A New Way to Spinnable Sols Derived from Modified Aluminumalkoxides

Code: EP6

W. GLAUBITT, D. SPORN AND R. JAHN

Fraunhofer Institut für Silicatforschung, Neunerplatz 2, D-97082 Würzburg, Germany

Abstract. The preparation of spinnable sols has been developed to obtain a new type of sol-gel derived pure alumina fiber. The starting material was aluminum sec-butoxide, which was modified in a first step with glycolether, e.g., isopropoxyethanol. This leads to a partial replacement of alkoxy groups via alcoholysis and a change of the precursor structure from a trimeric to a tetrameric one. In the second step, carboxylation, the transformation to six-coordinated aluminum could be observed. Due to the formation of a sol with Newtonian flow behavior after hydrolysis, gel fibers up to several kilometers long could be drawn directly from the clear colorless sol with spinning velocities up to 200 m/min. The addition of an organic filament-forming polymer is not necessary. The sol is spinnable for periods up to one year. The transformation of the gel fiber to α-Al$_2$O$_3$ occurs at 1150°C.

Keywords: α-aluminum fiber, polycrystalline α-Al$_2$O$_3$-fiber, spinnable sol

1. Introduction

Ceramic fibers are of increasing interest for the reinforcement of ceramics and metals. Pure α-Al$_2$O$_3$ fibers can be used for high temperature applications, provided their microstructure is stable. Sol-gel processing has been used for the synthesis of alumina fibers. Various aluminum compounds, such as aluminum salts [1, 2] and alkoxides [3, 4] were used as starting components. After hydrolysis and condensation an appropriate viscosity for spinning was reached. The critical points with regard to the spinning behavior are the time dependance of the viscosity and the achievement of Newto-

nian flow behavior which is most suitable for obtaining high spinning velocities. In [5] the synthesis of zirconia fiber from precursor sols with a stable viscosity was demonstrated.

This paper describes a new synthesis of alumina fibers by modifying aluminum sec-butoxide to prevent precipitation during the synthesis of spinnable sols. The influence of alcoholysis and carboxylation on the precursor structure is shown. The relationship between the structure of the modified precursor after hydrolysis and the resulting viscosity and flowing behavior have been investigated. Fibers which were spun continuously from such precursor sols could be converted into crack-free α-Al$_2$O$_3$ fibers by thermal treatment.
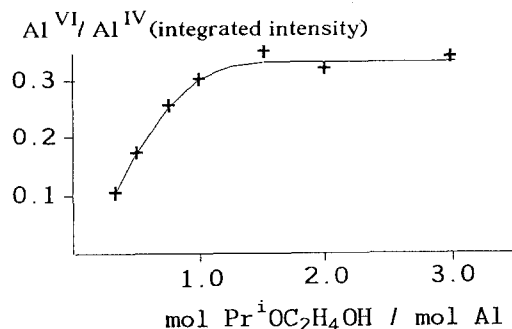
2. Alcoholysis

Glycolether, e.g. isopropoxyethanol, was reacted with aluminum sec-butoxide yielding a mixed alkoxide. The observed integrated intensities of the Al^{VI} and Al^{IV} peaks in liquid-state ^{27}Al NMR measurements reach a constant ratio near 1 : 3 after the replacement of 1.5 mol of secondary butoxy groups (Fig. 1). The structure of aluminum sec-butoxide transforms during the alcoholysis step from being trimeric to tetrameric, in which a six-coordinated aluminum core is encapsulated by three end groups consisting of four-coordinated alu-
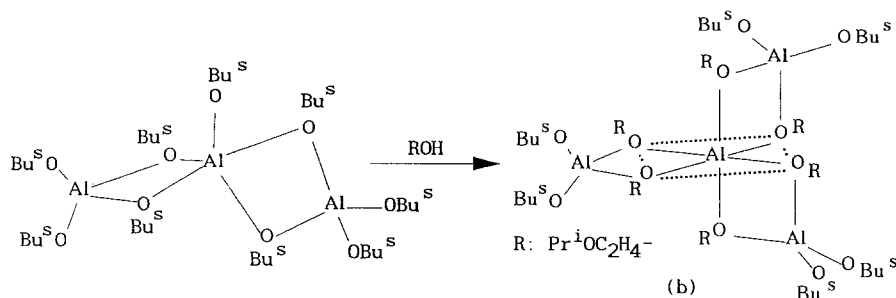

Fig. 1. Evolution of the ratio of Al^{VI} : Al^{IV} measured by ^{27}Al NMR as a function of the ratio of isopropoxyethanol to aluminium sec-butoxide.

