SOL - GEL α-Al₂O₃/Fe₂O₃ ABRASIVE GRAINS

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Boehmite derived alumina gels (grains and sticks) containing Fe_2O_3 in the range of 1 to 6 wt. % were sintered at 1350 °C for 3 hours. Relative density, strength and unexpectedly also the size of α-Al_2O_3 crystals increase with Fe_2O_3 content. A bimodal microstructure of anisotropic α-Al_2O_3 crystals is observed at and above 3 wt.% content of Fe_2O_3. Anisotropic growth of α-Al_2O_3 crystals is attributed to the presence of Fe^{2+} and to the specific nucleation effect of α-Fe_2O_3. Due to high strength and the relatively small size of α-Al_2O_3 crystals a Fe_2O_3 content of 3 wt.% seems most appropriate when applications of the material as abrasive grains are intended.

INTRODUCTION

Initiation of phase transformation by means of heterogeneous or epitaxial nucleation is widely used in the synthesis of materials for electronics [1]. In the field of large scale bulk material, the method is rather named seeding [2-9]. The method has been applied for about 20 years in the production of α-Al₂O₃ abrasive grains by the sol-gel process. In this case, there was only short time between the discovery of the method and its technological application. The first patent [6] and the journal publication [2] were issued practically simultaneously.

The method has been extended due to the existence of suitable raw material source of the aluminium compound: peptisable boehmite of Condea company (Germany). This boehmite is a by product of the synthesis of higher alcohols being characterised by high chemical purity, weak crystallinity and about 10 nm size of primary particles, which are aggregated. These aggregates are not strong and are peptisable in dilute acid solutions ($pH \cong 3$; $20 \leq$ wt.% of AlOOH) at temperatures of 50 - 70 °C. Addition of α-Al₂O₃ (1 - 3 wt.%) seed particles (< 0.5 μm) to boehmite sols results gradually in diphasic sols, gels and finally in highly uniform dense sintered microstructure even at lower temperature. Seed particles significantly enhance the rate of α-Al₂O₃ crystallisation as well as densification of materials to full density (e. g. abrasive grains) at about 1300 °C. This temperature is about 1000 °C lower than the temperature of the classical melting route (electric arc oven) of α-Al₂O₃ abrasive grains.

Nucleation and growth of α-Al₂O₃ in boehmite gel can be controlled not only by the α-Al₂O₃ phase itself, but also by phases that are isostructural with α-Al₂O₃ [3, 4], as are α-Fe₂O₃ and Cr₂O₃. The most frequently used seeds are α-Fe₂O₃, which are added into the system as fine α-Fe₂O₃ powder or Fe(NO₃)₃. 9H₂O. Unlike α-Al₂O₃, α-Fe₂O₃ seeds have a more complex influence on the mentioned system. The nucleation effect of α-Fe₂O₃ is followed by dissolution of Fe₂O₃ into the α-Al₂O₃ structure and partial reduction of Fe³⁺ to Fe²⁺ according to the redox equilibrium Fe³⁺/Fe²⁺. These processes result in anisotropic growth of α-Al₂O₃ crystals and, consequently, as is known [10], the bimodal microstructure can then increase the toughness of the material. Anisotropic grain growth of α-Al₂O₃ was recently attributed by Tartaj and Messing [11] to the presence and grain boundary segregation of Fe²⁺ ions.

The most important properties of α-Al₂O₃ abrasive grains are strength, toughness and the size of α-Al₂O₃ crystals. The aim of this work is to compare some mechanical properties and the microstructure of α-Al₂O₃ abrasive grains in dependence of α-Fe₂O₃ seed contents in the Al₂O₃ - Fe₂O₃ system.

