Journal of the European Ceramic Society **6** (1990) 107–110

Preparation Studies of Amorphous Al_2TiO_5

A. Feltz & F. Schmidt

Department of Chemistry of the Friedrich Schiller University, August-Babel-Strasse 2, Jena 6900, GDR

(Received 13 November 1989; revised version received 23 February 1990; accepted 26 February 1990)

Abstract

An amorphous form of Al_2TiO_5 containing only ~0·5% of volatile constituents is prepared by the sol–gel route by hydrolysis of $Al(OCH_2CH_2OC_2H_5)_3$/$Ti(OCH_2CH_2OC_2H_5)_4$ mixtures in 2-ethoxy-ethanol followed by evaporation of the solvent and stepwise heating up to 650°C. Only a small part is transformed into the crystalline state on annealing at 650°C, which is far below the formation temperature of Al_2TiO_5 (1280°C). In contrast to amorphous Mg_2TiO_4, decomposition takes place on annealing at low temperature. At 700°C, TiO_2 (rutile) is formed, followed by sudden crystallization of α-Al_2O_3 at ~930°C, measured by differential scanning calorimetry. Al_2TiO_5 and Mg_2TiO_4 are characterized by an endothermic formation enthalpy, indicating the role of the entropy term, which appears to be positive. Reaction sintering takes place more effectively starting from amorphous Al_2TiO_5.

Durch die Hydrolyse einer Mischung aus $Al(OCH_2CH_2OC_2H_5)_3$ und $Ti(OCH_2CH_2OC_2H_5)_4$ in 2-Ethoxy-Ethanol, anschließender Verdampfung des Lösungsmittels und stufenweisem Aufheizen bis 650°C wird eine amorphe Form von Al_2TiO_5 gebildet, die nur etwa 0·5% flüchtige Bestandteile des Sol–Gel-Verfahrenswegs enthält. Nur ein kleiner Teil wird beim Tempern bei 650°C weit unterhalb der Bildungstemperatur von Al_2TiO_5 (1280°C) in die kristalline Form umgewandelt. Im Gegensatz zu amorphem Mg_2TiO_4 findet die Zersetzung während des Temperns bei niedrigen Temperaturen statt. Bei 700°C wird TiO_2 (rutil) gebildet, gefolgt von einer plötzlichen Kristallisation von α-Al_2O_3 bei etwa 930°C, gemessen mit DSC. Al_2TiO_5 und Mg_2TiO_4 sind durch eine endotherme Bildungsenthalpie gekennzeichnet, was auf die Rolle des Entropietherms hinweist, der positiv zu sein scheint. Ausgehend von amorphem Al_2TiO_5 ist das Reaktionssintern effektiver.

On a produit une variété amorphe de Al_2TiO_5 contenant environ 0·5% de constituants volatils à partir du procédé sol–gel par hydrolyse de mélanges $Al(OCH_2CH_2OC_2H_5)_3$/$Ti(OCH_2CH_2OC_2H_5)_4$ dans l'éthylate-2-éthanol suivie de l'évaporation du solvant et d'un chauffage par paliers jusqu'à 650°C. Le taux de cristallisation est faible lors d'une recuit à 650°C, température très inférieure à la température de formation de Al_2TiO_5 (1280°C). Au contraire du Mg_2TiO_4 amorphe, une décomposition se produit au cours du recuit à basse température. La formation de TiO_2 (rutile) à 700°C est suivie de la cristallisation soudaine d'Al_2O_3 α à 930°C environ, mesurée par DSC. Al_2TiO_5 et Mg_2TiO_4 sont caractérisés par une enthalpie de formation positive indiquant le rôle du terme entropique qui se révèle être positif. Le frittage réactionnel s'effectue plus facilement à partir d'Al_2TiO_5 amorphe.

