



Composite material in the Al_2O_3 -20 vol% YAG system[#]

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Abstract

Within alumina particle suspension yttria precursor was precipitated with ammonium carbonate. Drying and calcination at 600°C resulted in the mixture of alumina and yttria particles, the latter being much finer than alumina particles. This mixture was additionally homogenized by short attrition milling in aqueous suspension of pH selected on the basis of zeta (ζ) potential measurements. It was found that acidic conditions (realized with HNO_3) resulted in hard agglomerates. Such powder shows poor sintering ability. Much better properties showed powders homogenized under basic conditions. They give dense materials composed of YAG inclusions within alumina matrix. YAG particles resulted from the reaction of Y_2O_3 with Al_2O_3 during heat treatment. Homogenization of the system mixed at pH=8, corresponding to the heteroflocculation conditions, is slightly better than observed at pH=10. YAG inclusions (20 vol%) increase hardness and fracture toughness of the material in comparison with pure alumina polycrystals.

Keywords: ceramic matrix composites; mechanical properties; Al_2O_3 -YAG system

I. Introduction

Unquestionable advantage of the ceramic oxide materials, also for high temperature applications, is their resistance to oxidation. A certain disadvantage of single-phase oxide materials is their susceptibility to creep at elevated temperatures. From this point of view ceramic matrix composites in the oxide-oxide systems arouse special interest [1,2].

Alumina is one of the most popular oxide materials with good mechanical properties. These properties can be improved by the second phase inclusions. From this point of view YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$) seems to be an interesting candidate. YAG shows coefficient of thermal expansion close to alumina and as a phase of the highest Al_2O_3 content among three phases in the alumina-yttria system (YAlO_3 and $\text{Y}_4\text{Al}_2\text{O}_9$), is chemically stable in contact with the alumina grains.

Some articles on the composites in the alumina/YAG system describe materials prepared by the directional eutectic crystallization [3–7]. This is an expensive and technically difficult method due to very high

temperature of the process. Only few papers concern the alumina-YAG materials prepared by the sintering technique [8–12].

Aim of the present study was to find proper preparation conditions resulting in dense Al_2O_3 /YAG composite. Mixtures of submicrometer α - Al_2O_3 and nanometric Y_2O_3 powders were used. It was assumed that reaction of yttria with alumina should lead to the formation of YAG particle inclusions within alumina matrix.

II. Experimental

Alumina (TM-DAR TAIMAY Chemicals, Japan) and yttria of purity 99.99% (Aldrich) were used in this study. Yttria was dissolved in nitric acid (analytical quality). The resulting $\text{Y}(\text{NO}_3)_3$ solution was introduced into alumina suspension of 50 vol% concentration. The vigorously stirred suspension was treated with $(\text{NH}_4)_2\text{CO}_3$ solution until the suspension reached pH = 8.5. Under such conditions quantitative yttrium precipitation occurs. The suspension was dried and calcined at 600°C for 60 min. with the rate of temperature increase of 5°C/min. Yttria amount corresponded to 20 vol% of YAG after the reaction with alumina. The resulting powder was attrition ground for 30 min. using zirconia 2 mm balls (TOSOH). Weight ratio of the powder to grinding media correspond-

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ed to 1 : 20. Homogenization was performed using pH = 3, 8 and 10 of the suspension. Acidic conditions were received by HNO₃ (1 : 10) additive. Since in this case pH of the suspension increased constantly during the process, presumably due to the adsorption of H₃O⁺ ions on the oxide surface, amount of nitric acid had to be replenished. No pH changes occurred under basic conditions achieved with ammonium carbonate (pH = 8) and ammonia (pH = 10) additives. The homogenized powders were dried at 100°C for 12 h and separated from the grinding media on a sieve. Cylindrical samples of 23 mm diameter and about 4 mm thickness were prepared by uniaxial pressing under 50 MPa and isostatic repressing under 300 MPa. No lubricant was added to the powders. Then the compacts were sintered in air at 1400, 1500 and 1600°C with the rate of temperature increase of 5°C/min and 2h soaking time.

