

Melt synthesis of Al_2TiO_5 containing composites and reinvestigation of the phase diagram Al_2O_3 – TiO_2 by powder X-ray diffraction

S. Hoffmann · S. T. Norberg · M. Yoshimura

© Springer Science + Business Media, LLC 2006

Abstract Recently the fabrication of ceramics starting from the appropriate melts of the educts has attracted increasing attention due to the easy shaping of work pieces and other advantages compared to powder sintering methods. We focused our interest on aluminum titanate (β - Al_2TiO_5) based ceramics which are interesting for high temperature applications due to the low thermal expansion coefficient. For this purpose we have investigated the titania-rich side of the Al_2O_3 – TiO_2 system (up to 50 mol% titania) under rapid cooling conditions with respect to the phase formation. By powder X-ray diffraction we could prove the solely formation of the known phases rutile and β - Al_2TiO_5 in agreement with the equilibrium phase diagram. Furthermore, powder pattern fitting has revealed the formation of solid solutions for both compounds.

Keywords Arc-imaging furnace · Powder pattern fitting · Aluminum titanate

1 Introduction

Recently the fabrication of ceramics starting from the appropriate melts of the educts has attracted increasing attention due to the easy shaping of work pieces and other

advantages compared to powder sintering methods. Furthermore, new phenomena are encountered when this method is used which offers the possibility to obtain new materials with a tailored microstructure. One of these phenomena is for instance the glass formation due to the rapid cooling even in systems with high alumina content without the well-known network-former like SiO_2 , B_2O_3 , or P_2O_5 [1, 2]. A proper heat treatment of such glasses can yield ceramics consisting of consolidated nanocrystallites without losing optical transparency. To add some more interesting features of this method which make it worth to investigate is the possible occurrence of directionally solidification and the formation of metastable compounds during cooling.

We have started to investigate the system Al_2O_3 – TiO_2 – ZrO_2 [3, 4] with respect to the phase formation and glass formation. In particular we were interested in ceramic composites containing β - Al_2TiO_5 which exhibits a low thermal expansion coefficient. Thus, β - Al_2TiO_5 is interesting for applications where a good thermal-shock-resistance is desirable for instance in ferrous and non ferrous metallurgy [5–8]. Another reported compound for this phase diagram is ZrTiO_4 which exhibits the phenomenon that the lattice parameters show a dependency on the cooling rate [9] due to different degrees of cation ordering.

In the course of experiments in the mentioned pseudo-ternary system we encountered difficulties in the interpretation of powder X-ray patterns which showed new reflections of an unknown crystalline phase. Therefore we decided to re-investigate the pseudo-binary system Al_2O_3 – TiO_2 (Fig. 1) [10] with respect to the phase formation under rapid cooling conditions in an arc-imaging furnace. Here we present the results of the powder X-ray pattern fitting [11] for the pure oxides and the titania-rich side of the phase diagram.

S. Hoffmann (✉) · M. Yoshimura
Materials and Structures Laboratory, Tokyo Institute of
Technology, Yokohama 226-8503, Japan
e-mail: stefan598@aol.com

S. T. Norberg
Ceramic Research Laboratory, Nagoya Institute of Technology,
Gifu 507-0071, Japan

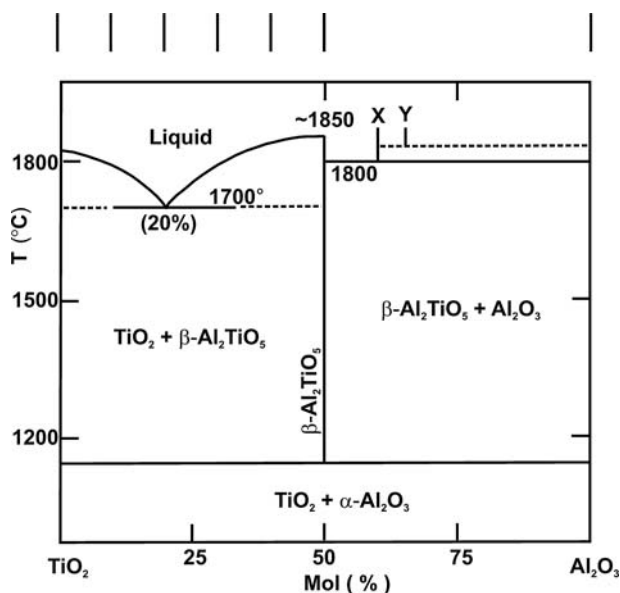


Fig. 1 Redrawn phase diagram proposed by Goldberg in 1968 (X and Y denote new compounds) [10] and examined compositions marked by bars above

