 2 wt% hydroxypropylcellulose (HPC) to A2 shifts the particle size distribution to

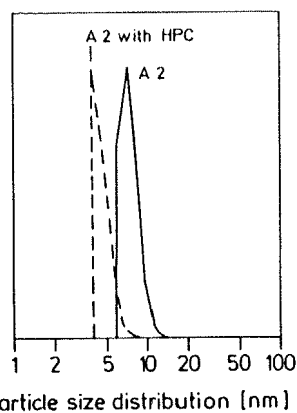
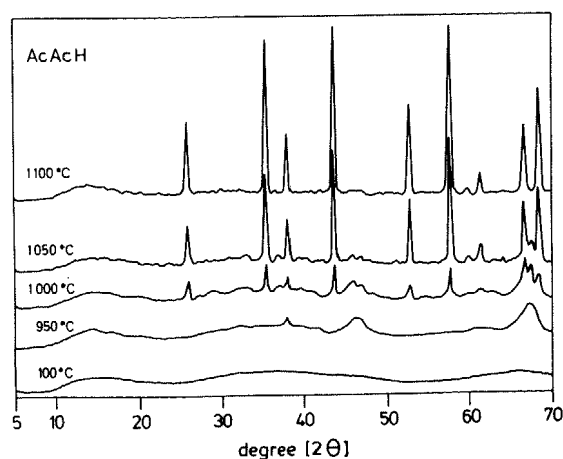


Fig. 3. Particle size distribution in the sol A2 with and without hydroxypropylcellulose.

smaller particle size (fig. 3), indicating the original sol A2 was agglomerated. The appearance of agglomerates may be due to the content of an amount nitric acid sufficient to neutralize hydroxyl groups or acetylacetonate anions and thereby causing a destabilization of the sol by shifting the  $\zeta$ -potential to the isoelectric point. Addition of more  $\text{HNO}_3$  leads to reprecipitation.

### 3.1.1. Crystallization

The crystallization behavior of the dried gel powders was measured between 100 and 1100 °C by X-ray diffraction. Figures 4 and 5 show X-ray diagrams of the samples A2 and E2.

Fig. 4. X-ray diagrams of  $\alpha$ -alumina formation in the acetylacetonate system.

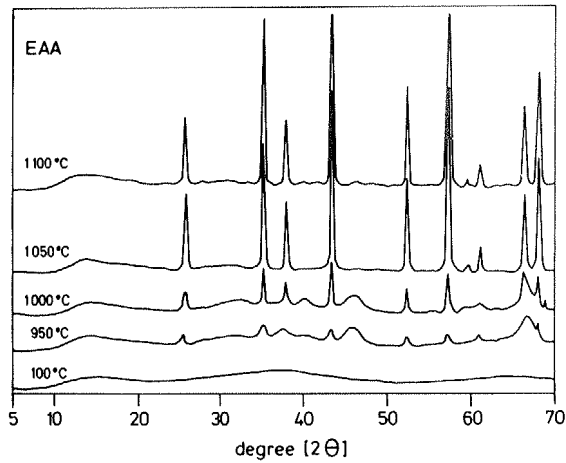


Fig. 5. X-ray diagrams of  $\alpha$ -alumina formation in the ethyl-acetoacetate system.

The dried gel powders are X-ray amorphous and did not crystallize up to 750 °C after heating for 2 h. Above this temperature two broad peaks of low intensity were detected which can be attributed to metastable alumina phases ( $\delta$ ,  $\theta$ ). However, the intensity of these peaks increased only slightly during further calcination. The first peaks of  $\alpha$ -alumina appeared at 950 °C (E2) and 1000 °C (A2), respectively, after heating for 2 h. Complete transformation to  $\alpha$ -alumina was achieved between 1050 and 1100 °C. Similar results were obtained for E1 and A1. Compared with other sol-gel synthesis of  $\alpha$ -alumina [15,16], e.g.  $\alpha$ -alumina crystallization from boehmite gels needs 1150 °C for 2 h, the crystallization temperature of  $\alpha$ -alumina from chelated aluminumhydroxides is rather low and often only be obtained by seeding [17]. Since reaction times do not differ, one can conclude a lower activation energy for  $\alpha$ -alumina crystallization from the amorphous alumina compared with metastable phases. This can be understood from a structural point of view indicating a structure for the amorphous state more similar to  $\alpha$ -alumina than for metastable phases. However, this assumption has to be proved by further experiments.