Alumina and alumina-yttria mixture were characterized by the specific surface area measurements using nitrogen adsorption (Quantachrome, Nova 1200).

The pH conditions of alumina/yttria powders mixing were selected on the basis of zeta (ζ) potential determination (Malvern, Zetasizer Nano-Z) separately for alumina and yttria powders. Gases emitted by the sample prepared under the acidic condition were analysed using mass spectrometer (Mass Spectrometer QMD 300 Thermostat, Balzers).

Green samples were characterized by pore size distribution measurements (Quantachrome, PoreMaster). Hydrostatic weighing allowed us to determine apparent density of the sintered samples. Fracture toughness and hardness were measured by the Vickers indentation using the Future Tech (Japan) equipment. In the former case load of 3 kgf and in the latter 10 kgf were applied. Critical stress intensity factor (K_{Ic}) was calculated using Niihara formula [13] for the Palmquist crack type fracture. Phase compositions of the sintered samples were determined by the X-ray diffraction (CuK_α radiation, equipment, X'Pert Pro, Panalytical).

III. Results and discussion

By the X-ray diffraction, it was found that the alumina/yttrium compound mixture transforms to the alumina and yttria mixture after heat treatment at 600°C. Amount of the latter corresponded to 20 vol. of YAG

after the reaction of Al₂O₃ and Y₂O₃ at sufficiently high temperature.

In Table 1 specific surface areas of alumina, alumina/yttria mixture after calcination at 600°C and yttria powders are shown. The latter was calculated basing on the known alumina and alumina/yttria specific surface areas and knowledge of the volume fraction of yttria in the mixture, assuming that inter-particle contacts is negligible; this is due to low calcination temperature of the system. Particle sizes of alumina and yttria differ essentially.

Fig. 1 shows zeta potential of the constituent powders vs. pH. It follows from these data that under acidic conditions yttria and alumina particles should repel each other. Similar situation occurs at pH = 10, although due to the lower zeta potential values these interactions should be much weaker than in the former case. At pH = 8 yttria particles charge is of the opposite sign than the one of alumina grains. So, alumina and yttria particles should attract each other and the particles of the same oxide should repel each other. This situation causes so called heteroflocculation effect which is considered to improve homogenization of the two component powder system [14].

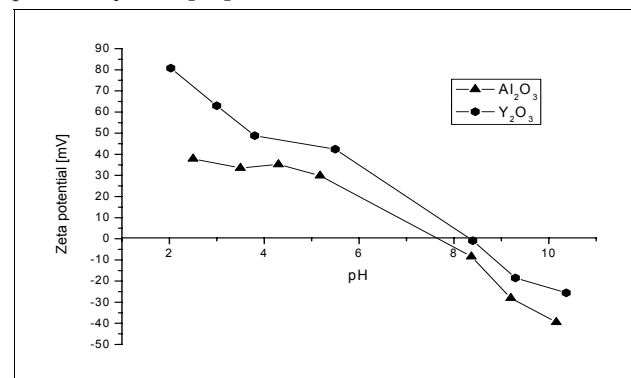


Figure 1. Zeta potential vs. pH of the alumina and yttria powders

It was found that suspension homogenized at pH = 3 after drying at 100°C forms succint, hard body difficult to grind in a mortar. Similar phenomenon was observed in the alumina-zirconia system [15]. No such behaviour occurred in case of the samples homogenized at pH = 8 and 10. These powders were fluffy, easy to disperse in a mortar.