2 Experimental

Five mixtures consisting of the oxides Al_2O_3 and TiO_2 were prepared with molar ratios according to the bars shown above the phase diagram in Fig. 1. The $\alpha\text{-Al}_2\text{O}_3$ (Sumitomo Chemicals type AKP-30 high purity) and TiO_2 (High Purity Chemicals Kōjundo Kagaku Kenkyū 99.99%, consisting of 96 wt% rutile and 4 wt% anatase according to X-ray powder pattern) were weighted and afterwards thoroughly mixed in a corundum mortar using ethanol, then dried in air and melted in an arc-imaging furnace. First the mixed oxides were completely melted by opening the shutter situated between the Xenon lamp and the sample. Then the obtained spherical specimens with a diameter of 2–3 mm were turned over and again melted to ensure a complete melting. The same was done for the pure oxides. To melt alumina a small amount of high-purity graphite was added to enhance the radiation absorption.

After melting the globules were crushed in a corundum mortar and then grinded for 30 min in ethanol. The powders had a gray to bluish-grey appearance. A home-built glass sample holder with a quadratic dip (0.5 mm depth) was side-loaded and measured with a X-ray powder diffractometer (Rigaku RINT 2000, Cu K_α radiation, 200 mA 50 KV) typically in the 2θ -range of $5\text{--}90^\circ$ with a scan speed of $0.7^\circ/\text{min}$ and a step width of 0.02° .

The recorded patterns were compared with reported patterns from ICDD [12]. After the identification of the crystalline compounds the patterns were fitted with structural models for $\alpha\text{-Al}_2\text{O}_3$ [13], TiO_2 (rutile) [14], and $\beta\text{-Al}_2\text{TiO}_5$ [15] taken from literature using the program

FULLPROF2000 [16]. The parameters for the zero-point shift, background, line shape, and unit cell were refined whereas the atomic coordinates and the isotropic atomic displacement parameters were fixed for the mixtures.

3 Results and discussion

Firstly we have investigated the pure oxides as well as the melted pure oxides by powder X-ray diffraction with respect to polymorphs and lattice parameters. In all alumina samples only the common α polymorph could be identified. The percentage error for the lattice parameters was less than 0.04% compared with reported values for $\alpha\text{-Al}_2\text{O}_3$ (NIST SRM674a) [17]. For the melted sample it was observed that manual grinding as long as 30 minutes is needed to record a powder pattern almost free from preferred orientation. In the case of titania the starting powder consists of the two polymorphs rutile and anatase. The quantitative evaluation yields 96 wt% rutile and 4 wt% anatase assumed that no amorphous material was present. During melting the sample became black and shiny indicating a change in the chemical composition. Consequentially new weak reflections were observed in the powder pattern beside the lines stemming from crystalline rutile. After melting no reflections of anatase were observed. We suppose that during melting the sample was slightly reduced and Magneli phases were formed [18]. The determined lattice parameters for both polymorphs agree well with the published data [14, 19] even though the amount of anatase in the starting material was comparably small.

After these preliminary experiments we started to analyze the molten mixtures in the same way. Essentially all samples consist of rutile and $\beta\text{-Al}_2\text{TiO}_5$ with variable ratio which is consistent with the known phase diagram (Fig. 1). For the mixture with equimolar ratio of alumina and titania, traces of $\alpha\text{-Al}_2\text{O}_3$ and $\text{Al}_6\text{Ti}_2\text{O}_{13}$ [20] could be identified beside $\beta\text{-Al}_2\text{TiO}_5$ as the main product. The results of the lattice parameter refinement for $\beta\text{-Al}_2\text{TiO}_5$ are given in Table 1 as well as the published data for pure $\beta\text{-Al}_2\text{TiO}_5$ [21]. We have found