EXPERIMENTAL PART

The boehmite gel used in this work was prepared from a commercial boehmite (Condea, 350 m² g⁻¹, ~ 10 nm particle size) by the commonly used procedure [2-4, 12]. Water-boehmite (18 wt.%) and Fe(NO₃)₃.9H₂O (1; 2; 3 and 6 wt.% on α-Al₂O₃) suspension was peptised by mixing it with HNO₃ ($pH \approx 2.5$) at 55 °C. The sols were mixed thoroughly until it gelled. The gels obtained were further slowly mixed on a hot plate, thickened (~ 26 wt.%) and extruded to sticks ($d \approx 0.4$ cm). Gel sticks were dried on air in vertical position and in a dryer at 90 °C. Dried sticks were cut to small cylinders ($d \approx 3.5$ mm and length ~ 5 mm) and used for diametrical compression tests (DCT) and crushed grains of the size 1.2 - 1.8 mm for measuring the strength of individual abrasive grains.

Gel samples were calcined at 550 °C for 1 hour to transform boehmite to γ-Al$_2$O$_3$. The samples were then sintered at 1350 °C for 3 hours in static air atmosphere. The heating rate was 10 °C min^{-1}.

Bulk density was measured according to Archimedes' law. Samples before weighing in water were hydrophobized by melted paraffin.

The strength of sintered abrasive grains was measured by force needed to crash an individual grain when linearly increasing the acting force. The diametrical compression test was performed similarly using cylindrical ($d \cong 3$ mm, length $\cong 5$ mm) samples and calculated according [13] to:

$$DCT = \frac{2F}{\pi dl} ,$$

where F is the acting force (N), d (mm) is the diameter and l (mm) the length of the sample.

These mechanical measurements enable fast mutual comparison of various samples. At least 10 tests were carried out from each sample. Dispersion of measured values are shown in the next part (table 1, figures 5 and 6).

Crystalline phases were identified by X-ray diffraction using CuK$_\alpha$ radiation (Dron 2.0). The microstructure of sintered samples was observed by SEM (Tesla BS 300).

Table 1. Mean size of crystals, l, anisotropic characteristics of crystals (% - portion, aspect ratio) on the surface and fracture vs. Fe₂O₃ content

| Fe₂O₃ (wt.%) | l (μm) | | anisotropic growth | | | |
| | surface | fracture | fracture | | surface | |
			portion (%)	ratio	portion (%)	ratio
1	0.95	0.86	-	-	-	-
2	1.22	1.02	-	-	-	-
3	1.53	1.37	4.7	1.83	6.4	2.12
6	2.73	2.12	8.8	2.12	9.8	2.44

RESULTS

The bulk density of sintered (1350 °C for 3 hours) samples increases with the Fe₂O₃ content (figure 1) in the system. Samples containing 3 wt.% of Fe₂O₃ reached the largest relative density (~ 99.5 %, figure 2). A little lower is the relative density for double content of Fe₂O₃. Deviation of experimental values (figure 2) from theoretical relative densities (calculation based on

densities of α-Al₂O₃ = 3.9869 and Fe₂O₃ = 5.2749 g cm^{-3} [14]) of samples is primarily caused by residual porosity, partly by non ideality of α-Al₂O₃/Fe₂O₃ solid solution and redox equilibrium of Fe^{3+}/Fe^{2+} ions.
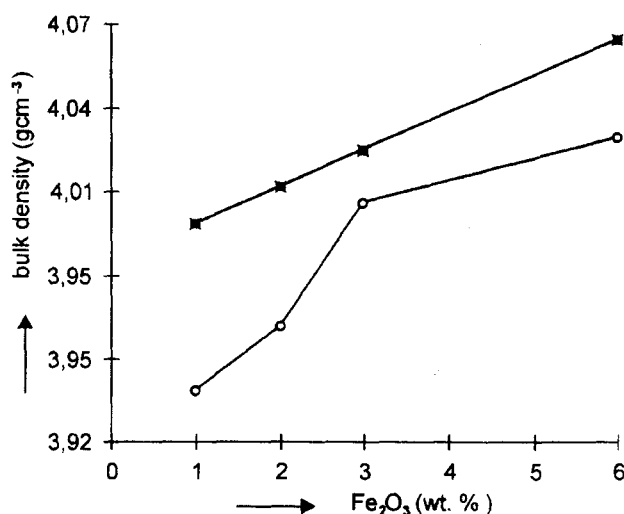

