STUDY OF CRYSTALLISATION OF Al$_2$O$_3$-Fe$_2$O$_3$ GELS BY MÖSSBAUER SPECTROSCOPY

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Boehmite derived alumina gels seeded (5 wt.%) with α-Al$_2$O$_3$, α-Fe$_2$O$_3$ and Fe(NO$_3$)$_3$ were examined by Mössbauer spectroscopy. Feric oxide orginated from Fe(NO$_3$)$_3$ was identified in defect alumina phases in two high disperse form as solid solution γ-(Al, Fe)$_2$O$_3$ and substituted hematite particles (α-(Fe, Al)$_2$O$_3$ ~ 6 nm). Dispersed Fe^{3+} ions reduce temperature of the crystallisation of α-Al$_2$O$_3$ (solution (Al, Fe$_2$O$_3$)) much more significantly than particulate seeds. Enhanced transformation has been attributed to solution effect of dispersed Fe^{3+} ions resulting in transparent ceramics sintered below 1300 °C.

INTRODUCTION

Synthesis of alumina ceramic fibres, films or membranes is more convenient from solution precursor than via traditional powder techniques. However, solution routes as is sol-gel process starting with boehmite have some difficulties connected with a series of topotactic metastable phase transformation (γ-δ-θ-Al$_2$O$_3$) before final crystallisation of thermodynamically stable α-Al$_2$O$_3$ [1, 5]. The first dehydrated product of γ-AlOOH is γ-Al$_2$O$_3$. This is spinel-based structure with disordered cation vacancies, which is not basically changing during topotactic transformations [1, 2]. The difficult α-Al$_2$O$_3$ nucleation in this system is directly responsible for unwanted porous microstructure evolution of boehmite-derived alumina. In order to overcome these problems, seeds are often used to lower the nucleation barrier, thus allowing the transformation to occur at a reasonable rate and at lower temperatures [3 - 6]. Small particles of α-Al$_2$O$_3$ or isostructural crystals with similar lattice parameters as is hematite (α-Fe$_2$O$_3$) are commonly used as seeding agents for boehmite gels. The seeding effect of α-Al$_2$O$_3$ crystals is generally postulated in the literature [3, 5, 6] as purely crystallographic. In the case of ferric oxide it is not so simple because it can be introduced into the system in the form of small particles α-Fe$_2$O$_3$ (hematite) or as a solution of Fe(NO$_3$)$_3$. For colloidal boehmite seeded with hematite particles or Fe(NO$_3$)$_3$ solution McArdle and Messing [7] reported, that nucleation efficiency of ferric nitrate solution is much higher than that of particulate seeds. This result was attributed to the higher oxide particle number concentration afforded by in situ formation of ferric oxide, resulting in higher nucleation frequency and seeds/matrix interfacial contact. This interpretation is supported by other authors [8] and is consistent with mentioned crystallographic seeding effect. Co-precipitated aluminium - ferric oxide phases from an alkoxide and Fe(NO$_3$)$_3$ solution [9] or Al, Fe nitrates [10] revealed a different phase transformation series as is reported above. The first crystalline phase in the both solution routes was single phase γ-(Al, Fe)$_2$O$_3$ of spinel structure. Polli at al. [10] postulated, that the phase γ-(Al, Fe)$_2$O$_3$ directly transforms to α-(Al, Fe)$_2$O$_3$ solid solution without the prior nucleation of ferric oxide seeds. Bey and Simpkin [9] reported, that enhanced formation of α-Al$_2$O$_3$ could arise from segregation of Fe-rich clusters within γ-(Al, Fe)$_2$O$_3$ matrix, which could nucleate α-Al$_2$O$_3$ at much lower temperatures and acts as seeds for α-Al$_2$O$_3$. The latest two effects of Fe^{3+} ions on crystallisation of α-Al$_2$O$_3$ are evidently different from epitaxic-crystallographic effect and it was earlier used by McArdle and Messing [7] as solution seeding effect. The aim of this work is to study crystallisation of α-Al$_2$O$_3$ in the gels derived from colloidal sols of γ-AlOOH-Fe(NO$_3$)$_3$-H$_2$O system. Occurrence of Fe^{3+} containing phases, as dominant seeding effect, is studied by Mössbauer spectroscopy.