Table 1 Determined lattice parameters for $\beta\text{-Al}_2\text{TiO}_5$ (SG: Cmcm) in dependence on the titania content of the starting mixture ([a] data from ICDD [21] for comparison)

TiO_2 (mol%)	a (Å)	b (Å)	c (Å)	V (Å ³)
90	3.5824(4)	9.463(1)	9.690(1)	328.5
80	3.5862(3)	9.4553(8)	9.6696(8)	327.9
70	3.5944(1)	9.4454(4)	9.6530(4)	327.7
60	3.5948(1)	9.4416(3)	9.6476(3)	327.5
50	3.5982(1)	9.4346(4)	9.6414(4)	327.3
50 ^[a]	3.5929(1)	9.439(2)	9.647(2)	327.2

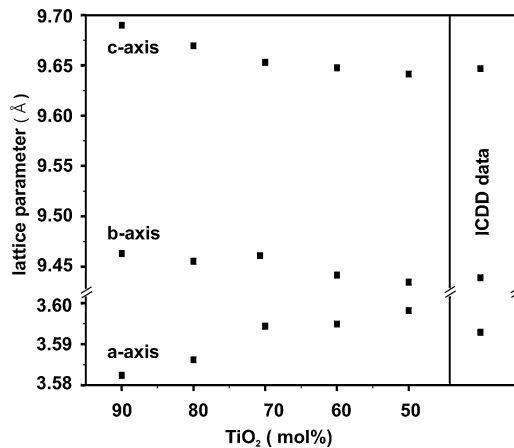


Fig. 2 Graphical presentation of the determined lattice parameters for β - Al_2TiO_5 (SG: Cmcm) in dependence on the titania content of the starting mixture and for comparison the data from ICDD [21] (standard deviations are given in Table 1)

that with increasing titania content the b and c axis elongate whereas the a axis shrinks (see Fig. 2). As a result the unit cell volume enlarges about 0.4% for the sample starting from a mixture with a molar ratio of 1:9 Al_2O_3 : TiO_2 compared with a sample prepared from an equimolar mixture. This volume expansion can be explained if assuming that a small extent of Al^{3+} can be replaced by the larger Ti^{3+} , which has an effective ionic radii of 0.67 Å [22] as compared to 0.535 Å for Al^{3+} and 0.605 Å for Ti^{4+} . The shortening of the a axis indicates a structural relaxation in this crystallographic direction when a bigger cation is incorporated into the crystal structure. Ishitsuka et al. [23] observed for a solid solution of ZrO_2 in β - Al_2TiO_5 that the length of the a axis hardly changes but the other directions are expanded as we observed for our case. Interestingly enough, the a axis of β - Al_2TiO_5 (setting in space group Cmcm) is the one contracting during heating [15, 24] and is therefore responsible for the small thermal expansion.

Due to the capability of the used fitting program to handle more than one compound, we simultaneously obtained the refined lattice parameters for all crystalline compounds. The result for rutile, the only polymorph of titania we have found by powder X-ray diffraction after rapid cooling, is presented in Fig. 3. The change of lattice parameters with increasing content of alumina in the starting mixture is very small, only a few thousandth Å compared to pure titania, which shows that only a small part of trivalent Al^{3+} can be incorporated into the rutile lattice. We observed a slight increase for both lattice parameters. In contrary, two detailed works on the solid solution of alumina in rutile reported a small shrinkage when the rutile lattice incorporates Al^{3+} [25, 26]. However, long termed annealed samples were investigated in these studies, which might be the reason for the observed difference.

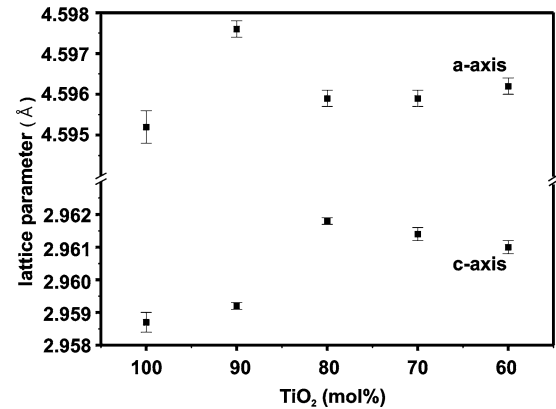


Fig. 3 Graphical presentation of the determined lattice parameters for rutile (SG: P42/mnm) in dependence on the titania content of the starting mixture