1 Introduction

Because of its low thermal expansion, tialite (Al_2TiO_5) has been extensively studied as a material with a great deal of promise for applications in thermal-shock-resistant insulation (for reviews see Refs 2 and 3). The compound is unstable at lower temperature. According to the phase diagram,[4] decomposition takes place below 1150°C. On the other hand, 1280°C has been reported as the lowest temperature of stability of Al_2TiO_5.[5] It has been shown that decomposition is inhibited by suitable doping or alloying, e.g. with $MgTi_2O_5$,[6] and at the same time improvement of mechanical strength has

Journal of the European Ceramic Society 0955-2219/90/$3.50 © 1990 Elsevier Science Publishers Ltd, England. Printed in Great Britain

been achieved.[7] Al_2TiO_5 appears to be a member of the group of compounds whose formation results from the positive value of entropy generating a negative free enthalpy to a greater extent with increase in temperature, until melting takes place. Obviously, random occupation of the cationic sites in the lattice of the pseudo-brookite structure leads to stabilization.

The reaction of $MgTiO_3$ and MgO above 987°C to yield Mg_2TiO_4 with inverted spinel structure has also been interpreted as an effect of entropy stabilization.[8] On the other hand, starting from an amorphous intermediate state, obtained by calcination of the residue which is formed by hydrolysis of solutions of $Mg(OCH_2CH_2OC_2H_5)_2$ and $Ti(OCH_2CH_2OC_2H_5)_4$ in 2-ethoxy-ethanol, Mg_2TiO_4 can be[9,10] prepared at ~600–700°C, i.e. under thermodynamically unstable conditions, as a highly dispersed powder of high sintering activity.

It is the aim of this paper to investigate whether tialite may also be formed as a metastable compound below the decomposition temperature of 1280°C via an appropriate precursor, which would open a possible method of preparation of Al_2TiO_5 powder with increased sintering activity. Kato *et al.*[5] have reported Al_2TiO_5 crystallization to a metastable state at 1250°C, starting from an amorphous powder prepared from a mixture of $Al(O\text{-}iC_3H_7)_3$ and $Ti(O\text{-}iC_3H_7)_4$ dissolved in iso-propanol after pouring into water.

2 Experimental Procedure

2-Ethoxy-ethanol (EEOH) can be used for preparation of solutions of mixtures of $Mg(OEE)_2$ and $Ti(OEE)_4$, which are promising for hydrolysis in homogeneous conditions. Preparation of $Ti(OEE)_4$ has been described from $TiCl_4$ dissolved in EEOH diluted with benzene at −18°C under the action of NH_3.[10] $Al(OEE)_3$ is formed by dissolution of Al splinters in 2-ethoxy-ethanol. The viscous liquid, consisting of trimeric units dissolved in benzene, is unvolatile even at 200°C and 1 Pa.[1]

Preparation of Al_2TiO_5 follows the reaction

$$2Al(OEE)_3 + Ti(OEE)_4 + 5H_2O \rightarrow Al_2TiO_5 + 10EEOH \quad (1)$$

Stoichiometric amounts of water were added dropwise under stirring as a 1 M solution in 2-ethoxy-ethanol to the mixture of $2Al(OEE)_3$ and $Ti(OEE)_4$ dissolved in the same solvent. The viscosity increases with time, and heating results in the formation of a white xero-gel. Evaporation of the solvent under vacuum and heating up to 200°C yields an amorphous residue, which still contains some alkoxide groups, presumably chemically bound; i.e. hydrolysis remains incomplete, which is in accordance with observations on the formation process of Mg_2TiO_4 following an analogous preparation route.[9,10]

Thermal decomposition of the amorphous residue has been investigated by thermogravimetry (TG), differential scanning calorimetry (DSC) and prolonged isothermal heating at selected temperatures. X-ray diffraction measurements allow us to locate changes in structure and phase transformation.

Studies of the sintering behavior of Al_2TiO_5, prepared by the sol–gel route (powder A: $25 \pm 2\,m^2/g$), and of coarse Al_2TiO_5 formed from Al_2O_3/TiO_2 by firing at 1500°C and grinding, for comparison (powder B: about $1\,m^2/g$), have been carried out with tablets which were densified by pressure (150 MPa) without granulometric pretreatment.