Fig. 2 shows pore size distribution curves in the powder compacts. Curves for the powders homoge-

Table 1. Specific surface area (S_w) and average particle size (D_{BET}) of the powders calcined at 600°C for 1h

Powder	Al ₂ O ₃	Al ₂ O ₃ + 20 vol.% Y ₂ O ₃	Y ₂ O ₃
S_w [m ² /g]	12.4	17.5	52.3**
D_{BET} * [nm]	121.3	-	22.9

* $D_{BET} = 6/S_w \cdot d$, where d is density, $d_{Al_2O_3} = 3.99$ g/cm³, $d_{Y_2O_3} = 5.01$ g/cm³

**calculated on the basis of the known alumina and alumina/yttria specific surface areas and applied volume fraction of yttria in the mixture with alumina. Yttria volume fraction corresponded to 20 vol.% of YAG after total reaction of Al₂O₃ and Y₂O₃

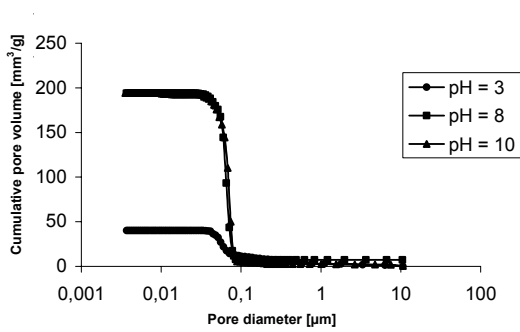


Figure 2. Cumulative curves of pore size distribution in the powder compacts. Powders homogenized under indicated pH of the suspensions

nized in suspensions of pH = 8 and 10 practically do not differ from each other. Significantly different is the plot corresponding to the powder homogenized in the suspension of pH = 3; pore volume in this case is much smaller and pore sizes are shifted towards lower values. In order to understand this behaviour gases emitted by the material during heat treatment in air atmosphere were detected. Fig. 3 shows emission of NO and NO₂ at elevated temperatures. These oxides can arise from decomposition of azeotropic nitric acid aqueous solution formed during drying of the powder homogenized in suspension of pH = 3 at 100°C. It cannot be excluded that due to the small powder particle sizes and related to this small capillary diameters, the azeotropic solution does not totally evaporate from the system during drying. Concentration of this azeotropic solution corresponds to 69.2 wt.% HNO₃ [16] (boiling temperature 122°C). It seems also possible that such concentrated nitric acid can react with alumina and yttria leading to the formation of the relative nitrates. Their decomposition

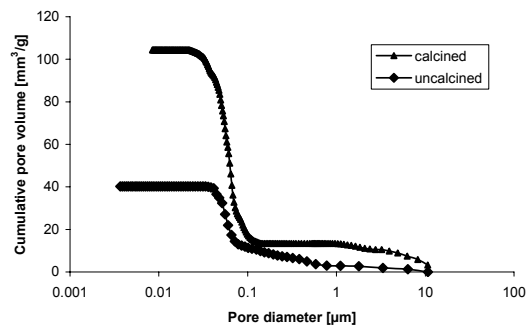


Figure 4. Cumulative curves of pore size distribution in the compacts derived from uncalcined and calcined (400°C) powders, homogenized under acidic condition (pH = 3)

can also be responsible for the nitrogen oxides emission. We were not able to observe them by the X-ray diffraction, most probably because of small content of the postulated phases.

Fig. 4 indicates strongly limited pore volume in the discussed compacts. It suggests that pores are filled with the product of alumina and yttria reaction with nitric acid and/or with the azeotropic nitric acid solution itself. This conclusion seems to be corroborated by the essential specific surface area increase of the powder subjected to calcination at 400°C for 2 h from the starting 3.88 m²/g to 12.67 m²/g after calcination. It indicates that due to the heat treatment the matter filling pores is removed. Simultaneously pore size distribution measurement in compact of the calcined powder shows distinct pore volume increase (Fig. 4) compared to that in compact of the powder dried at 100°C. In the former the bimodal pore size distribution is observed. This characteristic is a typical pattern for a powder composed of hard aggregates. It is well known that such powders do not densify effectively