### 3.1.2. Coatings

The different sols show interesting properties for the preparation of dense and crack-free trans-

parent alumina coatings. A low temperature for  $\alpha$ -alumina formation, a very small particle size, a solid high content of about 0.75 mol/l which is higher compared with conventionally used sols and an adjustable viscosity range (by dilution) of about 2 mPa s to 10 mPa s due to the organic modification are observed. Coatings from these sols were made by dip coating on fused silica plates ( $2 \times 5 \text{ cm}^2$ ). The wet films were dried at 25 °C for 2 h and then, according to the results of the X-ray studies, calcined up to 1100 °C within 12 h giving a transparent alumina coating about 1  $\mu\text{m}$  thick. This relatively fast procedure was chosen in order to test if the properties of the sols mentioned above lead to a crack-free drying and densification behavior.

From coating experiments, it was found that the AcAcH system exhibits better coating properties than the EAA system. Whereas gel films obtained from sols E1 and E2, respectively, cracked

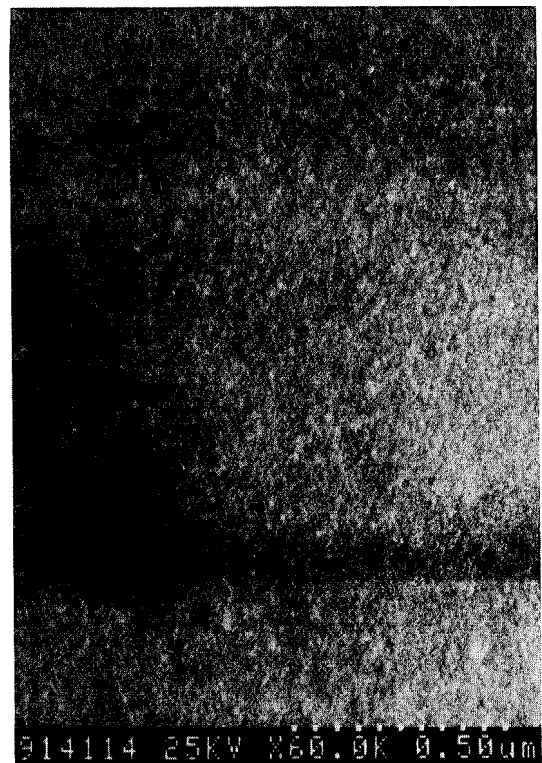


Fig. 6. SEM micrograph of an  $\alpha$ -alumina coating densified at 1100 °C (thickness  $\approx 1 \mu\text{m}$ ).

off during drying, coatings from sol A1 or A2 showed better adhesion to fused silica. The dried films were about 2  $\mu\text{m}$  thick and showed only a few microcracks. These differences can be understood in view of the sol composition.

As pointed out before, a mainly sterical stabilization can be assumed in the EAA system. Stabilization is caused by the bulky chelating agent, which increases the hydrophobicity of the sol particles. The hydrophobic character of the sol particles was proven by solubility tests using dried gel powders [13]. It was shown that a gel powder of the composition E1 gives a clear colloidal solution in toluene with particle sizes around 2 nm and a gel powder of the composition E2 can be easily dispersed in toluene leading to a translucent sol. In contrast, gel powders of A1 and A2 are not dispersible in toluene. Since the surface of silica glass is hydrophilic, no adhesion of hydrophobic sol particles can be achieved and the gel films crack off during drying. In contrast, acidification of sols A1 and A2 can lead to a partial neutralization of hydroxyl groups or acetylacetonate anions causing charged particles. The influence of the bulky chelating agent is reduced by this process and leads to improved adhesion. In addition, only a few cracks occur during drying of the wet gel film, showing the positive effect of the organic modification of the precursor. Figure 6 shows the microstructure of a coating (A2) calcined at 1100°C for 1 h. The fired coating is transparent and exhibits a very fine microstructure with particle grain size in the range < 10 nm.

These results directly display the advantage of the sol consisting of very small particles which did not grow during calcination. According to the X-ray studies it is known that the coating is pure  $\alpha$ -alumina. Some microcracks were found and this may be due to the non-optimized coating technique as well as the very fast drying and densification procedure. However, compared with alumina coatings obtained from pure aluminumalkoxides, the sol A2 gives a better microstructure.

#### 4. Conclusion

Chelation of aluminum-sec-butoxide leads to improved processing properties of the alkoxide during hydrolysis and condensation. Sols with particle size distributions in the range of 2 to 15 nm can easily be prepared. Agglomeration of these small particles is prevented by the chelating agent and gives rise to new synthesis methods of nanosized materials. Alumina coatings from these nanosized sols show an ultrafine microstructure. This shows clearly the potential of chemical modification of metal alkoxides for improving properties of sol-gel derived materials.

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