

EFFECT OF ORGANIC ADDITIVES ON CRYSTALLIZATION OF BOEHMITE GELS

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Monolithic planar boehmite gels of thickness of ~0.15 mm unseeded, seeded by Fe(NO₃)₃ and doped (3 wt.%) with organics (PVA, PEG and EG) were examined by photoluminescence spectroscopy, in-situ optical transmittance and SEM. Polymeric organic additives although burned up at low temperatures (550°C), leave microstructure traces, having significant effect on high temperature processes, crystallization and sintering. Actually, polymeric additives (PVA or PEG) cancel a profound positive high effect of Fe(NO₃)₃ to α -Al₂O₃ nucleation.

INTRODUCTION

Crystallization of α -alumina in boehmite derived alumina gels takes place either by a nucleation and growth mechanisms, or epitaxially on surface of seed crystals [1-3] (only single growth and/or nucleation and growth). The former process can be controlled by the dissolved ions (e.g. Fe³⁺ [4-9]) - "solution" mechanism - and the second one by the crystallographic character of solid seeds [1-3, 10-12].

Crystallization of "high temperature" phases is a key process in sol-gel synthesis of materials, determining thus their final properties. Monolithic gels are unsuitable for practical ceramics applications due to their low green strength and large volume drying and sintering shrinkage. Polymeric additives are commonly used to strengthen inorganic wet gels, or powder compacts [13]. Water soluble polymers [14-16], as polyvinyl alcohol (PVA) and polyethylene glycol (PEG) are ones most frequently applied for this purpose. Known is e.g. use of PVA [17] for strength increase of boehmite gel plates, used as membranes at low temperatures. However, the effect of PVA and similar polymers on high temperature processes (crystallization and sintering) was not until yet studied systematically. Actually, at these temperatures organic additives are no more present because of their previous pyrolysis. The question however remains how their low temperature effects

influence (predestine) microstructural and/or chemical changes at high temperatures. Next to SEM, two less frequent methods are used in this study. A home designed method to in-situ measure the optical transmittance [18] and the standard photoluminescence spectroscopy [8]. The first method relates to the creation and disappearance of the light scattering species inside the particulate xerogel film matrices. The second one was found to be an effective tool in observing the crystallization of boehmite gels [8].

We showed recently [8] that photoluminescence spectra of Cr³⁺ impurity traces, even at molar concentration below 1 ppm, enable sensitive monitoring of the α - and θ -Al₂O₃ crystallization in boehmite derived alumina unseeded and Fe(NO₃)₃ seeded gels. Chromium ions in α -Al₂O₃ manifest a sharp dominant R1, R2 doublet at ~693 nm. The characteristic luminescence in θ -Al₂O₃ is not as strong and sharp as that from α -Al₂O₃ with a R-line doublet at ~685 nm [8, 19].

As recently found out [9, 20], "seeding" of boehmite gel with Fe(NO₃)₃ solution (5 wt.% Fe₂O₃) leads to transparent corundum ceramics by sintering at relatively low temperatures ~1300°C. It is an interest to increase the mechanical strength of the wet gels by polymeric additives. The aim of this work is to examine an effect of polymeric (PVA and PEG) and monomer (EG) additives on crystallization of unseeded gel and gel seeded with 5 wt.% of Fe(NO₃)₃.

