



## Synthesis of alumina/YAG 20 vol% composite by co-precipitation

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### Abstract

*Co-precipitation of alumina/YAG precursor from aluminum and yttrium nitrate solution with ammonium carbonate results in dawsonite. Its crystallographic parameters differ from the compound precipitated with no yttrium additive. It suggests that yttrium ions become incorporated into the dawsonite structure. The DSC/TG and X-ray diffraction measurements show decomposition of dawsonite at elevated temperatures resulting in  $\gamma$ - $\text{Al}_2\text{O}_3$  and then  $\delta$ - and  $\theta$ -alumina modifications. Full transformation to  $\alpha$ - $\text{Al}_2\text{O}_3$  and YAG occurs at temperatures higher than 1230°C. Starting powder for the sintering experiments was prepared using the co-precipitated precursor calcined at 600°C. Seeding of such powder with 5 wt.%  $\alpha$ - $\text{Al}_2\text{O}_3$  results in material of 98% density at 1500°C. Much lower densification show compacts of unseeded powder.*

**Keywords:** ceramic matrix composites, alumina-YAG, co-precipitation

### I. Introduction

Generally, mechanical properties of alumina polycrystals can be improved by incorporation of selected inclusions into alumina matrix. One of the possible inclusion-phase is YAG ( $\text{Y}_3\text{Al}_5\text{O}_{12}$ ). This is one of three compounds in the alumina-yttria system characterized by the highest aluminium content. That is why it is stable in contact with alumina. Powder/sintering technique has been used by several researchers to prepare composites in this system.

Different techniques were applied to prepare powders for densification in the alumina/YAG system. Co-precipitation was one of them. Using aluminium and yttrium nitrates [1,2] or chlorides [3] treated with ammonia, gels were prepared. Their calcination resulted in powders of YAG content from 5 to 50 vol%. Such powders were densified either by hot pressing [1,2] or pressure-less sintering [3]. Sol-gel techniques should also be mentioned as a method of YAG-alumina composite fibers preparation [4,5]. In these cases corresponding alkoxides or chlorides were applied.

Another group of investigations on  $\text{Al}_2\text{O}_3$ /YAG composites is based on mixing alumina with yttria [6] or yttria precursors (yttrium chloride [7,8], yttri-

um alkoxides [9,10] and YAG powder [11]). Subsequent heat treatment of the powders resulted in composites of different YAG content. Recently, using an original technique has been elaborated to prepare composites of YAG content from 5 to 30 vol%. The method was based on the precipitation of yttria precursor within  $\alpha$ - $\text{Al}_2\text{O}_3$  powder suspension followed by calcination and sintering. Details of the method are described elsewhere [12].

The aim of the present investigation was preparation of composite powder with YAG concentration of 20 vol% by the co-precipitation method using ammonium carbonate as a precipitation agent. According to our knowledge this way has not yet been investigated by other researchers.

### II. Experimental

Yttria of high purity 99.9% (main impurities: 0.04 wt.% of  $\text{Cr}_2\text{O}_3$  and 0.03 wt.% of  $\text{Ag}_2\text{O}$ ) was dissolved in nitric acid of analytical quality and mixed with the aluminium nitrate solution also of analytical quality. Concentration of the  $\text{Al}(\text{NO}_3)_3 + \text{Y}(\text{NO}_3)_3$  solution was 0.62 mol/L and the Al/Y ratio corresponded to 20 vol% YAG after reaction within the system. The mutual solution of both nitrates was introduced to vigorously stirred solution of ammonium carbonate; pH = 8.5 of the precipitated suspension was kept constant during the process. Under such conditions the quan-

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titative yttrium and aluminium precipitation occurs, as determined by the ICP analysis of the filtrate. Surplus volume of the liquid was removed by the vacuum filtration, using Buechner funnel. The precipitate was washed three times with ethyl alcohol and then dried at 110°C overnight. Washing with alcohol allowed us to receive fluffy precipitate after drying and hence mechanically weak agglomerates of high porosity. It is well known that such powder properties improve sintering conditions [13].