4 Conclusion

The phase composition of the rapid cooled samples of the investigated part of the phase diagram Al_2O_3 - TiO_2 is in agreement with the published results [10]. The careful analysis of the recorded powder X-ray patterns revealed the formation of solid solutions for both rutile and β - Al_2TiO_5 under the experimental condition described above. This observation might have drastic consequences on the thermal behavior of composites synthesized by rapid cooling or even by high-temperature sintering methods.

Acknowledgments SH acknowledge JSPS post-doc fellowship No. P03752 and SN acknowledge JSPS post-doc fellowship No. P03707. Dr. T. Watanabe and Dr. T. Ishigaki are kindly acknowledged for their help in recording powder XRD patterns.

References

1. S. Araki and M. Yoshimura, *Int. J. Appl. Ceram. Technol.*, **1**, 155 (2004).
2. A. Rosenflanz, M. Frey, B. Endres, T. Anderson, E. Richards, and C. Schardt, *Nature*, **430**, 761 (2004).
3. A.S. Bereznoi and N.V. Gulko, *Dopov. Akad. Nauk*, **1**, 77 (1955).
4. P. Pena and S. DeAza, *Ceramica (Florence)*, **33**, 23 (1980).
5. H.A.J. Thomas and R. Stevens, *Br. Ceram. Trans. J.*, **88**, 144 (1989).
6. C.G. Aneziris, E.M. Pfaff, and H.R. Maier, *Key Eng. Mat.*, **132–136**, 1829 (1997).
7. I.J. Kim, K.S. Lee, and G. Cao, *Key Eng. Mat.*, **224–226**, 819 (2002).
8. I.J. Kim, H.C. Kim, I.S. Han, and C.G. Aneziris, *Key Eng. Mat.*, **280–283**, 1179 (2005).
9. Y. Park, Y.K. Kim, and H.G. Kim, *Ferr. Lett.*, **21**, 65 (1996).
10. D. Goldberg, *Rev. Int. Hautes Temper. et Refract.*, **5**, 181 (1968).
11. The Rietveld Method, edited by R.A. Young (Oxford University Press, Oxford, 1993).
12. The International Centre for Diffraction Data, PDF-2 release (1999).
13. N. Ishizawa, T. Miyata, I. Minato, F. Marumo, and S. Iwai, *Acta Cryst.*, **B36**, 228 (1980).
14. W. Gonschorek, *Z. Krist.*, **160**, 187 (1982).

15. B. Morosin and R.W. Lynch, *Acta Cryst.*, **B28**, 1040 (1972).
16. J. Rodriguez-Carvajal, in: Meeting on Powder Diffraction of the XV Congress of the IUCr (IUCr, Toulouse, 1990), p. 127.
17. M. Oetzel and G. Heger, *J. Appl. Cryst.*, **32**, 799 (1999).
18. B.G. Hyde and S. Andersson, *Inorganic Crystal Structures* (John Wiley & Sons, New York, 1989).
19. J.K. Burdett, T. Hughbanks, G.J. Miller, J.W. Richardson, and J.V. Smith, *J. Am. Chem. Soc.*, **109**, 3639 (1987).
20. S.T. Norberg, S. Hoffmann, M. Yoshimura, and N. Ishizawa, *Acta Cryst.*, **C61**, i35 (2005).
21. W. Syvinski and G. McCarthy, North Dakota State University, Fargo, ICDD Grant-in-Aid (1989).
22. R.D. Shannon, *Acta Cryst.*, **A32**, 751 (1976).
23. M. Ishitsuka, T. Sato, T. Endo, and M. Shimada, *J. Am. Ceram. Soc.*, **70**, 67 (1987).
24. G. Bayer, *J. Less-Common Met.*, **24**, 129 (1971).
25. R.A. Slepetyts and P.A. Vaughan, *J. Chem. Phys.*, **73**, 2157 (1969).
26. U. Gesenhues and T. Rentschler, *J. Solid State Chem.*, **143**, 210 (1999).