Figure 1. Bulk (experimental) and theoretical density of α-Al₂O₃/Fe₂O₃ sintered at 1350 °C for 3 hours vs. Fe₂O₃ content. ■ - Theoretical values, O - experimental values.
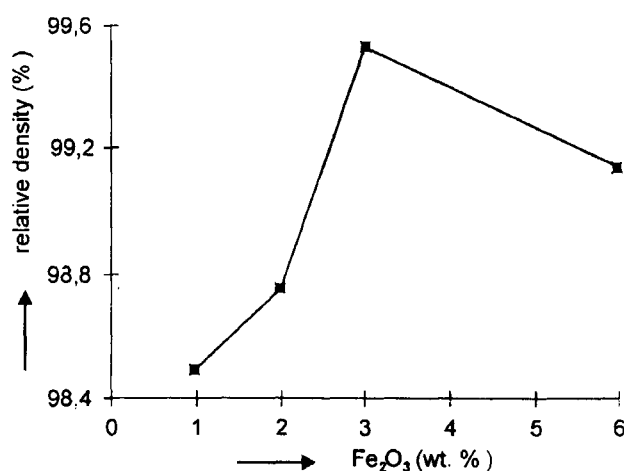

Figure 2. Relative density of α-Al₂O₃/Fe₂O₃ sintered at 1350 °C for 3 hours vs. Fe₂O₃ content.

The mean size of crystals (figure 3) is changed from about 0.5 to 2.5 μm and nearly linearly increases with Fe₂O₃ content. The size of crystals is little lower on the specimen surfaces than on fracture surfaces in all cases. The number of crystals per 100 μm^2 derived from their size unexpectedly decreases with Fe₂O₃ content (figure 4).

Measured mechanical parameters, strength of individual grains (figure 5) and DCT (figure 6) increased in the range of 1 - 3 wt.% of Fe₂O₃, but more significantly between 2 and 3 wt.%. These parameters

practically remained unchanged with larger content (6 wt.%) of Fe_2O_3. As can be seen from figures 5 and 6, bulk mechanical properties have similar course.
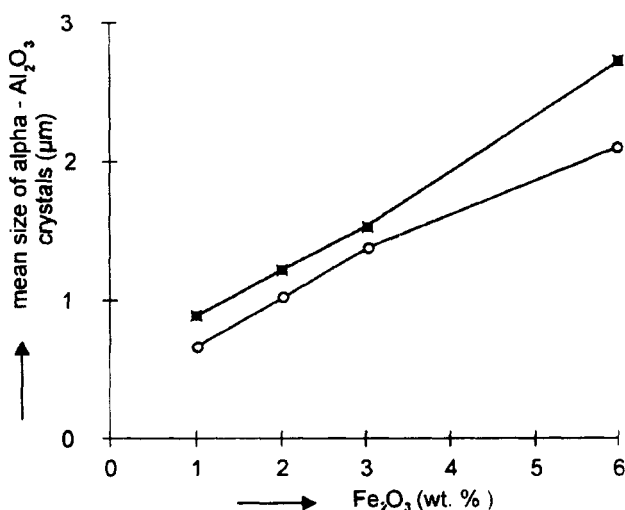