EXPERIMENTAL PART

Monolithic unseeded and seeded (α-Al$_2$O$_3$, α-Fe$_2$O$_3$ or Fe(NO$_3$)$_3$) boehmite gels were prepared from commercial boehmite (Condea, Pural SB ~ 240 m^2 g^{-1}, ~ 10 nm particle size) using the common procedure [3, 5]. Water boehmite suspension (15 wt.%) was peptised with nitric acid (*pH* ~ 2.5) by mixing at 55 °C. Unpeptized part of boehmite (~ 2 wt.%) was eliminated from the sol by centrifugation (10000 rpm).

The boehmite sol was seeded-mixed with α-Al_2O_3 (sample A) particles (< 0.2 μm and 5 wt.% on boehmite--derived alumina) hematite (samples H) particles (< 0.2 μm and 5 wt.% on Al_2O_3) or by solution of $Fe(NO_3)_3$, samples N, (5 wt.% Fe_2O_3 on Al_2O_3). The sols were poured into a plastic plane dishes. Thin layer of sol (~ 1 mm) gelled in about 1 h. Gel was allowed to dry at room temperature for 2 days and then it was crackled to large fragments (several cm²). Obtained gel fragments of thickness ~ 150 μm were used for experiments. Gels seeded with $Fe(NO_3)_3$ have red colour and are transparent while those with hematite particles are opaque. Gels were heated in atmospheric electric furnace in the temperature range 500 - 1500 °C with heating rate of 10 °C / min. Thermal analysis (DTA, TGA) of gels were carried out in air at a heating rate of 10 °C / min using V 1.9 DTA Instrument. Crystalline phases were identified by X-ray diffraction using CoK_α radiation (Dron 2.0). Mössbauer spectra were measured at room temperature and at 77 K using conventional Mössbauer spectrometer with source ^{57}Co in Rh matrix. Spectra were fitted using NORMOS program [12].

RESULTS

Crystallisation temperature (table 1) of α-Al_2O_3 in boehmite derived alumina gels depends on the used seeding compound (α-Al_2O_3, α-Fe_2O_3 or $Fe(NO_3)_3$) and preheating (24 h at 700 °C). In the comparison with unseeded sample the crystallisation temperature decreased about of 85 °C in sample A, 105 °C in samples H and in samples N about 195 °C. According to this result, one can suppose a qualitative difference between these two types of ferric oxide seeds. We supposed different response of samples H and N to the preheating treatment at temperatures enough high for supporting dissipation of Fe^{3+} ions in the alumina (defect phases) matrix, but lower because of preventing crystallisation of α-Al_2O_3. This temperature experimentally find is about 750 °C, therefore for preheating was chosen temperature 700 °C, but 24 hours. To verify this hypothesis, all samples were preheated at this temperature and time and afterwards the samples were examined by thermal analysis. As is shown in table 1, DTA gives a positive answer. Due to preheating--nucleation, the crystallisation temperature decreased even more about 40 °C only in the sample N. This indicates some possible difference in the crystallisation mechanism or different seeding effect of particulate α-Fe_2O_3 and ferric oxide originated from $Fe(NO_3)_3$ solution.

For further consideration, it is necessary to know the phase composition after heat treatments of both types of samples. Occurrence of phases was detected by means of XRD (table 2). Used boehmite results in defect alumina phases (γ, δ, θ-Al_2O_3) with very weak crystallinity (difficult XRD distinguishing) and as not important for following consideration presented in table 2. Contents of particulate α-Fe_2O_3 seeds

(sample H) begin to decline at the 900 °C and it is simultaneously associated with appearance of α-Al_2O_3 phase. As is known [7, 8] α-Al_2O_3 epitaxially nucleates and growths on the surface of α-Fe_2O_3 seeds. Ferric oxide is continuously dissolved in this new formed α-Al_2O_3 phase, which is turning to solid solution of Fe_2O_3 in Al_2O_3 or $(Al, Fe)_2O_3$, respectively. Ferric oxide (α-Fe_2O_3) disappears from the system after 1 h of annealing at the temperature of 1200 °C. From the point of view of ferric oxide phase detectable by XRD, samples N are quite simple. Own Fe_2O_3 phase was not detected throughout the used temperature range, even not after 24 h heating at the temperature of 600 or 700 °C, respectively.