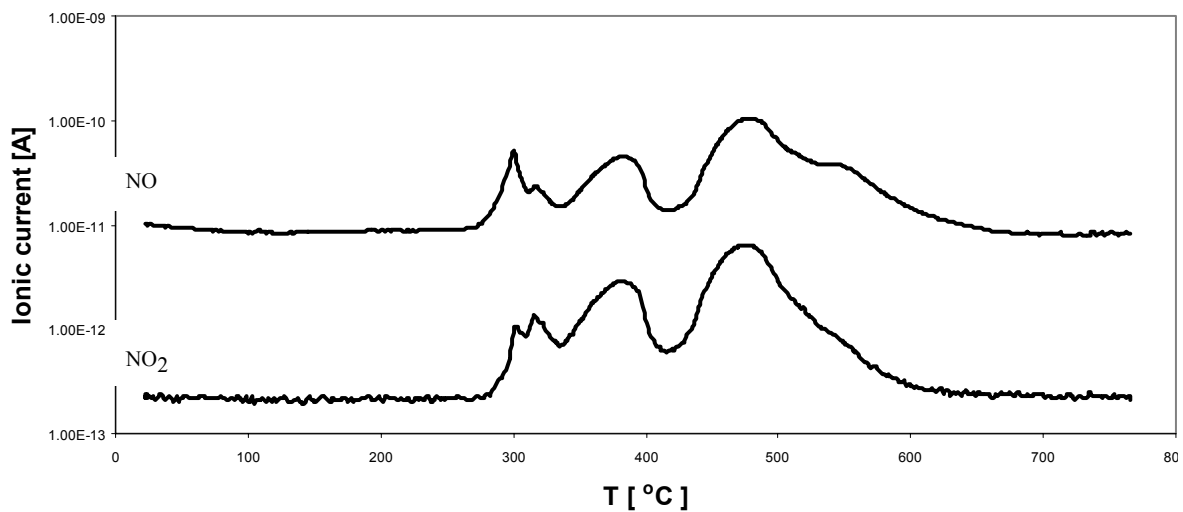


Figure 3. Nitrogen oxides emitted from the compact prepared from powder homogenized in the suspension of pH = 3 (measurement done by mass spectrometer in air atmosphere and heating rate of 10°C/min)

Table 2. Relative density (% theoretical density) of alumina and alumina/YAG composite sintered at indicated temperatures

Material / pH of homogenization	1500°C	1600°C
Al ₂ O ₃	99.38 ± 0.04	99.05 ± 0.11
Al ₂ O ₃ - Y ₂ O ₃ / pH = 3	93.13 ± 0.07	94.02 ± 0.05
Al ₂ O ₃ - Y ₂ O ₃ / pH = 8	100.00 ± 0.08	100.00 ± 0.08
Al ₂ O ₃ - Y ₂ O ₃ / pH = 10	99.58 ± 0.06	100.00 ± 0.10

± denotes confidence interval at 0.95 confidence level

during sintering which is really the case as it is indicated by the data in Table 2.

Next two figures (Figs. 5 and 6) indicate small but detectable differences in the inclusion distribution in the materials derived from the powders homogenized at pH = 8 (Fig. 5) and pH = 10 (Fig. 6). In the latter case we observe clusters of inclusions, not visible in the material homogenized under the heteroflocculation conditions. However, better homogenization of the system processed at pH = 8 shows essentially smaller alumina grains compared to that treated at pH = 10.

Data presented in Table 3 indicate that YAG particle inclusions effectively increase hardness and fracture toughness of the dense material in comparison with dense, pure polycrystalline alumina. No essential difference is observed in properties of the materials derived from the powders homogenized in suspensions of pH = 8 and 10. Plausibly the difference in homogenization of these two systems, although visible (see Figs. 5 and 6) is too small in order to affect hardness and fracture toughness of the materials. Fig. 7 shows microstructure of the pure polycrystalline alumina. Comparing Figs. 5 and 7 we conclude that YAG inclusions arrest alumina grain growth. Consequently one Vickers indent in case of pure alumina is situated within