Figure 3. Mean size of α-Al_2O_3 crystals in sintered body (1350 °C for 3 hours) vs. Fe_2O_3 content.
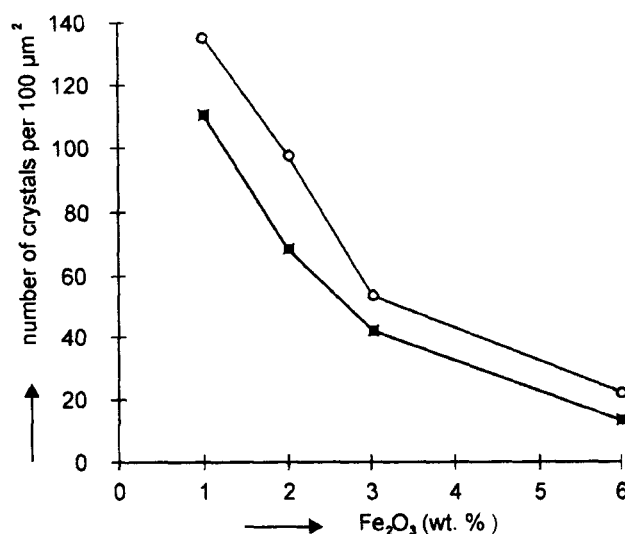■ - fracture, O - surface

Figure 4. Number of α-Al_2O_3 crystals for sintered body (1350 °C for 3 hours) vs. Fe_2O_3 content.
■ - fracture, O - surface

The microstructure of sintered samples (figures 7 and 8) significantly depends on Fe_2O_3 content. Unseeded samples (figures 7a, b) show the known porous vermicular microstructure [4, 5, 11, 12]. The shape of α-Al_2O_3 crystals is isometric in samples containing 1 and 2 wt. % of Fe_2O_3 (figures 7c-f). Elongated crystals are appeared at 3 wt.% (figure 8a, b) and this anisotropic growth is further extended with larger content of Fe_2O_3 (figures

$8c$-d). The crystal size generally increases with Fe_2O_3 content (table 1). The microstructure of samples with $Fe_2O_3 \geq 3$ wt. % is bimodal, the number of elongated

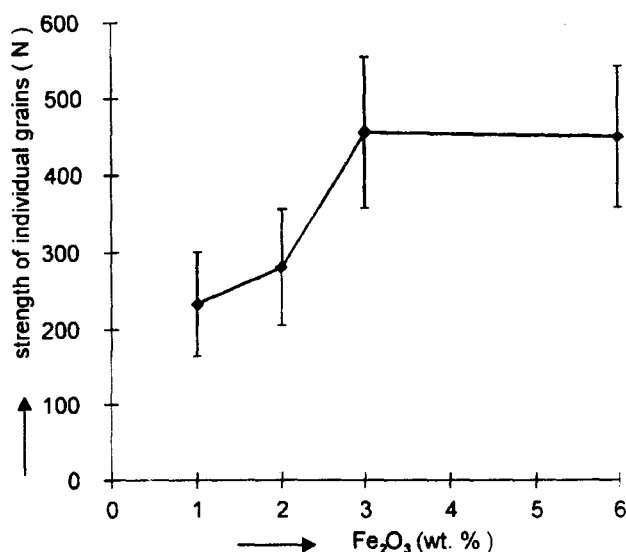Figure 5. Strength of individual α-Al_2O_3/Fe_2O_3 abrasive grains (size ~ 1 mm) sintered at 1350 °C for 3 hours vs. Fe_2O_3 content.
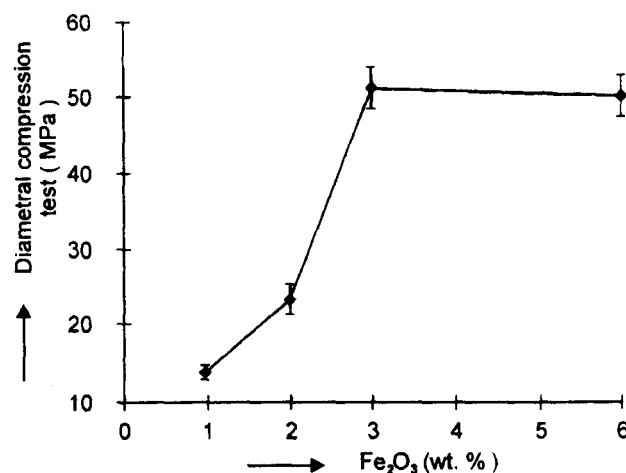

Figure 6. Diametrical compression test of sintered body (1350 °C for 3 hours) vs. Fe_2O_3 content.

crystal (% - portion) and their aspect ratio increased with Fe_2O_3 content (table 1).

