Effects of Silica and Titania Modification Additions on the Microstructure of Sintered Alumina

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Abstract—The way in which silica and titania modification additions are introduced into alumina is shown to have a strong effect on the microstructure of sintered Al_2O_3 -SiO₂-TiO₂ materials. By combining molecular layering and mechanical mixing, materials with a controlled pore structure can be obtained.

INTRODUCTION

One way of controlling the properties of ceramics is by doping preceramic materials. Changes in the chemical composition of the starting system are, as a rule, accompanied by changes in the phase composition and microstructure of the sintered material, which have a crucial effect on its mechanical, thermal, catalytic, sorption, and other properties. According to numerous studies (see, e.g., [1, 2]), the effectiveness of a modification addition depends not only on its nature but also on its content and the way it was introduced. Earlier work [3, 4] has shown that the properties of Al_2O_3 - SiO_2 -TiO₂ materials depend significantly on the modification procedure-molecular layering or mechanical mixing. For example, the addition of titania to alumina via molecular layering ensured rapid thermal densification at relatively low temperatures and allowed us to obtain ceramics with a narrow pore size distribution (micronscale ceramic membranes) [5]. With other procedures, this was impossible. In some instances, particularly when a few additions markedly different in chemical nature are to be introduced, a combination of different procedures may prove effective [6]. The purpose of this work was to examine the effect of the synthesis procedure on the phase composition and microstructure of alumina ceramics.

EXPERIMENTAL

We used the synthesis procedure described in detail earlier [5]. The starting reagents were gamma alumina (State Standard GOST 8136-85) containing less than 0.05 wt % impurity cations, OSCh 9-2 titania (TU 6-09-01-629-83) in the rutile phase, silica (TU 6-09-17-48-82) in the form of silica gel

(silokhrom), extrapure-grade titanium tetrachloride (TU 6-05-2118-77), and analytical-grade silicon tetrachloride (TU 6-01-22-75). The samples were sintered isothermally at 1520, 1570, or 1620 K for 1 h.

Phase composition was determined by x-ray diffraction (DRON-3, CuK_{α} radiation) [6].

To obtain comprehensive information about the pore structure of the materials, we carried out a detailed microstructural analysis, in conformity with IUPAC Recommendations [7], using mercury porosimetry, optical microscopy, electron microscopy, and pycnometry [8].

Pore size distributions in the range from 1 nm to several hundred microns were derived from mercury porosimetry (Karlo Erba instrument), optical microscopy, and pycnometry data. Microstructures were examined under an EPIQUANT Carl Zeiss metallographic microscope fitted with a Videotest 2.0 Ista image analysis system. Polished sections were prepared as described in [9]. Distributions by the equivalent circle radius r_{eq} were obtained by processing each frame until the coefficient of variation stabilized. Total porosity was determined by pycnometry as described in [8].

Fracture surfaces were examined by scanning electron microscopy (SEM) with a JSM-35C instrument at an accelerating voltage of 15 kV. Gold films 5.0 to 10.0 nm in thickness were deposited onto the specimen surface using a JFC-1100 unit.

The samples studied are characterized in Tables 1 and 2.

RESULTS AND DISCUSSION

According to XRD data (Table 2), the phase composition of sintered Al_2O_3 -SiO₂ materials depends

Sample no.	Preparation procedure	Weight fraction		
		Al ₂ O ₃	SiO ₂	TiO ₂
1	Molecular layering of SiO ₂ (6 cycles)	0.8884	0.1116	-
2	Mixing	0.8516	0.1484	-
3	Molecular layering of SiO_2 (6 cycles) + mixing with SiO_2	0.8530	0.1071* + 0.0399**	-
4	Molecular layering of SiO_2 (6 cycles) + mixing with TiO_2	0.8530	0.1071	0.0399
5	Mixing of Al_2O_3 , SiO_2 , and TiO_2	0.8176	0.1424	0.0399
6	Molecular layering of SiO_2 (6 cycles) and TiO_2 (1 cycle)	0.8530	0.1071	0.0399

 Table 1. Characteristics of the starting samples

* Amount of SiO₂ introduced by molecular layering.