A series of heat-treated H samples examined by Mössbauer spectroscopy is in good agreement with the previous XRD observation. Figure 1 shows representative spectra of H samples recorded at RT. Mössbauer spectrum of the sample annealed at 700 °C was fitted by one sextet with the hyperfine splitting $H_{ef} = 51.5$ T that corresponds to hematite (figure 1*a*). The mutual interaction of the two components γ-Al_2O_3 and α-Fe_2O_3 of the system appears at the temperature of 900 °C. The corresponded spectrum (900 °C / 1h, figure 1*b*) shows formation of a new phase with iron oxide content, we

Table 1. Crystallisation temperature of α-Al_2O_3 as DTA exoterms (heating rate 10 °C/min) in dependence of used seeds (A - α-Al_2O_3, H - α-Fe_2O_3, N - $Fe(NO_3)_3$ solution) and preheating (700 °C / 24 h).

Sample	t (°C), DTA exoterms	
--		preheated
unseeded	1195	1195
seeded A	1110	1110
seeded H	1090	1088
seeded N	1000	960

Table 2. Occurrence of α-Al_2O_3 and α-Fe_2O_3 phases as identified by RTG diffraction for H samples and N samples after indicated annealing.

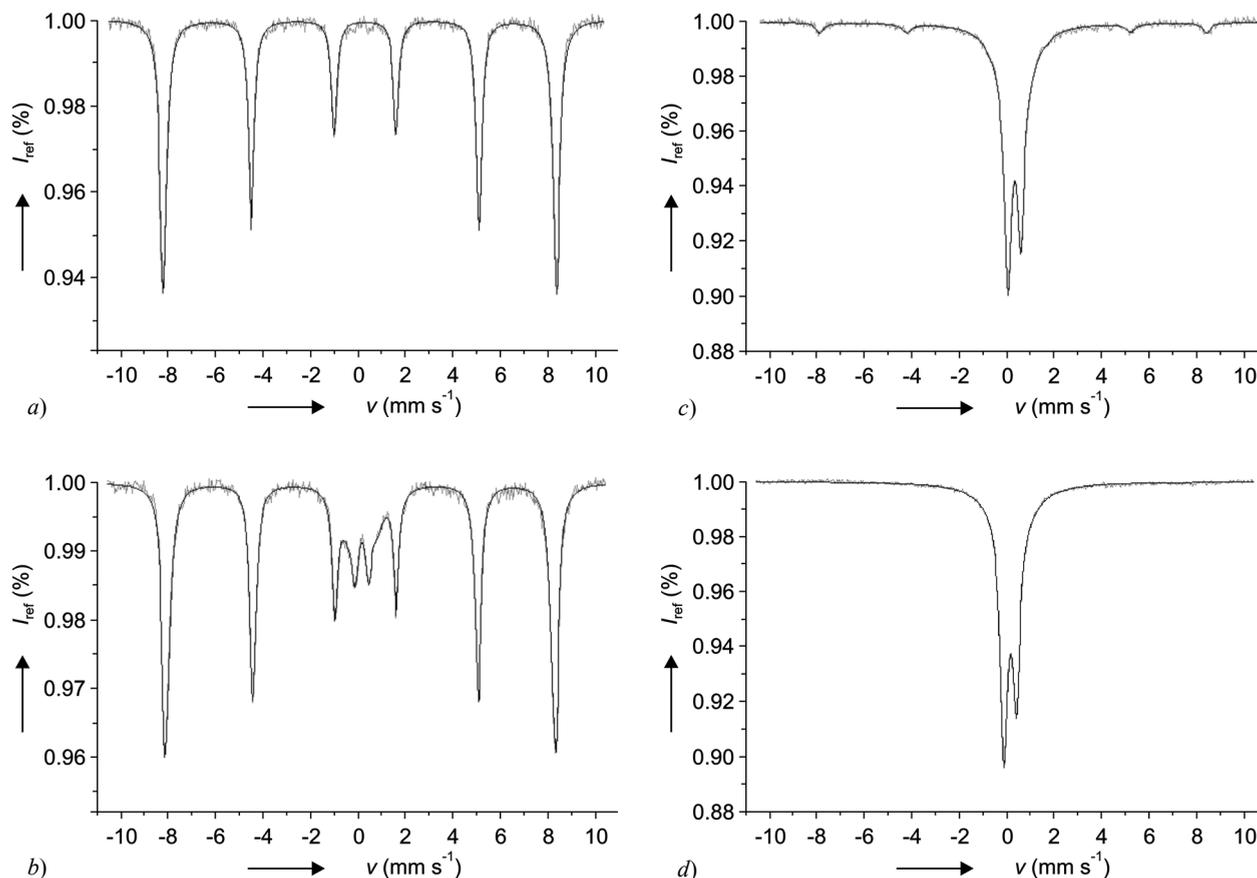| annealing		phases	
t (°C)	τ (h)	H	N
25	-	α-Fe_2O_3	-
500	1	α-Fe_2O_3	-
700	24	α-Fe_2O_3	-
800	1	α-Fe_2O_3	α-$(Al, Fe)_2O_3$
900	1	α-Fe_2O_3, α-Al_2O_3	α-$(Al, Fe)_2O_3$
1000	1	α-Fe_2O_3, α-Al_2O_3	α-$(Al, Fe)_2O_3$
1100	1	α-Al_2O_3, α-Fe_2O_3	α-$(Al, Fe)_2O_3$
1200	1	α-$(Al, Fe)_2O_3$	α-$(Al, Fe)_2O_3$