X-ray analysis of sintered samples revealed only one set of α-Al_2O_3 reflections with shift of d_{hkl} values in dependence of Fe_2O_3 content (e. g. for 6 wt.% of Fe_2O_3, the shift is in the range of 0.22-0.89 % of α-Al_2O_3 d-values).

The intensity of green colour of sintered samples increased with Fe_2O_3 content.

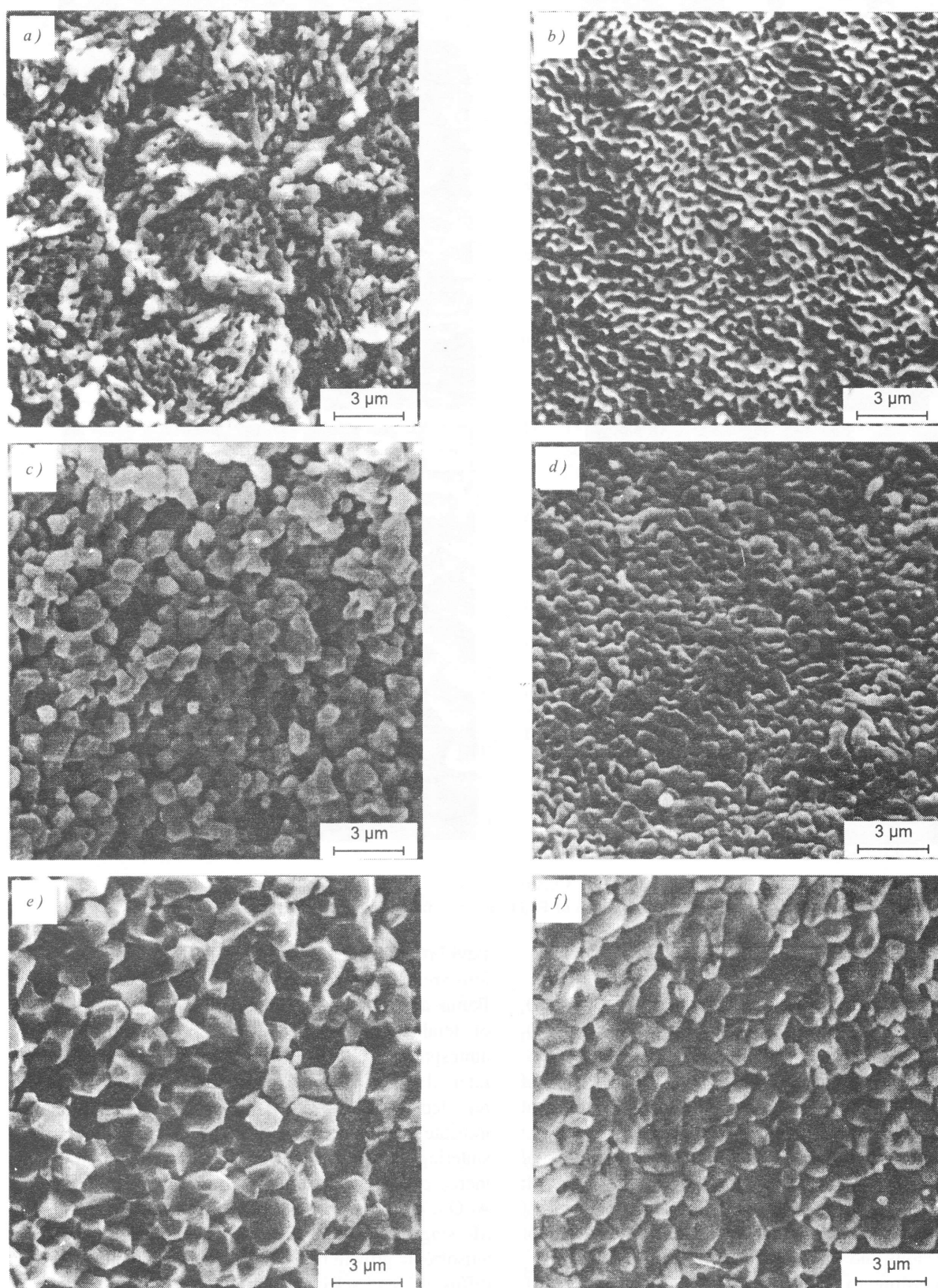Figure 7. SEM pictures of sintered bodies (1350 °C for 3 hours).