DSC/TG measurements (Netzsch STA 449 F3 Jupiter) were used to follow the phenomena occurring during heat treatment of the powder sample. The rate of temperature increase was 10°C/min and atmosphere was synthetic air with the flow rate of 40 cm<sup>3</sup>/min. Phase composition of the samples, heated with our DSC/TG equipment to the predetermined temperatures corresponding the particular heat effects and then quickly cooled down was determined by the X-ray diffraction (CuK $\alpha$  radiation, equipment X'PertPro, Panalytical). Powder for sintering experiments was prepared by calcination the co-precipitated material at 600°C for 1 h. It was characterized by the specific surface area measurements using nitrogen adsorption (Quantachrome, Nova 1200) and by the observation under transmission electron microscope (JEOL JSM-5400). It is well known that transformation of low temperature modification of alumina (as in this case) to its  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> form (korundium) usually retards densification of the system during sintering. Most probably this is due to the large difference in specific volume of the high and low temperature Al<sub>2</sub>O<sub>3</sub> modifications and related to this change of the pore substructure in the green compact. However, it was demonstrated that seeding of such powder with some  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> additive promotes low-to-high temperature alumina modifications and improves densification of the whole powder compact [14]. That is why 5 wt.%  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder (TM DAR TaiMai Chemicals, Japan) was added to the material prepared by calcination at 600°C. Mixing was performed by 2 h ball milling in ethyl alcohol with 5 mm zirconia (TOSOH) grinding media. Cylindrical samples of 23 mm diameter and 5 mm thickness were uniaxially compacted under pressure of 5 MPa and isostatically repressed at 300 MPa. Sintering was performed in air atmosphere at 1500°C and 1600°C with the rate of temperature increase of 5°C/min and 2 h soaking time. Hydrostatic weighing allowed us to determine apparent density of the sintered samples. Microstructures were observed with the scanning electron microscope (FEI Nova Nano SEM 200). Mean intersect of alumina and YAG grains was used as a measure of their sizes.

In case of dense samples fracture toughness and hardness were measured by the Vickers indentation using Future Tech (Japan) equipment. Under 1 kgf load no cracks occurred what allowed us to assess hardness

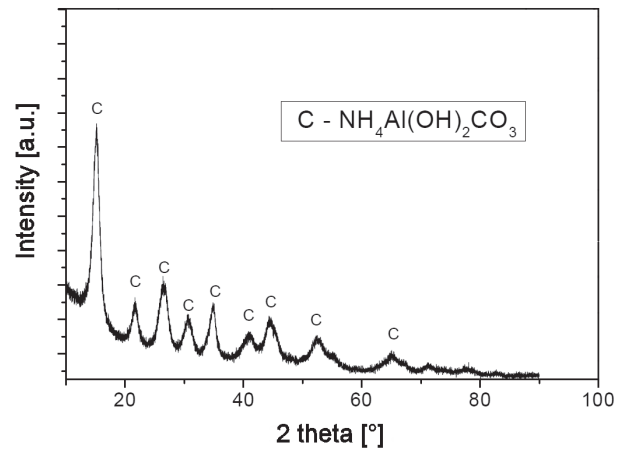


Figure 1. X-ray diffraction pattern of the co-precipitated material

of the material. Higher load (3 kgf) lead to the radial cracks. Their lengths were used to calculate fracture toughness according to Niihara *et al.* [15] formula.

### III. Results and discussion

Figure 1 shows X-ray diffraction pattern of the co-precipitated material. The phase can be identified as dawsonite (NH<sub>4</sub>Al(OH)<sub>2</sub>CO<sub>3</sub>). There is no any phase which could be attributed to yttrium containing phase. Most probably yttrium ions are present in the dawsonite structure. This conclusion is corroborated by the essentially different lattice parameters of the material co-precipitated with yttrium and prepared by the same technique but without this additive (Table 1). The differences are higher than error of these measurements (0.0002 nm).

Table 1. Crystallographic parameters of dawsonite

Dawsonite	<i>a</i> [nm]	<i>b</i> [nm]	<i>c</i> [nm]
With yttrium	0.66724	1.19030	0.57105
Without yttrium	0.66267	1.19350	0.57148