Fig. 2. Alcoholysis of aluminum sec-butoxide leading to a proposed structure of a mixed aluminum alkoxide.
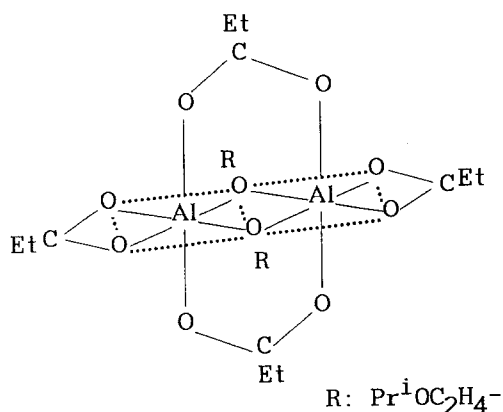

Fig. 3. Schematic representation of structures of aluminum carboxylate in excess of propionic acid.

minum atoms [6]. It is suggested that the inner-sphere complex is formed by the glycolether groups due to the lower steric hindrance and higher electronegativity compared to the secondary butoxygroups. Alcoholysis is demonstrated schematically in Fig. 2.

3. Carboxylation

The formation of soluble aluminum carboxylates was carried out by the reaction of propionic acid and aluminum sec-butoxide modified by glycolether (iso-propoxyethanol, ethoxyethanol and methoxyethanol). Potentiometric and gaschromatograph measurements indicate a rapid reaction of 1.5 mol propionic acid per mol Al and a loss of 1.5 mol sec-butanol per mol Al, whereas all isopropoxyethoxy groups are retained on aluminum. Asymmetric stretching vibrations of carboxylate groups at 1670, 1626 and 1575 cm^{-1} are clearly observable in IR spectra. The bands of the corresponding symmetric vibrations are found at 1370, 1453 and 1478 cm^{-1}. These bands may be as-
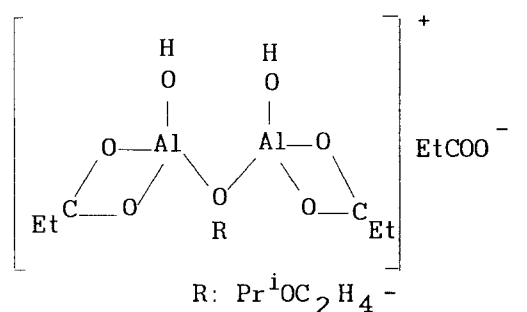

Fig. 4. Proposed structure of sol molecule.

signed to monodentate, bridging and chelating bonds, respectively.

The viscosity of the stirred solution shows a sharp maximum during addition of propionic acid as soon as 1.5 mol is consumed by one mol of the aluminum species. In addition a proportion of the Al atoms present is not observable on the recorded liquid-state ^{27}Al NMR spectrum [7]. This supports the idea of polymerization of the tetramers, linked by bridging carboxylates. Further carboxylation in an excess of propionic acid removes 0.5 mol iso-propoxyethanol per mol Al gradually. The asymmetric stretching vibration of the attached monodentate carboxylate decreases markedly and the ^{27}Al NMR spectra only reveal six-coordinated Al atoms with normal intensity.

Taking all these facts into account we believe that all terminal butoxygroups of the tetramer (see Fig. 2b) are replaced by carboxylates of the types mentioned and the inner-sphere complex remains stable. With an excess of propionic acid, however, the inner-sphere complex changes also and only one isopropoxyethoxy-group remains attached to aluminum. It may be concluded that the structure of aluminum carboxylate with an excess of propionic acid can be represented as depicted in Fig. 3.
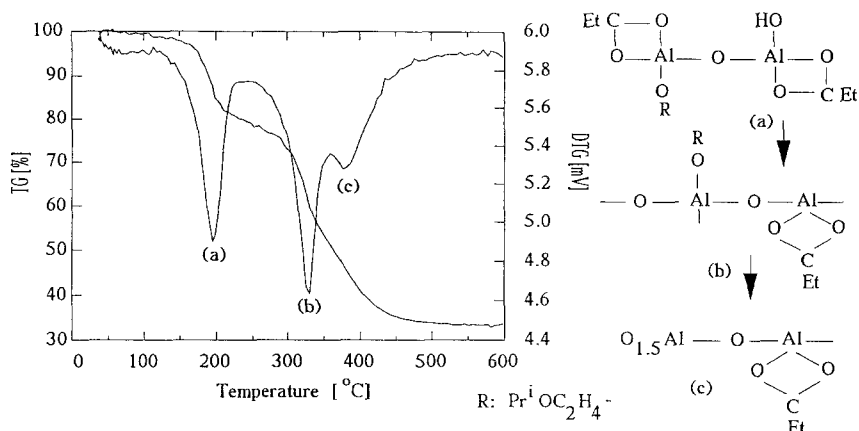
Fig. 5. Thermal decomposition and proposed structure of aged gel fiber molecule I and suggestions of cleavage mechanism (a–c).