EXPERIMENTAL

Monolithic AlOOH and AlOOH-Fe(NO₃)₃ (5 wt.% Fe₂O₃) gels were prepared from commercial boehmite (Condea Pural) and aqueous solution of Fe(NO₃)₃·9H₂O, using previously described procedure [3, 7, 8]. Water boehmite suspension (15 wt%) was peptized by mixing it with HNO₃ (*pH* ≅ 2.5) at ~55°C. Unpeptized part of boehmite (~2 wt.%) was removed from the sol by centrifugation (10 000 rpm). Aqueous solutions of PVA (average MW 49 000), or ethylene glycol (EG, reagent grade chemical) were finally added to the boehmite sols, to have their 3 wt.% content with respect to alumina. Transparent sol was poured on a plastic plate. Thin layer of sol (~1 mm) gelled in about 15 min. Gel was allowed to dry at room temperature for 2 days, cracking spontaneously to planar fragments (1-2 cm²). Gel fragments (~1 cm²) of ~150 μm thickness were thermally pre-treated as specified in table 1. Gels were further heated at a rate of 10°C/min in static air, or dynamic O₂ atmosphere in the temperature range 550-1350°C and cooled immediately. The in-situ measurements of the optical transmittance of gel fragments up to ~1300°C (heating rate of 10°C/min) were performed using device described previously [20]. The "white" light source (LED) was used in experiments. Photoluminescence spectra were measured at room temperature using DILOR-JOBIN YVON-SPEX LABRAM 010 confocal microscope laser Raman system. A He-Ne laser, operating at a wavelength of 632.8 nm with a power of 15 mW was used as an excitation source. Bulk density was measured by Archimedes method. The microstructure of sintered samples was observed by SEM (Tesla BS 300).

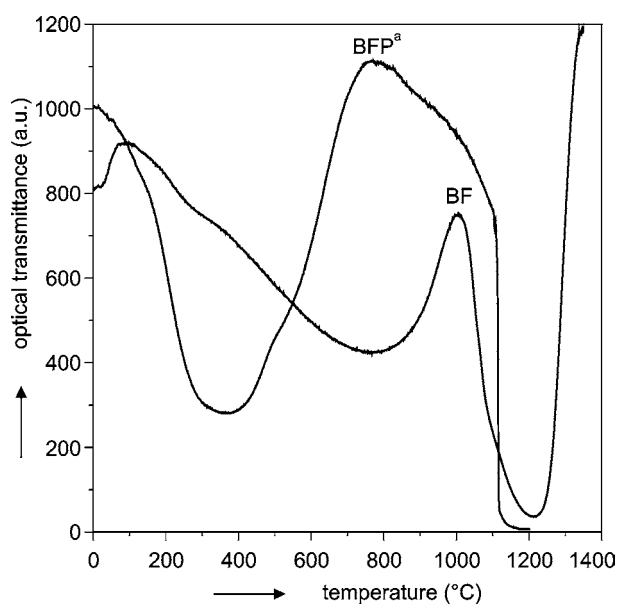
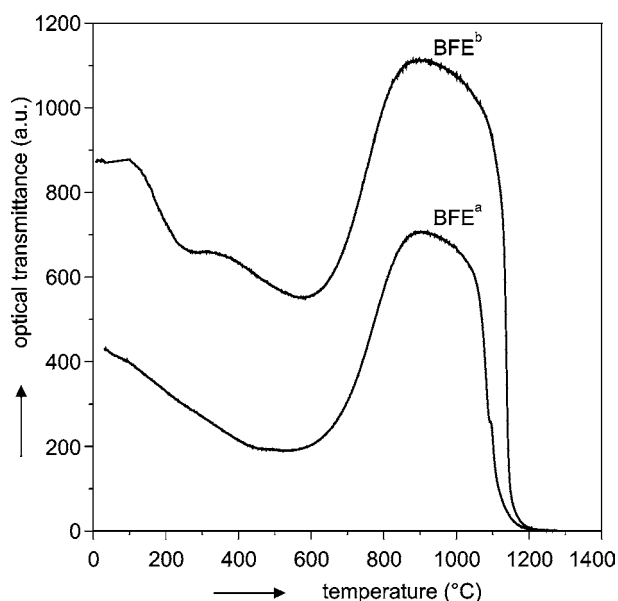
RESULTS