Figure 1. Mössbauer spectra recorded at room temperature of the sample H (hematite particles seeds, 5 wt.%) after heat treatments. *a*) 700 °C / 1 h, *b*) 900 ° C / 1 h, *c*) 1100 °C / 1 h, *d*) 1350 °C / 3 h.

have found that 81 % of iron is in magnetically ordered component which correspond to hematite (α-Fe$_2$O$_3$). The six line pattern was fitted with - two sextets. This is typical for slightly substituted hematite [12]. The substitution of Fe^{3+} by Al^{3+} is relatively well documented. Such substitutions by diamagnetic ions reduce the hyperfine field [12 - 15]. The rest of iron (19 %) is in paramagnetic phase in Fe^{3+} valence state. In the sample 1100 °C / 1h (figure 1*c*) we have identified only 8 % of substituted hematite and the rest of iron in paramagnetic phase with Fe^{3+} ions. In the sample 1350 °C / 3h only paramagnetic phase can be identified. Paramagnetic doublet (figure 1*c, d*) corresponds to the highly dispersed iron (Fe^{3+}) in the system that can be present only in the form of solid solution of Fe$_2$O$_3$ in α-Al$_2$O$_3$ or α-(Al, Fe)$_2$O$_3$, respectively. The formation of the new phase α-(Al, Fe)$_2$O$_3$ is in direct connection with the decrease of hematite content in the system. No further changes are observed after heating at 1500 °C/3h (figure 1*d*).

In the Mössbauer spectrum of sample N heated at 600 or 700 °C for 24 h (figure 2*a, b*) we have identified two doublets which correspond to Fe^{3+} [16, 17] in the form of highly dispersed iron species (i. e., solid-solution, surface-phase or small iron oxide particles). Used alumina gel heat treated at 550 °C has the surface area about 280 m^2 g^{-1}. On such large surface, 5 wt.% of Fe$_2$O$_3$, it can be dispersed on atomic or in Fe^{3+} level. From the composition of this sample can be determined, that approximately one Fe^{3+} ion belongs to one nm^2 of the gel (γ-Al$_2$O$_3$) surface. However, according to XRD no other phase is present than only weak crystallised γ-Al$_2$O$_3$, it follows, that by Mössbauer spectra is detected solid solution of Fe$_2$O$_3$ in γ-Al$_2$O$_3$ or γ-(Al, Fe)$_2$O$_3$, respectively. These spectra (figure 2*a, b*) obviously differ from spectra for the stable α-Al$_2$O$_3$ phase (figure 1*d*) in parameters of the doublets. The shape and Mössbauer parameters of the spectra for sample heated at 700 °C / 24 h and 800 °C / 1 h (figure 2*c*) are the same as the previous one (figure 2*b*). It suggests that no changes were observed by means of Mössbauer spectroscopy.

The radical change was observed in the spectrum after one hour heating at 900 °C of preheated samples at 700 °C / 24 h. The spectrum (figure 2*d*) has the same parameters as that of the sample H after heating at 1350 and 1500 °C (figure 1*d*). Such behaviour indicate the transformation of one iron disperse form γ-(Al, Fe)$_2$O$_3$ to another one α-(Al, Fe)$_2$O$_3$.