3 Results

Figure 1 shows the results of heat-flux DSC measurements. Up to ~650°C, 60% of the weight of the xero-gel treated at 200°C in vacuum is lost. Residual units of 2-ethoxy-ethoxide become oxidized on heating in air, giving rise to exothermic enthalpy effects in the curve between 250 and 450°C. Maintaining the temperature at 650°C for 3 h yields amorphous Al_2TiO_5. Only ~0·5% volatile constituents remain.

Decomposition of amorphous Al_2TiO_5 at temperatures below 1280°C is shown in Fig. 2. A two-step reaction takes place. As can be seen from the X-

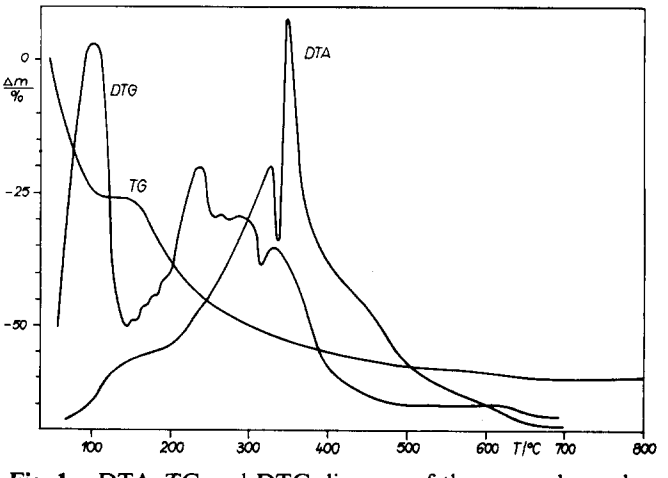

Fig. 1. DTA, TG and DTG diagram of the xero-gel powder prepared by hydrolysis of $2Al(OEE)_3/Ti(OEE)_4$ dissolved in 2-ethoxy-ethanol followed by evaporation of the solvent and drying of the amorphous residue at 100°C. Heating rate for DTA and TG is 10 K/min in air.

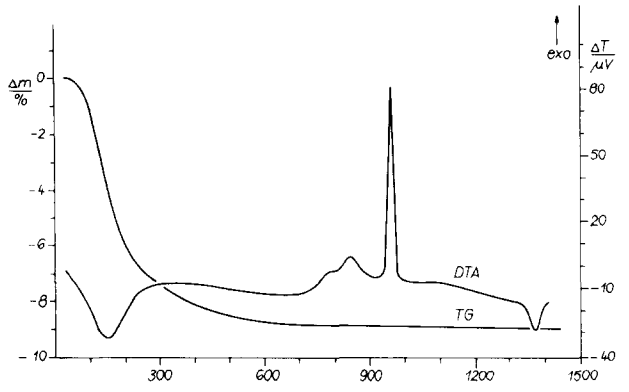

Fig. 2. DTA and TG diagram starting with an amorphous precursor prepared by annealing of the xero-gel powder for 200 h at 600°C in air (heating rate 10 K/min).

ray diffraction pattern of Fig. 3(b), only a very small fraction of amorphous Al_2TiO_5 becomes transformed into the crystalline state in the metastable range of temperature. After annealing for 130 h at 680°C some weak and broadened peaks appear, which seem to correspond to crystalline Al_2TiO_5. Maintaining the temperature at 700°C, near the first exothermic peak of Fig. 2, clearly indicates the formation of rutile (Fig. 3(c)). Only a very small fraction of α-Al_2O_3 appears at this stage in the powder mixture

$$Al_2TiO_5 \rightarrow xTiO_2 + \frac{5-2x}{5} Al_{10/(5-2x)}Ti_{5(1-x)/(5-2x)}O_5 \quad (2)$$

Annealing at 850°C shows an increased fraction of α-Al_2O_3 and rutile in the X-ray diffraction pattern (Fig. 3(e)). In the dynamic regime of DTA, sudden crystallization of α-Al_2O_3 and remnant TiO_2 is observed at ~930°C (Fig. 2):

$$\frac{5-2x}{5} Al_{10/(5-2x)}Ti_{5(1-x)/(5-2x)}O_5 \rightarrow Al_2O_3 + (1-x)TiO_2 \quad (3)$$