Optical transmittance

Preliminary experiments revealed that the final (1270°C) in-situ optical transmittance (OT) decreases continually with polymeric additives to 3 wt.%. The 3 wt.% level and all higher contents kept the final OT at zero. Used 3 wt.% content of organics was picked up on this boundary. OT results of samples B, BFP^a, BFE^a, BFE^b at ascending temperature are given in figures 1 and 2. The OT courses reflect microstructural and phase changes with temperature [18], discussed later. Seeded (Fe(NO₃)₃) boehmite gels (BF) shows an interesting pattern [20], where OT after an intermediate decrease at ~1200°C increases again even over its initial value. All samples with organics additives (BFP^a, BFP^b, BFE^a, BFE^b) differ from the above mentioned seeded BF sample, containing no organic additive, in a total irreversible loss of OT at ~1100°C. Sample BFE^b however visually shows same little OT when ex-situ heated at 1350°C. From a view point of OT, the samples with organic additives, seeded with Fe(NO₃)₃ behave, as unseeded boehmite gel without organics (sample B).

Table 1. Gel admixtures and heating rates to calcination temperature (1 h at 550°C).

dopant (heating rate)	B	BF	BFP ^a	BFP ^b	BFE ^a	BFE ^b
Fe ₂ O ₃ (5 wt.%)		+	+	+	+	+
PVA (3 wt.%)			+	+		
EG (3 wt.%)					+	+
10°C/min	+	+	+		+	
0.1°C/min				+		+

Figure 1. Optical Transmittance of samples BF and BFP^a vs. temperature at heating rate of 10°C/min.Figure 2. Optical Transmittance of samples BFE^a and BFE^b vs. temperature at heating rate of 10°C/min.

Microstructure

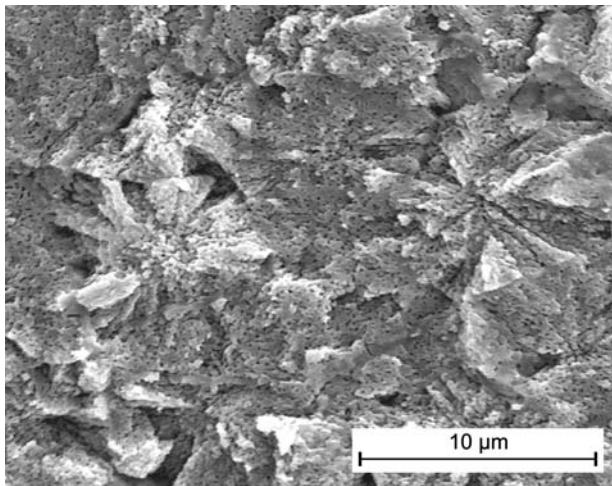
OT results correlate with SEM microstructure of fracture surfaces (figure 3). Sample BF (figure 3b) has typical microstructure of polycrystalline ceramic microstructure without visible porosity. On the other hand, unseeded (B, figure 3a) is highly porous (RD = 74.7 %, table 2) after sintering (1350°C) with evident single crystal colonies [3, 21] of the size from 12 to 15 μm . Such a microstructure is known from literature as vermicular [22] one. Microstructure of sample BFP^a (figure 3c) is very similar to that of unseeded sample (B, figure 3a), only the mentioned single crystal colonies are less evident.

Low heating rate (0.1°C/min) to calcination temperature of sample containing PVA (sample BFP^b) has no effect on microstructure of the sintered material.