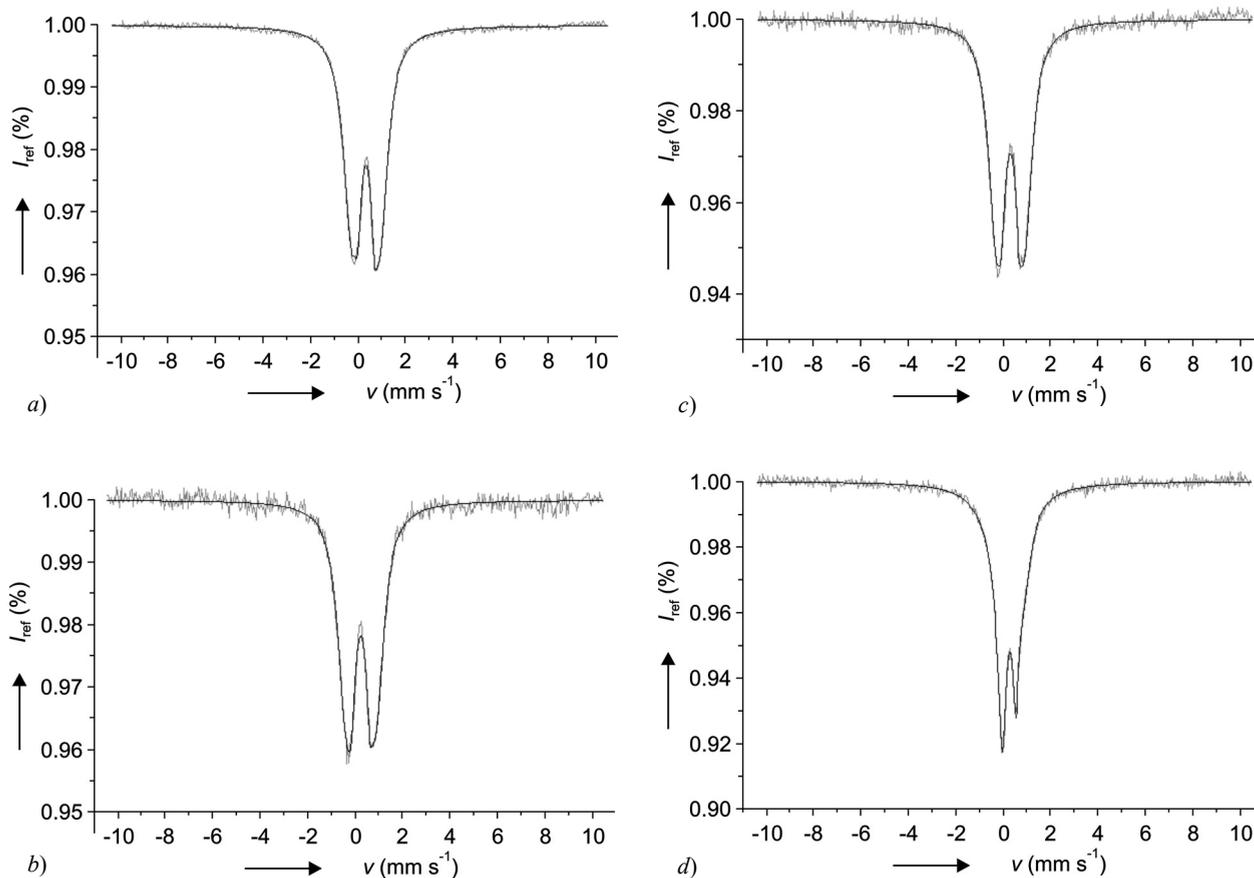There are no problems to distinguish between different magnetically ordered phases when they are

Figure 2. Mössbauer spectra recorded at room temperature of the sample N (seeded with Fe(NO$_3$)$_3$, 5 wt.% of Fe$_2$O$_3$) after heat treatment.
a) 600 °C / 24 h, *b)* 700 °C / 24 h, *c)* 700 °C / 24 h + 800 °C / 1 h, *d)* 700 °C / 24 h + 900 °C / 1 h.