a), *b*) − unseeded; *c*), *d*) − seeded, 1 wt. % Fe_2O_3; *e*), *f*) - seeded, 2 wt.% Fe_2O_3; *a*), *c*), *e*) - fracture; *b*), *d*), *f*) - surface
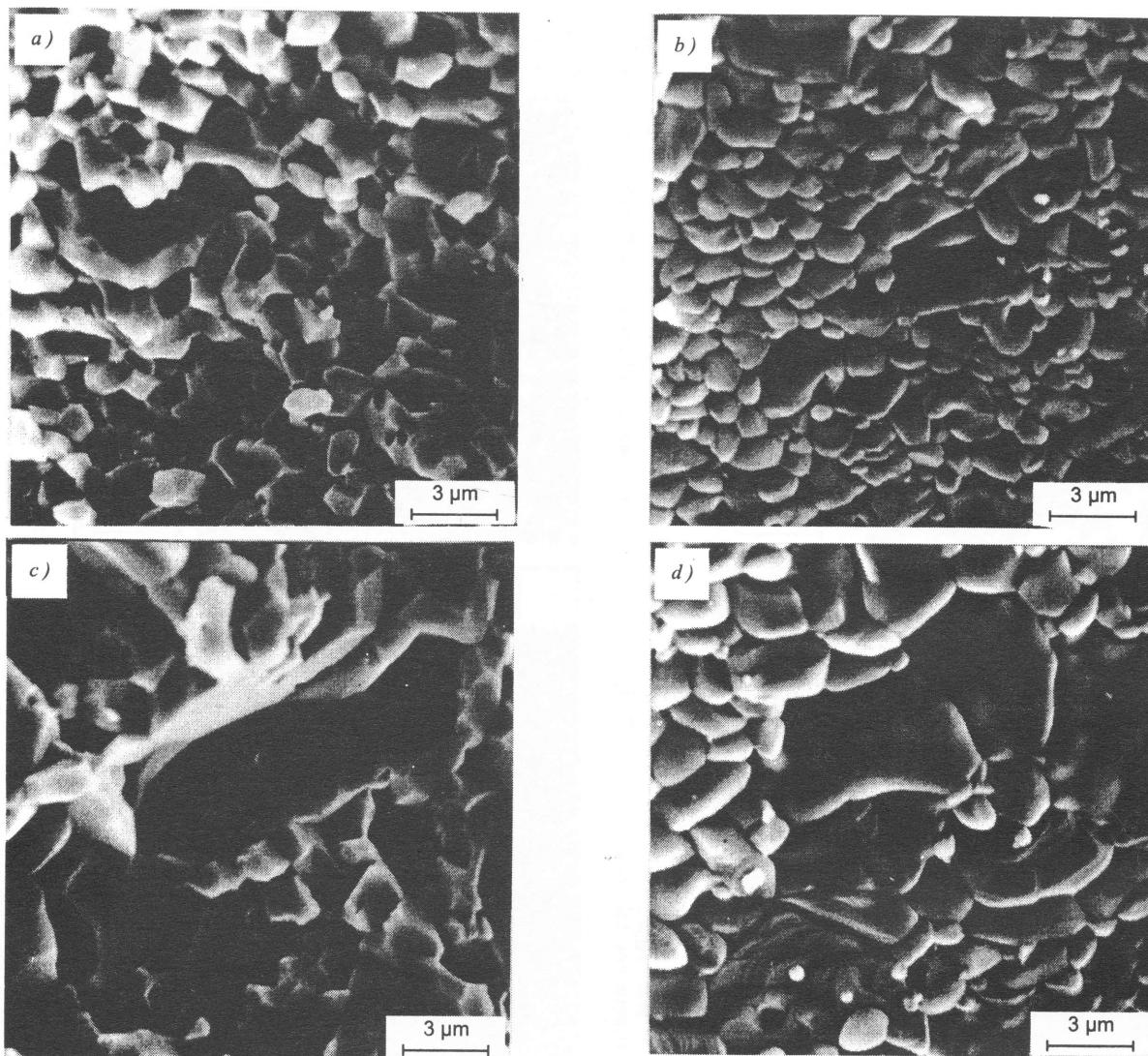
Figure 8. SEM pictures of sintered bodies (1350 °C for 3 hours).
a), *b)* – seeded, 3 wt. % Fe_2O_3; *c)*, *d)* - seeded, 6 wt. % of Fe_2O_3; *a)*, *c)* – fracture; *b)*, *d)* - surface