1–2 alumina grains. On the other hand, in the composite the indent meets 10–20 alumina and YAG grains. Grain and interface boundaries hinder plastic deformation of the matter by the Vicker pyramid. This seems to explain higher composite hardness compared to alumina polycrystals sintered under identical conditions. Sintering conditions influence phase composition of the resulting material. It was found by the X-ray diffraction that in the material sintered at 1400°C reaction between Al₂O₃ and Y₂O₃ is not completed. The following phases were found in this sample: Y₂O₃ (0.7 wt.%), YAG - Y₃Al₅O₁₂ (15.6 wt.%) YAM - Y₄Al₂O₉ (0.2 wt.%) and YAP - YAlO₃ (0.6 wt.%). Their content was determined by the Rietveld method. Unlike them, samples sintered at 1500°C and 1600°C contain only two phases, i.e. α-Al₂O₃ and YAG (Fig. 8).

IV. Conclusions

Precipitated with (NH₄)₂CO₃, yttria precursor within alumina grains transforms to Y₂O₃ at 600°C. Its reaction with alumina during sintering results in the formation of YAG inclusions within alumina matrix at sintering temperature of 1500°C or higher. At 1400°C the reaction is not completed; the system contains Y₂O₃, YAM, YAP, YAG and of course α-Al₂O₃.

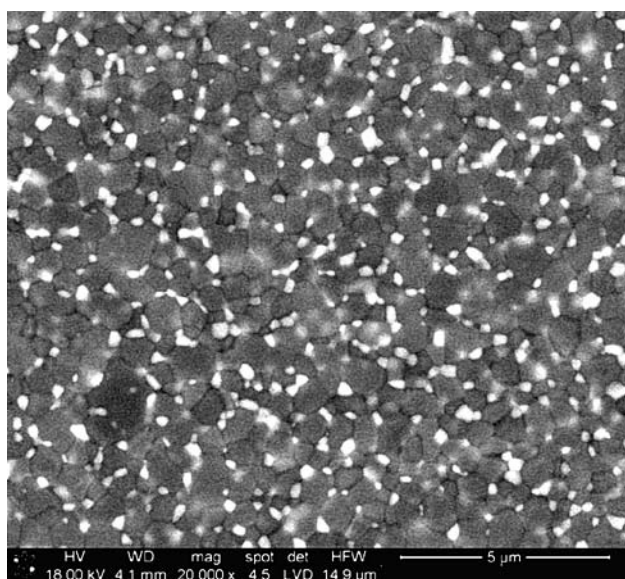


Figure 5. SEM micrographs of the material derived from the powder homogenized in suspension of pH = 8 sintered at 1600°C

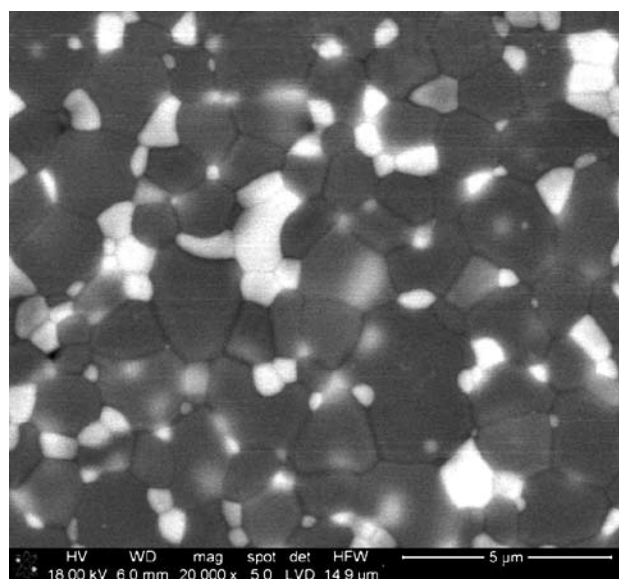
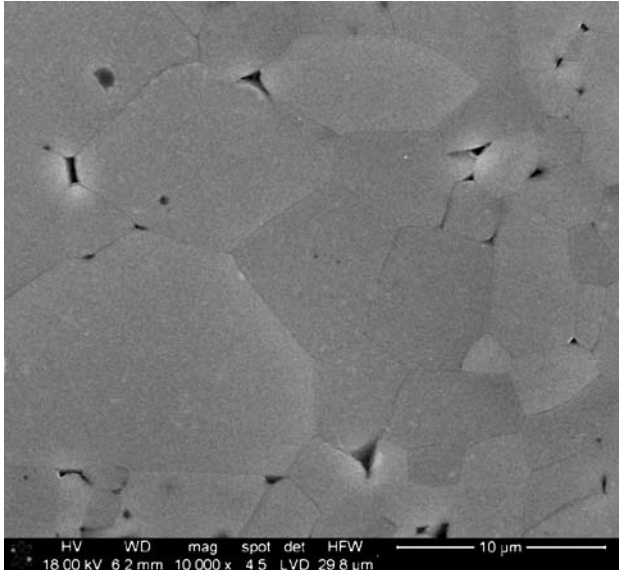