present in the well-crystallised form, with low degree or without any substitution. Both substitution and presence of small superparamagnetic particles make the situation more complicated [12 - 15]. In these cases, it is necessary to perform other supplementary measurements at low temperature. The room temperature Mössbauer spectra of such samples consist mainly of paramagnetic doublet (e.g. figure 2*a, b*) accompanied by a hyperfine split sextet with very broad lines indicating the presence of magnetic component in the sample. The spectra measured at liquid nitrogen temperature reveal that the relative area of doublet decreases, whereas the total area of magnetically split component increases. In order to prove the presence of small hematite particles in our samples we have performed measurement at liquid nitrogen temperature (77 K) on sample 700 °C / 24 h (figure 3). According to that measurement, about 30 % of iron is in magnetically split component, which can correspond to the hematite particles of the size approximately 6 nm. To prove this conclusion the Mössbauer measurement at more temperatures (at least at liquid helium) should be done. Larger part of iron (about 70 %) is present as solid solution γ-(Al, Fe)$_2$O$_3$. Similar results were obtained in [17].
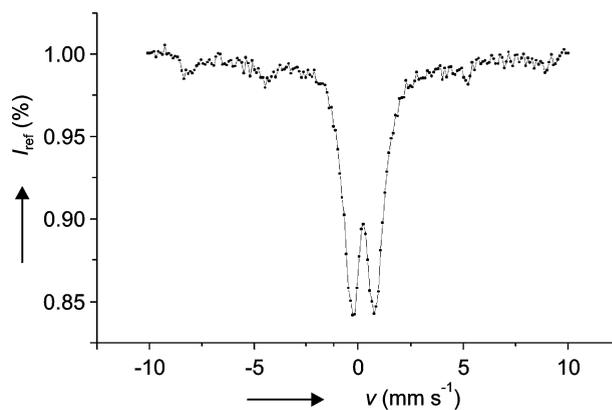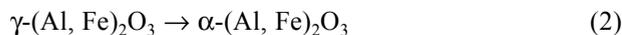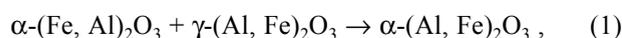

Figure 3. Mössbauer spectra of the sample N (seeded with Fe(NO$_3$)$_3$) after annealing at 700 °C for 24 h, recorded at 77 K.

DISCUSSION

We have proved in agreement with [7, 8], that nucleation efficiency of iron nitrate on weight basis is much higher than direct seeding with α-Al$_2$O$_3$ or

α-Fe$_2$O$_3$ particles. There is also probably some difference in α-Al$_2$O$_3$ and α-Fe$_2$O$_3$ seeding effect arising from interaction of α-Fe$_2$O$_3$ with defect alumina phases before own nucleation, as is proved by Mössbauer spectroscopy (figure 1*b*). According to the equilibrium phase diagram Al$_2$O$_3$ - Fe$_2$O$_3$ [18], the maximum solubility of Al$_2$O$_3$ in Fe$_2$O$_3$ is 25 wt.% and Fe$_2$O$_3$ in Al$_2$O$_3$ 7 wt.%, but metastably can be extended according [10] up to at least 20 wt.% Fe$_2$O$_3$. Surface solution of Al^{3+} on α-Fe$_2$O$_3$ seeds makes the process of transformation of γ, $\theta \to \alpha$-Al$_2$O$_3$ easier due to different properties (e.g. mobility) of Fe^{3+} and Al^{3+} ions in oxides. Diffusion coefficients (cm^2 sec^{-1}) of atoms in Fe$_2$O$_3$ are more than 10 orders higher than those for atoms in Al$_2$O$_3$ [19]. The mobility causes conversion of cubic γ-Fe$_2$O$_3$ to hexagonal α-Fe$_2$O$_3$ at $\sim$ 600 °C lower than those needed for the formation of α-Al$_2$O$_3$. Similar effect of Fe^{3+} and Al^{3+} ions on transformation can be expected in mutual solid solutions of Al$_2$O$_3$ - Fe$_2$O$_3$. The transformation temperature of these solid solutions can be somewhere between 600 and 1200 °C. By the other words, higher seeding efficiency of α-Fe$_2$O$_3$ in comparison of α-Al$_2$O$_3$ seeds is caused by mutual interaction of Fe$_2$O$_3$ seeds and alumina matrix.

In N samples, Fe$_2$O$_3$ is formed in situ from Fe(NO$_3$)$_3$ in γ-AlOOH / γ-Al$_2$O$_3$ matrix. This system was studied many times [20 - 23] for the purpose of catalytic applications, where the goal was to achieve high dispersity of Fe$_2$O$_3$. With agreement with these studies, samples N contain up to 800 °C two high disperse forms of iron oxide, a solid solutions γ-(Al, Fe)$_2$O$_3$ (about 70 % Fe$_2$O$_3$) and high substituted hematite particles of the size $\sim$ 6 nm (about 30 % of Fe$_2$O$_3$). Seeding frequency of such small particles is very high - approximately 3 . 10^{16} cm^{-3} (calculated from the particle size, weight content and densities). These hematite particles are de facto solid solution of Al$_2$O$_3$ in Fe$_2$O$_3$. Preheating (nucleation) effect was observed only in these samples (seeded with Fe(NO$_3$)$_3$) which can be explained only by extension of α-(Fe, Al)$_2$O$_3$ solid solution. Transformation of γ, $\theta \to \alpha$-Al$_2$O$_3$ simply passes through growth of nanometer sized hematite crystals without need of epitaxial nucleation (1) and/or by direct transformation of γ to α solid solution as proved Poli et al. [10] in monophase (Al, Fe)$_2$O$_3$:

$$\alpha\text{-(Fe, Al)}_2\text{O}_3 + \gamma\text{-(Al, Fe)}_2\text{O}_3 \to \alpha\text{-(Al, Fe)}_2\text{O}_3 \, , \quad (1)$$

$$\gamma\text{-(Al, Fe)}_2\text{O}_3 \to \alpha\text{-(Al, Fe)}_2\text{O}_3 \quad (2)$$

According to the presented results, the seeding effect of Fe$_2$O$_3$ originated from Fe(NO$_3$)$_3$ can be attribute to the solution effect.

CONCLUSION

It has been shown that among used seeds (α-Al$_2$O$_3$, α-Fe$_2$O$_3$ and Fe(NO$_3$)$_3$) only Fe(NO$_3$)$_3$ has preheating (e.g. 700 °C) – nucleation effect on crystallisation of α-Al$_2$O$_3$ phase from boehmite derived alumina gels.

Characteristic feature of Fe(NO$_3$)$_3$ seeded gels is the presence of two highly dispersed iron oxide phases, substituted hematite (α-(Fe, Al)$_2$O$_3$ of the particle size $\sim$ 6 nm and about 30 wt.%) and solid solution of γ-(Al, Fe)$_2$O$_3$ (about 70 wt.%) occurred before transformation to the α-Al$_2$O$_3$ phase.

Both solid solution of α-(Fe, Al)$_2$O$_3$ and γ-(Al, Fe)$_2$O$_3$ transform directly to the stable α-(Al, Fe)$_2$O$_3$ phase, so the seeding effect of Fe(NO$_3$)$_3$ / Fe$_2$O$_3$ can be attributed as solution effect or effect of Fe^{3+} dispersed ions, respectively resulting in transparent ceramics sintered below 1300 °C.

References

1. Zhou R.S., Snyder R. L.: Acta Crystalogr. *B47*, 617 (1991).
2. Levin I., Brandon D.: J. Am. Ceram. Soc. *81*, 1995 (1998).
3. Shelleman R. A., Messing G. L., Kumagai M.: J. Non-Crystalline Solids *82*, 277 (1986).
4. Suwa Y., Roy R., Komarneni S.: J. Mater. Sci. Lett. *5*, 21 (1986).
5. Pach L., Roy R., Komarneni S.: J. Mat. Res. *5*, 278, (1990).
6. Kotula P. G., Erickson D. D., Carter C. B.: in *Mat. Res. Soc. Symp. Proc.* Vol. 319, 57-62 (1994).
7. McArdle J. L., Messing G. L.: Adv. Ceram. Mat. *3*, 387 (1988).
8. Oberbach Th., Günther C., Werner G., Tomandl G.: cfi/Ber. DKG *74*, 719 (1997).
9. Bye G. C., Simpkin G. T.: J. Am. Ceram. Soc. *57*, 367 (1974).
10. Polli A. D., Lange F. E., Levi C. G., Mayer J.: J. Am. Ceram. Soc. *79*, 55 (1996).
11. Morup S., Knudsen J. E.: Acta Chimica Hungarica, 121, *147* (1986).
12. Murad E., Johnson J. H.: in G. J. Long: *Mössbauer Spectroscopy Applied to Inorganic Chemistry Volume II*, pp. 407-582, Plenum Press, New York 1984.
13. Morup S., Topsoe H., Lipka J.: Journal de Physique *C6*, 287 (1976).
14. Hoy G. R.: in G. J. Long: *Mössbauer Spectroscopy Applied to Inorganic Chemistry Volume I*, pp. 195-222, Plenum Press, New York 1984.
15. Topsoe H., Dumesic J. A. and Morup S.: in R. L. Cohen: *Applications of Mössbauer Spectroscopy Volume II*, pp. 55-188, Academic Press, New York 1980.
16. Ernstsen V., Morup S.: Hyperfine Interactions *70*, 1001 (1992).
17. Sontheimer F., Nagy D. L., Deasi I., Lohner T., Ritter G., Seyboth D., and Wegener H.: Journal de Physique *C6*, 443 (1974).
18. Muan A., Gee C. L.: J. Am. Ceram. Soc. *39*, 207 (1956).
19. Kingery W. D., Bowen H. K., Uhlmann D. R.: in *Introduction to Ceramics, Second Edition*, p. 239, J. Wiley & Sons, New York 1976.