DISCUSSION

Figures 1 and 4 show, that the number of α-Al_2O_3 crystals per unit area is indirectly proportional to Fe_2O_3 content. The number of α-Al_2O_3 nucleation sites has to increase with Fe_2O_3 content, i. e. with concentration of seeds. This fact immediately indicates that the number of α-Al_2O_3 crystals observed on SEM pictures is not identical, but significantly smaller than the number of α-Fe_2O_3 seeds (nuclei). This apparent paradox is a result not only of nucleation of α-Al_2O_3 on the surface of seeds, but also an effect of simultaneous diffusion of Fe^{3+}/Fe^{2+} ions and the growth of α-Al_2O_3 crystals.

According to Al_2O_3 - Fe_2O_3 phase diagram [15], Al_2O_3 can dissolve ~ 9 wt.% of Fe_2O_3 at 1200 °C and about 20 wt.% (maximum value) at 1420 °C. However, metastable solubility is according to Polli, Lange and

Levi [16] extended up at least to 30 wt.% of Fe_2O_3. Fe^{3+} ions are partially reduced also in air furnace atmosphere. Ikuma and Gordon [17] reported that only about 2 wt.% of total Fe^{3+} is reduced to Fe^{2+} at 1450 °C in air atmosphere. Solubility of Fe^{2+} in α-Al_2O_3 entering the interval 0.7 - 1.9 wt.% is much lower at 1450 °C, as reported by Muan [18]. All these literature information indicate that the presence of Fe^{2+} ions is possible at used sintering temperature. This idea is supported by an increase of green colour caused by Fe^{2+} in sintered Al_2O_3/Fe_2O_3 samples. According to work of Tartaj and Messing, Fe^{2+} ions are responsible particularly for anisotropic growth of α-Al_2O_3 due to generally enhanced diffusivity and selective grain boundary segregation.

In agreement with literature sources [11, 14-18] there was also observed an anisotropic growth of α-Al_2O_3 at Fe_2O_3 content ≥ 3 wt.% in this work. However,

we suppose, that besides the effect of anisotropic growth, there is a nucleation one. The latter effect is based on the number of nuclei, diffusion path and on the size of primarily formed α-Al$_2$O$_3$ crystals. At high content of seeds (6 wt.% of Fe$_2$O$_3$), the diffusion path for dissolution of Fe$_2$O$_3$ into formed α-Al$_2$O$_3$ crystals is short, unlike that for low content of seeds (1 wt. % Fe$_2$O$_3$).