Figure 6. SEM micrographs of the material derived from the powder homogenized in suspension of pH = 10 sintered at 1600°C

Table 3. Properties of the sintered Alumina-YAG composite

Material / pH of homogenization	1500°C		1600°C	
	HV [GPa]	K_{IC} [MPa·m ^{1/2}]	HV [GPa]	K_{IC} [MPa·m ^{1/2}]
Al ₂ O ₃	16.96 ± 1.02	4.50 ± 0.27	16.33 ± 0.90	4.37 ± 0.32
Al ₂ O ₃ - Y ₂ O ₃ / pH = 8	20.43 ± 1.72	5.97 ± 0.28	20.83 ± 1.51	6.19 ± 0.44
Al ₂ O ₃ - Y ₂ O ₃ / pH = 10	19.29 ± 0.91	5.88 ± 0.27	21.10 ± 0.61	6.24 ± 0.38

**Figure 7. SEM micrograph of pure alumina sintered at 1600°C**

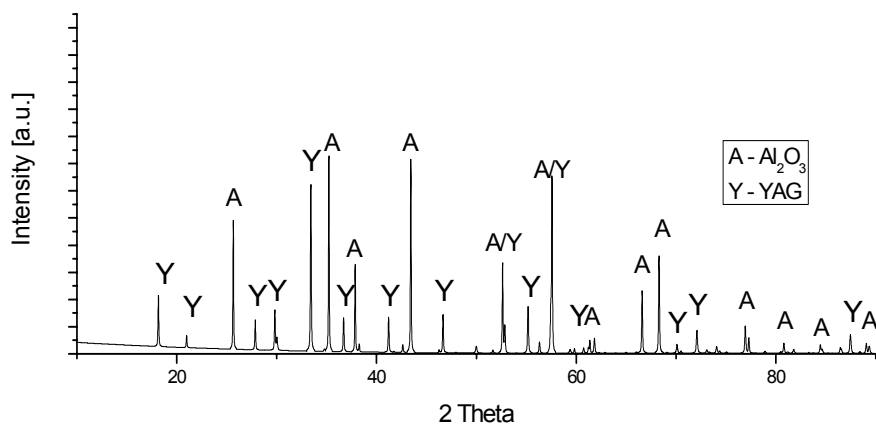
Powders of yttria content corresponding to 20 vol% YAG were homogenized by short attrition milling in the suspensions with different pH values. Level of pH was selected on the basis of the zeta potential measurements. Acidic conditions (pH = 3) were reached by the nitric acid additive. It leads to the powder composed of hard agglomerates which limits densification of the system. Densification of the material derived from the powder mixed under basic conditions is much higher. Slightly better homogenization of the system occurs when mixing of Al₂O₃ and Y₂O₃ pow-

ders was performed in suspension with pH = 8 compared to pH = 10 with no detectable influence on properties of the material.

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**Figure 8. X-ray diffraction pattern of the sample derived from the powder homogenized in the alkaline suspension sintered at 1500°C**

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