** Amount of SiO₂ introduced by mixing.

strongly on the preparation procedure. If SiO_2 , all or part of it, is introduced by molecular layering (samples 1, 3), the dominant phases in the heat-treated material are mullite and θ -Al₂O₃. Unreacted silica is likely to be amorphous. The only exception is sample 1 heattreated at 1570 K (Table 2), in which γ -Al₂O₃ grains were not coated with a continuous mullite layer [4, 10]. so that part of the alumina transformed into the α form. Raising the silica content—by increasing the number of layering cycles [4] or the amount of SiO_2 in the mixture-or temperature leads to the formation of a protective mullite coating on the γ -Al₂O₃ surface and stabilizes nonequilibrium forms of alumina (Table 2) [4]. At lower firing temperatures, these forms are stabilized by a silica layer (samples 1, 3) [4, 11]. If silica is introduced by mixing, γ -Al₂O₃ converts into the α form, which coexists with mullite and cristobalite (1570, 1620 K).

In the Al_2O_3 -TiO₂-SiO₂ system, the phase composition of heat-treated materials depends not only on the firing conditions but also on the way in which SiO₂ and TiO₂ were introduced. The samples were found to contain mullite, α -Al₂O₃, and/or θ -Al₂O₃. Titania as an individual phase was not detected. It seems likely that titania substitutes isomorphously into other phases [12, 13] and enters into the composition of the intergranular glassy phase [14]. It is of interest to note that the samples prepared only by mixing (sample 5) or only by layering (sample 6) have similar phase compositions after heat treatment at $T \ge 1570$ K but differ markedly in phase composition after heat treatment at 1520 K (Table 2). In sample 5 heat-treated at 1520 K, all of the alumina is converted into the α form, whereas sample 6 contains only about 8% α -Al₂O₃, the rest of the alumina being θ -Al₂O₃. Sample 4 heat-treated at 1520 K is similar in phase composition to sample 6 fired under the same conditions. After heat treatments at 1570 and 1620 K. sample 4 contains mullite; the unreacted alumina is

present as θ - and α -Al₂O₃; the fraction of the latter increases somewhat with firing temperature. The observed phase changes in the titania-containing samples can be explained by the fact that titania accelerates not only the formation of mullite [5], which stabilizes

Table 2. Phase composition of the samples heat-treated for 1 h

Sam-	<i>T</i> , K	Weight fraction				
ple no.		Al ₆ Si ₂ O ₁₃	α -Al ₂ O ₃	θ -Al ₂ O ₃	cristobalite	
1	1520	0	0	1	0	
	1570	0.51	0.20	0.29	0	
	1620	0.68	0	0.32	0	
2	1520	0	0.58	0.42	0	
	1570	0.32	0.60	0	0.08	
	1620	0.32	0.57	0	0.11	
3	1520	0	0	1	0	
	1570	0.56	0	0.44	0	
	1620	0.71	0	0.29	0	
4	1520	0	0	1	0	
	1570	0.38	0.04	0.58	0	
	1620	0.46	0.07	0.47	0	
5	1520	0	1	0	0	
	1570	0.30	0.70	0	0	
	1620	0.33	0.67	0	0	
6	1520	0	0.08	0.92	0	
	1570	0.25	0.75	0	0	
	1620	0.38	0.62	0	0	



Fig. 1. Pore size distributions in samples (a) 3, (b) 4, (c) 5, and (d) 6; r_{eq} is the equivalent circle radius.

the unstable forms of alumina [4, 10], but also the γ -Al₂O₃ $\longrightarrow \alpha$ -Al₂O₃ phase transition [14]. Depending on the area of the interface between the starting reagents and the relative, temperature-dependent rates of these processes, TiO₂ either impedes or accelerates the $\gamma \longrightarrow \alpha$ transition.

The phase changes under consideration have a significant effect on the microstructure of the materials. Optical examination of the pore structures of the materials prepared by layering (samples 1, 6), mixing (samples (2, 5), or a combination of these techniques (samples 3, 4), followed by firing at 1620 K (Table 1), shows that the pore size distributions each have only one maximum (Fig. 1).

Combining porosimetry and SEM data, we obtained pore size distributions in the form of histograms in the range from 1 nm to several hundred microns (Fig. 2). All diagrams are seen to have three maxima. At the same time, the pore structure depends substantially on the preparation procedure and chemical composition. Note, first of all, that the introduction of SiO_2 by molecular layering reduces the fraction of the smallest pores:

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the peak in the range $r_{eq} = 1-100$ nm is lower in comparison with the sample prepared by mixing γ -Al₂O₃ and fine-particle SiO₂ (Figs. 2a, 2b). This can be explained by the fact that molecular layering leads to filling of those pores which make the largest contribution to the specific surface area. In the case under consideration, these are the pores in γ -Al₂O₃ particles, ranging in size from 1 to 100 nm [15]. Since heat treatment of sample 1 gives rise to the γ -Al₂O₃ $\longrightarrow \theta$ -Al₂O₃ transformation, accompanied by no significant changes in the volume, shape, or microstructure of alumina particles (Fig. 3), the pore structure of γ -Al₂O₃ formed after the introduction of SiO₂ by molecular layering must remain intact upon this transformation.