For a high number of nuclei (seeds), the number of small α-Al$_2$O$_3$ crystals is also high, and consequently the interphase energy is large. This situation leads to fast growth of crystals at sintering temperature (1350 °C). On the other hand, for a low number of seeds, the diffusion path is longer and more primarily formed small α-Al$_2$O$_3$ crystals conserve their identity during sintering. Unexpectedly one can conclude that many seeds (nuclei) brings few crystals (large size) and oppositely few seeds (nuclei) brings many crystals (smaller size) in the studied system.

From the viewpoint of mechanical properties, which are important for application of the material as abrasive grains, the content of Fe$_2$O$_3$ should be about 3 wt.%. Higher contents show no effect on strength of abrasive grains and cause growth of grains being inconvenient for abrasive grains.

CONCLUSION

Iron oxide introduced into boehmite sol as Fe(NO$_3$)$_3$. 9H$_2$O is an efficient nucleation (seed) agent in the thermal transformations of defect alumina phases (γ, δ, θ) to α-Al$_2$O$_3$.

The mean size of α-Al$_2$O$_3$ crystals (0.5 - 2.5 μm) increases with Fe$_2$O$_3$ content (1 - 6 wt.%), i. e. unexpectedly with number of α-Fe$_2$O$_3$ seeds. The intensity of green colour (presence of Fe^{2+}) of sintered (1350 °C) bodies increases in a similar way.

Both bulk density and mechanical strength (strength of individual grains and diametrical compression test) increase significantly between 2 and 3 wt. % of Fe$_2$O$_3$ content. The strength increase is attributed to anisotropic growth of α-Al$_2$O$_3$ crystals.

Anisotropic growth is related to the presence of Fe^{2+} ions and to the specific nucleation effect of α-Fe$_2$O$_3$ joined with dissolution of Fe$_2$O$_3$ into α-Al$_2$O$_3$.

Acknowledgement

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Submitted in English by the authors.

SÓL - GÉL α-Al₂O₃/Fe₂O₃ BRÚSNE ZRNÁ

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Al$_2$O$_3$ gél (zrná a tyčinky), pripravený z böhmitového sólu, obsahujúceho 1 až 6 % hmot. Fe$_2$O$_3$ sa spekal 3h pri teplote 1350 °C. Oxid železitý, vnášaný do systému ako Fe(NO$_3$)$_3$. 9H$_2$O je účinným nukleačným činidlom kryštalizácie α-Al$_2$O$_3$ z defektných γ, δ, θ - Al$_2$O$_3$ fáz. Stredná veľkosť kryštálov (0,5 - 2,5 μm) neočakávane rastie s obsahom Fe$_2$O$_3$ (1 až 6 hmot. %) tzn. s počtom nukleačných miest α-Al$_2$O$_3$. V rovnakom zmysle sa zvyšuje aj intenzita tmavozeleného sfarbenia súvisiaca s prítomnosťou Fe^{2+} iónov. Objemová hmotnosť a mechanická pevnosť (pevnosť jednotlivých zŕn a pevnosť v priečnom ťahu) sa zvyšuje s obsahom Fe$_2$O$_3$, najmä v rozmedzí 2 až 3 hmot. %. Zvýšenie pevnosti sa vysvetľuje výskytom predĺžených kryštálov α-Al$_2$O$_3$. Anizotropný rast kryštálov α-Al$_2$O$_3$ súvisí s prítomnosťou Fe^{2+} iónov a špecifickým nukleačným efektom α-Fe$_2$O$_3$ spojeným s rozpúšťaním Fe$_2$O$_3$ v α-Al$_2$O$_3$. Pre aplikáciu materiálu ako brúsnych zŕn je výhodný obsah Fe$_2$O$_3$ okolo 3 % hmot., kedy sa pozoruje vysoká mechanická pevnosť pri malých kryštáloch α-Al$_2$O$_3$.