Furthermore, Fig. 2 shows the formation of crystalline Al_2TiO_5 by reverse equations (2) and (3), indicated by an endothermic enthalpy effect at 1340°C. Endothermic Al_2TiO_5 formation from the constituent oxides has already been observed.[11,12]

The results of the sintering experiments are shown in Fig. 4. Despite smaller green density ρ_0 after densification by pressure of the samples prepared as an amorphous product annealing from the xero-gel at 680°C, higher densities ρ_t are attained during sintering at 1500°C than for the coarser powder B formed by grinding of Al_2TiO_5 which had been separately prepared from the constituent oxides. The dependence on time of the density $\rho_{rel.}$ and the shrinkage parameter $\alpha = (\rho_t - \rho_0)/(\rho_{th} - \rho_0)$ reveals

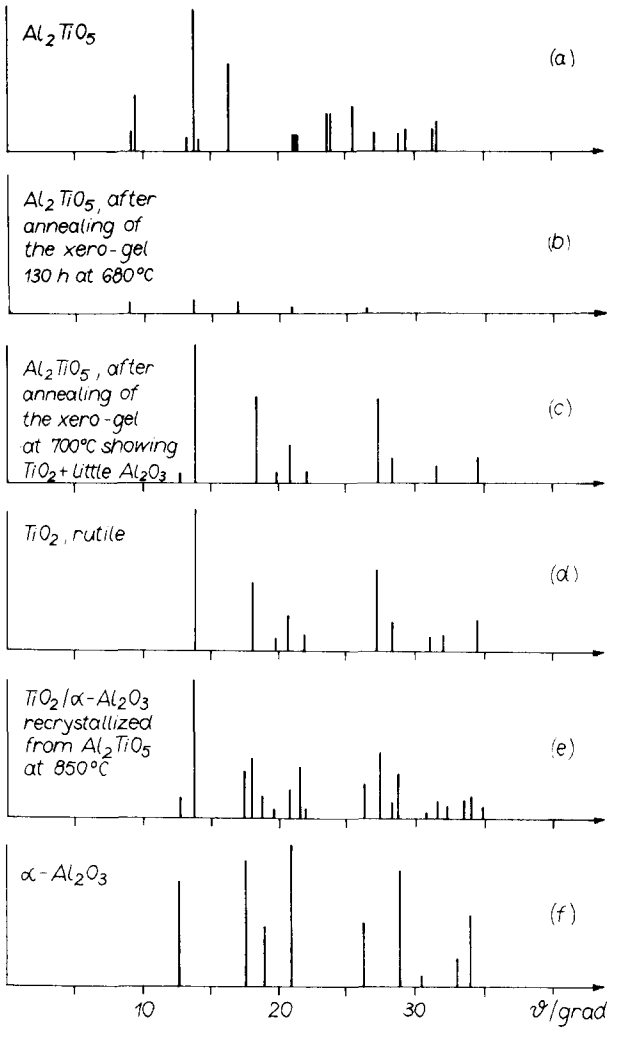

Fig. 3. X-ray diffraction diagrams of crystalline Al_2TiO_5 (a) and of highly amorphous Al_2TiO_5 (b), from which crystallization of rutile at 700°C arises (c), and of the mixture of rutile and α-alumina at 850°C (e), which is confirmed by the diagrams for rutile (d) and α-Al_2O_3 (f) for comparison.