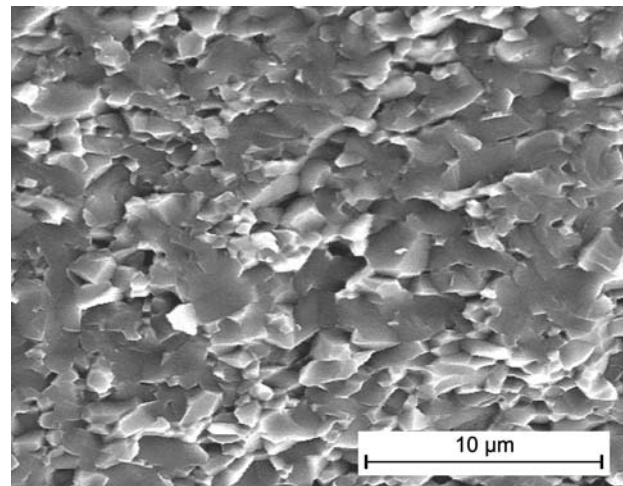
Similar behavior shows also sample with PEG. Contrary, low heating rate causes significant change, in a case when the organic additive is a monomeric EG (sample BFE^b), neither single crystal colonies nor pores are visible in figure 3d. Its small visual OT correlate with its nearly theoretical density (table 2). Very low OT of this sample compared with sample BF is a result of tiny porosity and larger interphase - smaller crystals (figure 3d).

Photoluminescence

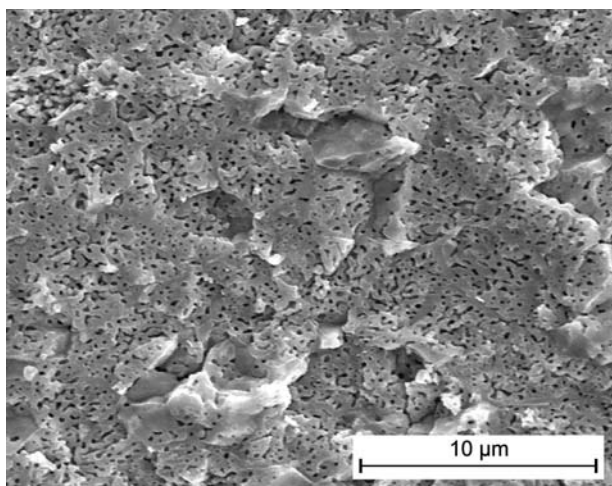
In agreement with above results also photoluminescence spectra on figures 4 and 5 confirm marked impact of the organic additives on the boehmite gels crystallization.



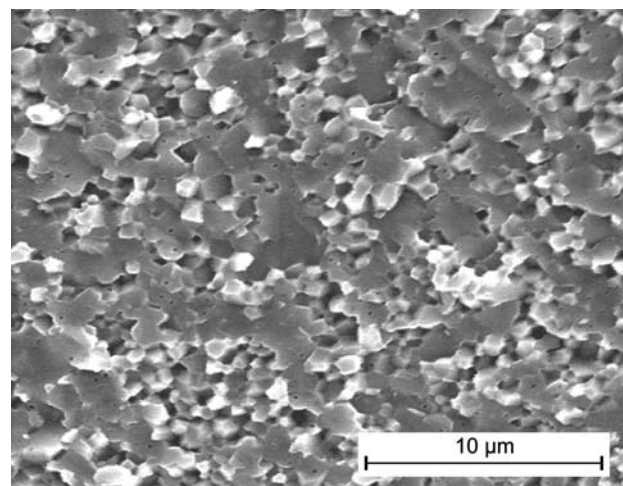
a)



b)

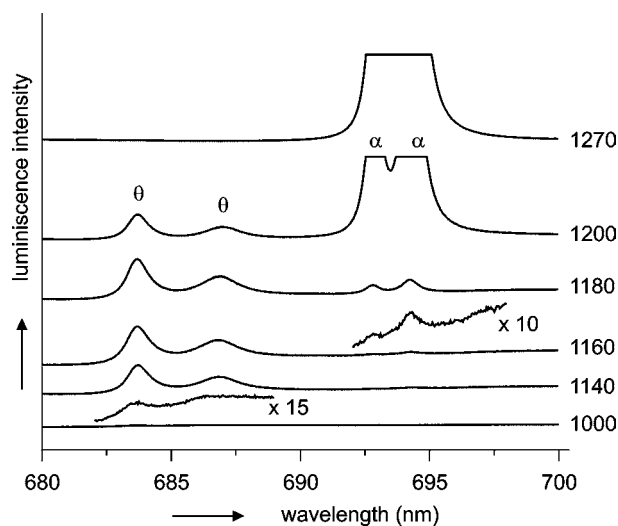


c)