When silica is introduced by mixing, the peak at $r_{eq} = 1-100$ nm shifts to larger pore sizes, and the peak at $r_{eq} = 100-3000$ nm decreases (Fig. 2b). Since the latter range covers almost the entire range of SiO₂ aggregate sizes, $d < 5 \,\mu$ m, we infer that sintering of the samples prepared by mixing leads to the filling of spaces between alumina particles close in size to SiO₂ aggre-



Fig. 2. Pore size distributions in samples (a) 1, (b) 2, (c) 3, and (d) 4. Light, dark, and gray areas represent porosimetry, optical microscopy, and combined data.

gates. The growth of the smallest pores present in the alumina particles is associated with the volume reduction upon the γ -Al₂O₃ $\longrightarrow \alpha$ -Al₂O₃ phase transition: $V_{x,A1,Q} = V_{x,A1,Q}$

 $\frac{V_{\gamma-Al_2O_3} - V_{\alpha-Al_2O_3}}{V_{\alpha-Al_2O_3}} \times 100\% \simeq 9\%.$ At the same time, the

pores in the range $d_{eq} = 5-10 \ \mu\text{m}$ between spherical γ -Al₂O₃ particles of dimensions 10–30 μm (the major size range in Al₂O₃, see Fig. 3) remain unfilled. Therefore, the combined introduction of silica—mixing of SiO₂ with γ -Al₂O₃ particles precoated with SiO₂—must reduce the fractions of pores in both size ranges ($r_{eq} = 1-100$ and 100–3000 nm), as observed in experiment (Fig. 2c). In this case, the total porosity is 60%, and the fraction of pores with dimensions lying in a range as narrow as $r_{eq} = 3.2-5.6 \ \mu\text{m}$ amounts to 40%. Beyond this range, the distribution is almost uniform, with barely discernible maxima at $r_{eq} < 3 \ \mu\text{m}$ (Fig. 2c).

The pore structure of the Al₂O₃-SiO₂-TiO₂ materials sintered at 1620 K depends little on the way in which the additions were introduced and is determined mainly by the presence of TiO₂. This can be explained by the increased rate of the γ -Al₂O₃ $\longrightarrow \alpha$ -Al₂O₃ phase transition in comparison with the Al₂O₃-SiO₂ system (Table 2). The γ - α transition is accompanied by sharp

changes in the pore structure. The specific surface area decreases by more than one order of magnitude, from $\simeq 200$ to $\simeq 10 \text{ m}^2/\text{g}$ [10], and, hence, the amount of the smallest pores also decreases---we observe a decrease in the fraction of these pores and a shift of the maximum at $r_{eq} = 1-100$ nm to higher r_{eq} values (Fig. 2). The increase in pore size is also, to some extent, due to the volume changes accompanying the $\gamma \rightarrow \alpha$ phase transition, which have the most pronounced effect on the largest pores (Fig. 2). In this respect, the materials containing titania (samples 4–6) differ from the Al_2O_3 – SiO_2 material (sample 2), close in phase composition. The likely reason is that the introduction of titania accelerates sintering of the particles located between large alumina particles [2, 3]. The resulting links between alumina particles form a rigid skeleton, thereby increasing the dimensions of free spaces. In sample 2, the rate of mullite formation is appreciably slower [5], and the unreacted, amorphous silica crystallizes into cristobalite, which poorly sinters at the temperatures in question (Table 2) and fills spaces between alumina particles.

The introduction of titania also has a strong effect on the microstructure of alumina particles. Instead of spherical, nanoporous $\gamma(\theta)$ -Al₂O₃ particles, we observe



Fig. 3. SEM micrographs of samples (a, b) 3 and (c, d) 6; (a, c) ×1000, (b, d) ×10000.

spherical aggregates of densely packed submicronsized α -Al₂O₃ particles (Figs. 3c, 3d).

CONCLUSION

The phase composition and microstructure of Al_2O_3 -SiO₂ materials are shown to depend substantially on the way the silica was introduced. By combining molecular layering and mechanical mixing, we obtain materials with a controlled pore structure. This system is therefore potentially attractive for the preparation of high-porosity materials containing micronand submicron-sized pores with a narrow size distribution.

The introduction of even small amounts of titania by either technique has a dramatic effect on the microstructure of the sintered material.

ACKNOWLEDGMENTS

This work was supported by the RF Ministry of Education (Universities of Russia/Basic Research Program) and the Russian Foundation for Basic Research, project no. 98-03-32063.

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