4. Hydrolysis

During hydrolysis 0.5 mol isopropoxyethanol per mol Al leaves the aluminum compound. Bridging and monodentate carboxylates are not observable in the sols (IR spectra). The strong band at 1575 cm^{-1} represents the chelating bonds mentioned. With respect to the solid-state ^{27}Al MAS-NMR spectrum showing two well separated peaks of similar intensities at 3 ppm and −10 ppm assigned to two types of six-coordinated Al-atoms we propose that the structure of the molecule of the spinning solutions is like that shown in Fig. 4.

The viscosity of the solution remains low during the first stage of hydrolysis and increases sharply up to a very high value of 2000 Pas immediately after adding 0.5 mol H_2O per mol Al. The sol hydrolyzed with 1.0 mol H_2O per mol Al shows a viscoelastic curve on increasing the shear rate. On reducing the shear rate back to zero, the curve converts to one exhibiting Newtonian flow behavior. The latter curve is desired for spinnable solutions [8]. Gel fibers up to several kilometers long could be drawn directly form the clear colourless sol with spinning velocities in the vicinity of 200 m/min. The addition of an organic filament forming polymer is not necessary. The sol is spinnable for periods up to one year.

5. Drying and Aging

After spinning, the excess of propionic acid and alcohol evaporates and the solid matter content of the gel fiber rises to 24% Al_2O_3, which matches well with the theoretical 24.9% Al_2O_3 of the proposed sol molecule. The solid yield increases slowly during aging for weeks at room temperature, due to a loss of propionic acid. Up to 0.5 mol propionic acid per mol Al leaves the fiber and we assume that the condensation reaction first occurs with the aging of the gel fiber I (see Fig. 5). The resulting gel fiber remains crack-free, highly flexible and soluble in propionic acid.

6. Thermal Decomposition

Thermal decomposition of aged gel fiber as observed by thermogravimetric analysis (TGA) shows a three-stage process. The first stage ranges between 150 and 250°C. According to weight loss and mass spectra recorded we believe that a condensation reaction of 0.5 mol propionate groups per mol Al occurs. This temperature treatment leads to the formation of a less flexible fiber, partly soluble in propionic acid. An oligomeric or polymeric material consisting of an Al–O backbone with carboxylates and alkoxides is suggested II (see Fig. 5). The second stage of the weight loss between 250 and 360°C is due to the decomposition of the alkoxide and may be catalysed by traces of water (Fig. 5b). The corresponding mass spectrum of the third stage above 360°C reveals a peak at the mass of 86 assigned to pentanone, which is in accordance with the behavior of aluminumlaurates in this temperature range (Fig. 5c) [9]. IR spectra of the fibers recorded at every stage show a OH-band at 3450 cm^{-1} of much lower intensity than that of boehmite. The intensity of the OH-band decreases not before the fiber is heated above 400°C. The total weight loss yields a solid matter content of the gel fiber of 31%. This is in good accordance with the

theoretical content of the aged gel fiber (30.4%). TGA showed a exotherm peak at 870°C followed by another at 1150°C. According to X-ray diffraction patterns it is due to the conversion of amorphous alumina to crystalline γ-Al_2O_3 and finally α-Al_2O_3. The final fiber diameter is in the range of 10–14 μm.

7. Conclusions

The stepwise modification of aluminum sec-butoxide, at first by glycolether and subsequently by propionic acid, leads to a soluble aluminum carboxylate. Hydrolysis of the aluminum carboxylate gives a sol with a long term stability of viscosity. The sol has Newtonian flow behavior and allows spinning velocities up to 200 m/min. The final diameter of the α-Al_2O_3 fiber is in the range of 10–14 μm.

Acknowledgment

References

1. Maki, T. and Sakka, S., J. Non-Cryst. Solids **100**, 303 (1988).

2. Lucuta, P.G., Halliday, J.D., and Christian, B., J. Mater. Sci. **27**, 6053 (1992).

3. Ikoma, H., Katayama, S., Sekine, M., and Nomiya, Y., Am. Ceram. Soc., Annual Meeting, Indianapolis, 1989.

4. Yogo, T. and Iwahara, H., J. Mater. Sci. **27**, 1499 (1992).

5. Yogo, T., Kodama, S., and Iwahara, H., J. Mater. Sci. **28**, 105 (1993).

6. Kriz, O., Casensky, B., Lycka, A., Fusek, J., and Hermanek, S., J. Magn. Reson. **60**, 375 (1984).

7. Akitt, J.W., Gessner, W., and Weinberger, M., Magn. Reson. Chem. **26**, 1047 (1988).

8. Sakka, S. and Yoko, T., J. Non-Cryst. Solids **147 & 148**, 394 (1992).

9. Rai, A.K. and Mehrotra, R.C., J. Indian Chem. Soc. **40**, 359 (1963).