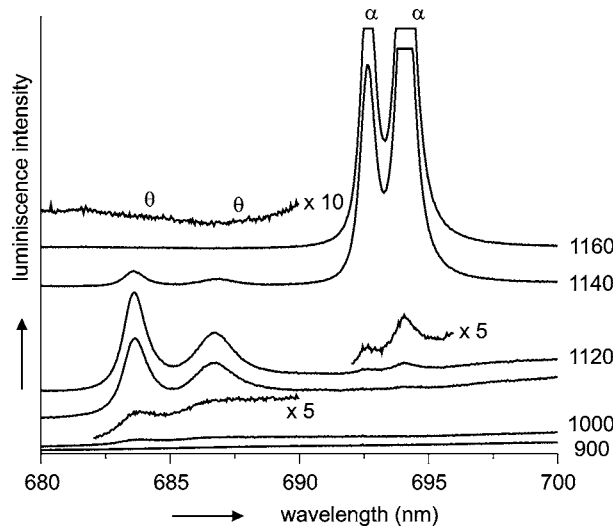


d)

Figure 3. SEM pictures of the fracture surface of samples: a) sample B, b) sample BF, c) sample BFP^a and d) sample BFE^b, sintered at 1350°C.



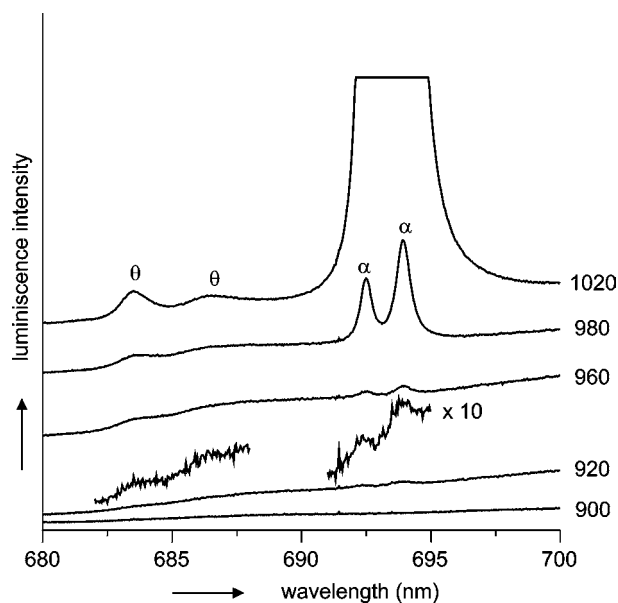
a)



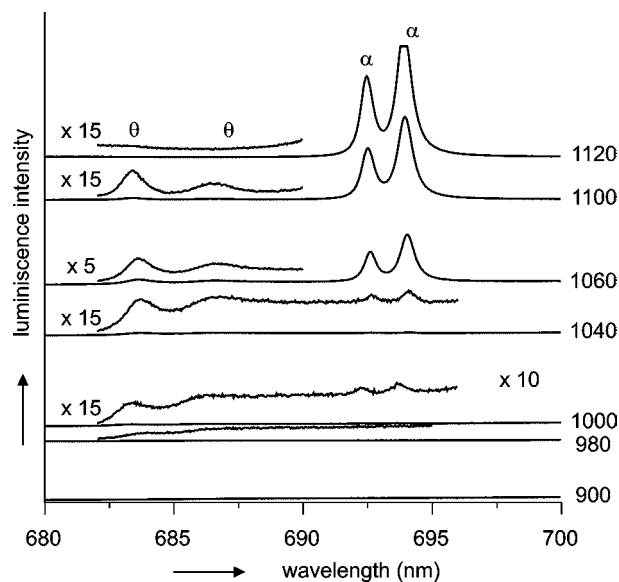
b)

Figure 4. Photoluminescence spectra of a) samples B and b) samples BFP^a heated at 10°C/min to 900-1270°C without holding time. Characteristic doublets are marked as "θ" and "α" respectively.