20. Hoffmann D. P., Houalla M., Proctor A., Fay M. J., Hercules D. M.: Appl. Spectroscopy *46*, 208 (1992).
21. Hoffmann D. P., Houalla M., Proctor A., Fay M. J., Hercules D. M.: Appl. Spectroscopy *46*, 489 (1992).
22. Clark F. T., Springman M. C., Willcox D., Wachs I. E.: Journal of Catalysis *139*, 1 (1991).
23. Ramselaar W. L. T. M., Crajé M. W. J. R., Hadders H., Gerkema E., de Beer V. H. J., and van der Kraan A. M.: Appl. Catalysis *65*, 69 (1990).

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KRYŠTALIZÁCIA Al$_2$O$_3$ – Fe$_2$O$_3$ GÉLOV A MÖSSBAUEROVA SPEKTROSKOPIA

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Keramické Al$_2$O$_3$ vlákna, povlaky a membrány sa pripravujú metódou sól-gél vychádzajúc z peptizovateľného böhmitu. Problémovým procesom prípravy týchto materiálov je kryštalizácia gélov spôsobená obtiažnou nukleáciou α-Al$_2$O$_3$. Aby sa kryštalizácia mohla riadiť, a tým aj vlastnosti, pridávajú sa do systému nukleačné prísady – očkovadlá. Sú to jemné kryštály (< 0.2 μm) α-Al$_2$O$_3$ alebo izoštruktúrne α-Fe$_2$O$_3$ a Cr$_2$O$_3$ [1 - 5], ktorých nukleačný efekt má kryštalografický – epitaxný charakter. Oxid železitý sa líši od ostatných očkovadiel tým, že ho možno vniesť do systému okrem partikulárnej formy aj ako roztok Fe(NO$_3$)$_3$. Objektom štúdia tejto práce Mössbauerovou spektroskopiou je nukleačný efekt Fe$_2$O$_3$ vznikajúceho in situ z Fe(NO$_3$)$_3$ pri tepelnom spracovaní gélov. Böhmitové soli stabilizované s HNO$_3$ (*pH* ÷ 2.5) a očkované s α-Al$_2$O$_3$, α-Fe$_2$O$_3$ a Fe(NO$_3$)$_3$ sa transformovali na gély voľným sušením. Teplota kryštalizácie gélov (table 1) klesá v poradí bez očkovadla → α-Al$_2$O$_3$ → α-Fe$_2$O$_3$ → → Fe(NO$_3$)$_3$ a predohrev (700 °C / 24 h) sa prejavil ďalším znížením teploty kryštalizácie na géloch očkovaných s Fe(NO$_3$)$_3$. Vo vzorkách H, očkovaných s α-Fe$_2$O$_3$ kryštalizuje priamo tuhý roztok α-(Al, Fe)$_2$O$_3$ pri súčasnom zániku fázy α-Fe$_2$O$_3$ (table 2). Vo vzorkách N (očkované s Fe(NO$_3$)$_3$) nebola RTG fázovou analýzou detegovaná samostatná fáza Fe$_2$O$_3$, ale len fáza α-(Al, Fe)$_2$O$_3$ od teploty 800 °C. Podľa Mössbauerovej spektroskopie Fe$_2$O$_3$ je vo vzorkách prítomný vo vysoko disperznej forme ako tuhý roztok (približne 70 hmotn.%) γ-(Al, Fe)$_2$O$_3$ a vo forme substituovaných kryštálov hematitu (približne 30 hmotn.%) o veľkosti ~ 6 nm. Nukleačný efekt rozptýleného Fe$_2$O$_3$ v tuhých roztokoch γ-(Al, Fe)$_2$O$_3$ a α-(Fe, Al)$_2$O$_3$ – hematit nemá charakter kryštalografický, ale roztokový, tzn. ide o vplyv iónov Fe^{3+} na transformáciu defektných Al$_2$O$_3$ fáz (γ, δ, θ) na termodynamicky stálu α-Al$_2$O$_3$ fázu.