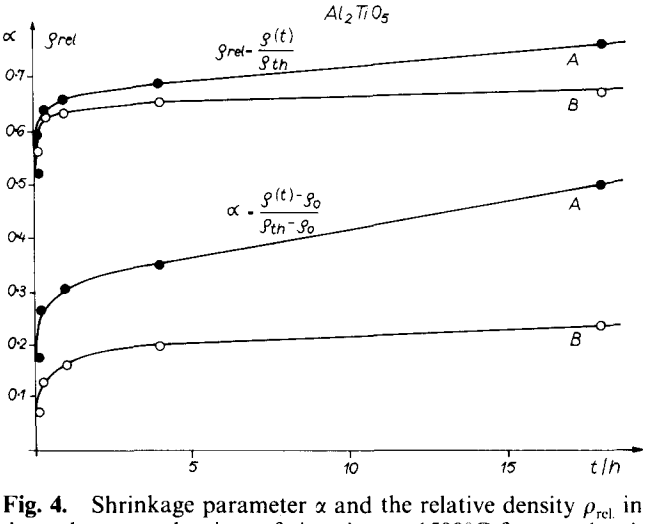

Fig. 4. Shrinkage parameter α and the relative density $\rho_{rel.}$ in dependence on the time of sintering at 1500°C for powder A prepared by the gel route and for powder B prepared in the conventional way at 1500°C followed by grinding.

the higher sintering activity of the amorphous form of Al_2TiO_5.

4 Discussion

Sol–gel techniques have already been applied to the preparation of powders in the system Al_2O_3–TiO_2.[5] Hydrolysis of mixtures of $Ti(OC_3H_7)_4$ and $Al(OC_3H_7)_3$ of different ratios resulted in crystallization of anatase containing up to 22 mol% Al_2O_3 in solid solution.[13] On the other hand, rutile seems to have only a comparatively limited solubility for Al_2O_3.[14,15] Thomas and Stevens[16] studied reaction sintering of an intimate mixture of Al_2O_3 and TiO_2 formed by coprecipitation from $Al(OC_3H_7)_3$ and $Ti(OC_3H_7)_4$ dissolved in isopropanol and added dropwise to water, followed by drying and calcination at 950°C. Because of shorter diffusion pathways, amorphous Al_2TiO_5 is expected to provide advantages. Studies on the mechanism in comparison with the results of Freudenberg and Mecellin[17] are in preparation.

Figure 5 shows the DTA diagram of metastable Mg_2TiO_4 crystallized at 700°C from an amorphous modification which is obtained on heating of the xero-gel prepared by hydrolysis of $2Mg(OEE)_2$/$Ti(OEE)_4$ mixtures in 2-ethoxy-ethanol.[9,10] Decomposition takes place in part, during heating at 10 K/min because Mg_2TiO_4 is unstable below 987°C, yielding an intimate $MgTiO_3$/MgO mixture. Above this temperature, Mg_2TiO_4 is formed and, as for Al_2TiO_5, the reaction enthalpy is negative, which clearly indicates the role of entropy. The value of $-T\Delta S$ overcomes $+\Delta H$, yielding a negative value of ΔG. Indeed, Al_2TiO_5, like Mg_2TiO_4, appears to be a compound which is stabilized by the positive value of the entropy term. Presumably, random distribution of the Al and Ti atoms on the sites of the pseudo-brookite structure are the reason for the formation of the compound.

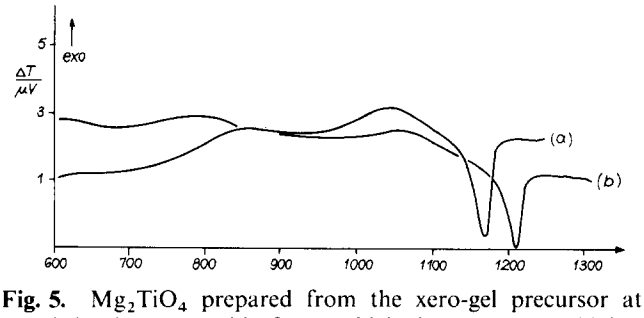

Fig. 5. Mg_2TiO_4 prepared from the xero-gel precursor at 700 C in the metastable form, which decomposes at higher temperatures into MgO and $MgTiO_3$, yielding an endothermic formation enthalpy in the DTA regime with 5 K/min (a) and 10 K/min (b).

5 Conclusions

Hydrolysis of $2Al(OEE)_3/Ti(OEE)_4$ mixtures dissolved in 2-ethoxy-ethanol allows preparation of an amorphous form of Al_2TiO_5, which shows an increased sintering activity.