PVA as a polymeric additive (figure 4b) induces qualitatively the same course of crystallization of Fe(NO₃)₃ seeded gels as is observed in unseeded and gels without organics (figure 4a). The BFP^a crystallization temperatures are lower as for B samples, but the crystallization sequence is identical, as if the polymer removed the nucleation effect of a present iron oxide seeding. Evidently, θ-Al₂O₃ crystallizes in both cases as the primary phase, which transforms to α-Al₂O₃ at higher temperatures. Contrary, applied monomeric EG additive (figure 5b) influences only crystallization temperatures but not the transformation sequence of Fe(NO₃)₃ seeded gels (figure 5a). Luminescence spectra



a)



b)

Figure 5. Photoluminescence spectra of a) samples BF and b) samples BFE^a heated at 10°C/min to 900-1120°C without holding time. Characteristic doublets are marked as "θ" and "α" respectively.

of both BF and BFE^a samples reveal that crystallization of θ-Al₂O₃ phase does not precede considerably crystallization of α-Al₂O₃, it means α-phase is created by a direct transformation $\gamma \rightarrow \alpha$ -Al₂O₃.

Table 2 summarizes the crystallization courses observed by photoluminescence spectroscopy. A single θ-Al₂O₃ phase temperature range is large for BFP^a (~100°C) and especially for B samples (~140°C), on the contrary it does not exist in BF and is negligible in BFE^a and BFE^b.

Table 2. Phase compositions of originally monolithic boehmite gel, boehmite gel seeded by Fe₂O₃ and boehmite gels doped with organic additives heated at 10°C/min to 900-1270°C without holding time by photoluminescence (PL). Relative densities of samples sintered at 1350°C for 1 h.

T (°C)	samples				
	B	BFB	BFP ^a	BFE ^a	BFE ^b
900					
920		θ, α			
940		θ, α			
960		θ, α		θ	
980		θ, α		θ	θ
1000	θ	θ, α	θ	θ, α	θ
1020	θ	θ, α	θ	θ, α	θ, α
1040	θ	α	θ	θ, α	θ, α
1060	θ		θ	θ, α	θ, α
1080	θ		θ	θ, α	α
1100	θ		θ	θ, α	α
1120	θ		θ, α	α	α
1140	θ		θ, α	α	α
1160	θ, α		α	α	α
1200	θ, α				
1270	α				
relative density (%)	74.7	≈100	79.1	99.6	99.9

DISCUSSION

The organic additives, although macroscopically removed (in our case during calcination ending at 550°C) leave in gels apparently the own traces, influencing thermal processes above 1000°C, influencing thus also the final properties of Al₂O₃ ceramics. The positive influence of examined organic additives on mechanical properties at low temperature becomes a negative influence at high temperatures, if a tendency exists to obtain highly dense, or transparent materials.

In generally, a creation of the light scattering species in a sample particulate matrix decreases its optical transmittance. Contrary, their vanishing causes an increase in the optical transmittance. The final optical transmittance of samples (at the end of experiments) is in agreement with microstructure results. The fully dense sample with facetal crystal growth (BF, figure 3b) is free from light scattering species and shows the high final optical transmittance. The samples containing organic additives, with vermicular crystal growth and high residual porosity, are opaque (figure 3a,c). The reason for an opacity is more or less a fractal structure of the samples, rough grain boundaries and a presence of pores. In the nearly dense sample BFE^b (figure 3d) the remnant pores are believed to be responsible for the extinction of the sample transmittance.

As mentioned samples with organic additives seeded with Fe(NO₃)₃ behave, from a view point of OT, as undoped and unseeded boehmite gels [21]. The additives in generally may collide from a part with self assembling process of the colloidal boehmite particles in the final period of the gel drying, enhanced by a presence of the Fe³⁺ ions [7-9], or they may exert an intermediate reductive environment during their pyrolysis, negative for the function of Fe³⁺ ions in nucleation of Al₂O₃.

Samples BFP^a, BFE^b heat treated 24 hour in continuous oxygen atmosphere at temperature 800°C (still no crystallization α-Al₂O₃) does not show any changes in comparison to the previous properties so traces influence rather the spatial-microstructural character and not the chemical or the residual one.

The organic additives in any case contribute to certain porosity after firing of the gel, which causes a decrease in number of the transport contacts of ions in the sintering and recrystallization process. The clue is a decrease of the general interactive coordination of colloidal particles what results, as already shown [3, 23] in a fall of number of potential sites of nucleation, nucleation density (number of nuclei per cm³). On the other side, the presence of Fe³⁺ ions (from Fe(NO₃)₃) raises the nucleation density [8, 9], while the presence of the organic polymeric additives it reduces or cancels. The PVA spatial effect on the nucleation is so intensive, that even very slow heating rate (0.1°C/min) doesn't cancel it and gel microstructure does not cure any more. System behaves thus, as if contained no nucleation agent - Fe₂O₃. Unseeded gel containing no PVA has nucleation density about 10⁸ nuclei/cm³ [24]. Contrary, for seeded (Fe(NO₃)₃) it is much higher ~10¹⁵ nuclei/cm³ [9]. On the other hand, the negative nucleation influence of EG as monomer is essentially smaller, appears only partly at heating rate 10°C/min and practically ceases at heating rate 0.1°C/min.

Because of their spatial effect, the organic polymeric additives, (resp. porosity remaining after their burning up) interrupt the crystallization continuity much more than the monomeric additive.

CONCLUSION

Polymeric additives (PVA, PEG, 3 wt.%) increased the green strength of monolithic boehmite gels, but decreased the bulk density of the material after sintering.

The cause is believed to be confined in the different spatial, microstructural character of samples after burning of organic additives. Therefore the influence of monomeric EG is at the same conditions lower and still decreases at slow heating rate (0.1°C/min) than it is with polymeric PVA and PEG.

Traces in gels result in the decreasing of interactive coordination of particles, what evidently leads to a fall of the nucleation density of α -Al₂O₃.

In seeded gel (5 wt.% Fe₂O₃ from Fe(NO₃)₃), PVA (3 wt.%) addition decreased the nucleation density in 7 orders. System behaved thus, as if was not seeded. PVA in this system increased the crystallization discontinuity.

Acknowledgement

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VPLYV ORGANICKÝCH ADITÍV NA KRYŠTALIZÁCIU BÖHMITOVÝCH GÉLOV

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Kryštalizácia monolitických planárnych böhmitových gélov o hrúbke ~0,15 mm, ktoré boli neočkované alebo očkované s Fe(NO₃)₃, obsahujúcich 3 % hmot. organických aditív (PVA, PEG a EG), sa sledovala fotoluminiscenčnou spektroskopiou, in-situ optickou transmitanciou a REM. Použitie organické polymérne látky, napriek tomu, že vyhoria pri nízkych teplotách (550°C), zanechajú v systéme mikroštruktúrne stopy (znížia vzájomnú koordináciu böhmitových častíc), ktoré majú významný vplyv na vysokoteplotné procesy, kryštalizáciu a spekanie. Polymérne aditíva (PVA alebo PEG) podstatne rušia nuklečný (očkovací) efekt Fe(NO₃)₃ na kryštalizáciu α -Al₂O₃ v sledovaných böhmitových géloch. Za prítomnosti PVA alebo PEG sa očkovaný gél (5 % hmot. Fe₂O₃ z Fe(NO₃)₃) chová tak, ako keby nebol vôbec očkovaný.