References

1. Schmidt, F. & Feltz, A., Herstellung keramischer Pulver IV, Zur Struktur von $Al(OCH_2CH_2OC_2H_5)_3$. *Z. Chem.*, **30** (1990) 109.
2. Hennicke, H. W. & Lingenberg, W., The formation and decomposition of aluminium titanate. I The reaction of formation of aluminium titanate. *Ber. Dtsch. Keram. Ges.*, **62**(9, 10) (1985) 439–44; II The decomposition reaction of aluminium titanate. *Ber. Dtsch. Keram. Ges.*, **63**(3) (1986) 100–6.
3. Hahn, Ch., Verbesserung von Aluminiumtitanat-Keramik. *Sprechsaal*, **118**(12) (1985) 1157–66.
4. Lejus, A. M., Goldberg, D. & Reveolevschi, A., New compounds formed between rutile TiO_2 and oxides of trivalent and tetravalent metals. *C.R. Hebd. Séanc. Acad. Sci., Paris*, Sér. C, **263** (1966) 1223–6.
5. Kato, B., Daimon, K. & Takahashi, J., Decomposition temperature of β-Al_2TiO_5. *J. Am. Ceram. Soc.*, **63**(5, 6) (1980) 355–556.
6. Ishitsuka, M., Sato, T., Endo, T. & Shimada, M., Synthesis and thermal stability of aluminium titanate solid solutions. *J. Am. Ceram. Soc.*, **70**(2) (1987) 69–71.
7. Ohya, Y., Hamano, K. & Nakagawa, Z., Microstructure and mechanical strength of aluminium titanate ceramics prepared from synthesized powders. *Yogyo-Ky Kai-Shi*, **91** (1983) 290–7.
8. Wechsler, B. A. & Navrotsky, A., Thermodynamics and structural chemistry of compounds in the system MgO–TiO_2. *J. Solid State Chem.*, **55** (1984) 165–74.
9. Feltz, A. & Schmidt, F., Herstellung keramischer Pulver I, $Ti(OCH_2CH_2OC_2H_5)_4$ und die Darstellung von Mg_2TiO_4 als metastabile Verbindung. *Z. Chem.*, **11** (1987) 414–15.
10. Schmidt, F. & Feltz, A., Herstellung keramischer Pulver II, Über die Bildung von Mg_2TiO_4, $MgTiO_3$, $MgTi_2O_5$ durch Hydrolyse von 2-Ethoxy-ethylaten. *Z. Anorg. Allg. Chem.*, **573** (1989) 208–14.
11. Bayer, G., Thermal expansion characteristics and stability of pseudobrookite-type compounds, Me_3O_5. *J. Less-Common Met.*, **24** (1971) 129–38.
12. Gani, M. S. J. & McPherson, R., The enthalpy of formation of Al_2TiO_5. *Thermochim. Acta*, **7** (1973) 251–2.
13. Yamaguchi, O. & Mukaida, Y., Formation and transformation of TiO_2 (Anatase) solid solution in the system TiO_2–Al_2O_3. *J. Am. Ceram. Soc.*, **72** (1989) 330–3.
14. Hamelin, M., Solid state reactions at elevated temperatures in the systems TiO_2–Al_2O_3, TiO_2–Cr_2O_3, TiO_2–Cr_2O_3–Al_2O_3. *Bull. Soc. Chim. Fr.* (1957) 1421–31.
15. Flörke, O. W., The reaction of TiO_2 with Cr_2O_3; comparison with other oxide pairs. *Ber. Dtsch. Keram. Ges.*, **38**(4) (1961) 133–49.
16. Thomas, H. A. J. & Stevens, R., Reaction sintering studies on aluminium titanate. *Science of Ceramics 14, Proc. Int. Conf. Science of Ceramics*, Canterbury, 1987. The Institute of Ceramics, Shelton, Staffordshire, UK, pp. 273–8.
17. Freudenberg, B. & Mecellin, A., Aluminium titanate formation by solid-state reaction of coarse Al_2O_3 and TiO_2 powders. *J. Am. Ceram. Soc.*, **71**(1) (1988) 22–8.