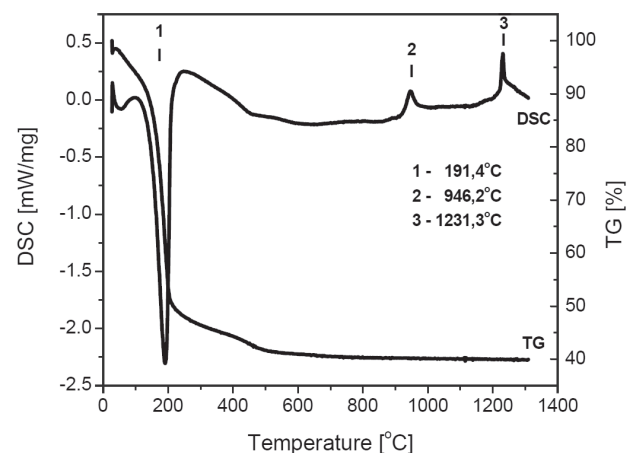
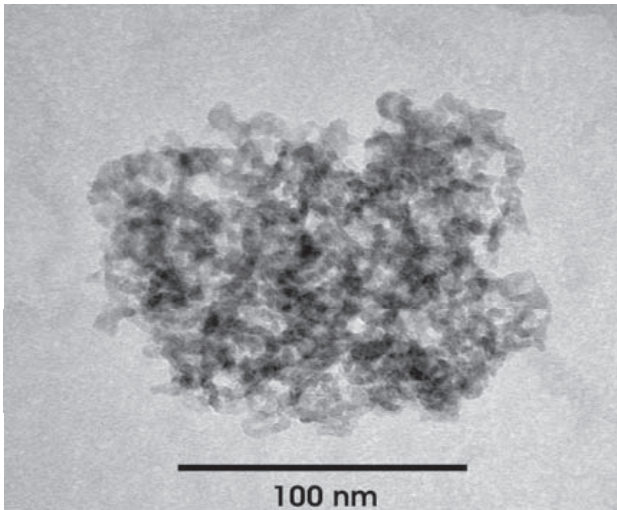


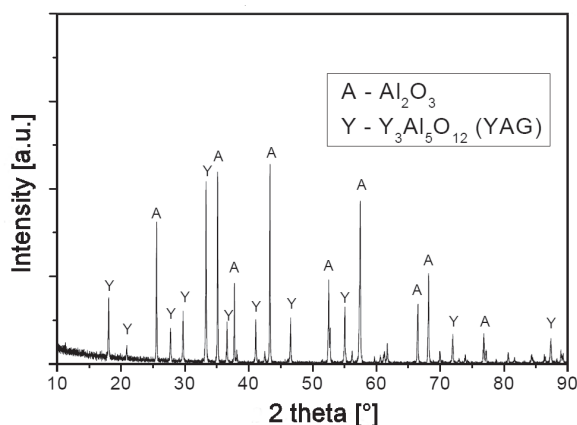
Figure 2. DSC/TG curves of the co-precipitated material. Yttria content corresponds to YAG 20 vol% after the reaction of the system

**Table 2.** Apparent ( $D_{app}$ ) and relative density ( $D_{ref}$ ), open porosity ( $P_{open}$ ), hardness ( $HV$ ) and fracture toughness ( $K_{IC}$ ) of samples sintered at indicated temperatures

Sample	$D_{app}$ [g/cm <sup>3</sup> ]	$D_{ref}$ [%]	$P_{open}$ [%]	$HV$ [GPa]	$K_{IC}$ [MPa·m <sup>1/2</sup> ]
AY+ $\alpha$ , 1500°C	3.985±0.006	97.16±0.14	-	17.32±0.38	3.86±0.34
AY+ $\alpha$ , 1600°C	4.053±0.006	98.78±0.16	-	17.66±0.25	4.15±0.39
AY, 1500°C	3.059±0.002	74.58±0.07	20.65	-	-
AY, 1600°C	3.155±0.007	76.91±0.18	12.46	-	-

**Figure 3.** TEM micrographs of the co-precipitated powder calcined at 600°C

The DSC/TG measurements (Fig. 2) demonstrate endothermic effect at low temperature accompanied with the large weight losses which could presumably be related to the dawsonite decomposition. At temperatures higher than 600°C no weight losses occur. In the sample calcined at this temperature X-ray diffraction reveals  $\gamma$ - $Al_2O_3$ . Specific surface area of this powder was 315 m<sup>2</sup>/g. Recalculating this value to the equivalent particle size we obtain value of about 3 nm. TEM micrograph (Fig. 3) shows much higher agglomerates com-

**Figure 4.** X-ray diffraction pattern of the co-precipitated material calcined in DSC/TG equipment at 1360°C temperature

posed of the smaller particles of the sizes corresponding to this assessment.

X-ray diffraction of the sample heated up to 800°C shows still  $\gamma$ - $Al_2O_3$ . Further increase of temperature to 1100°C results in the mixture of  $\delta$ - $Al_2O_3$  and  $\theta$ - $Al_2O_3$ . So the exothermic effect of the peak temperature 946°C should be attributed to the phase transition from  $\gamma$ - to  $\delta$ - and  $\theta$ - $Al_2O_3$  modifications. At 1198°C, that is few degrees before peak temperature of the highest exothermic effect (see Fig. 2) we observe  $\alpha$ - $Al_2O_3$ , YAH (hexagonal  $YAlO_3$ ) and YAP (rhombohedra  $YAlO_3$ ). At somewhat higher temperature (1300°C) only  $\alpha$ - $Al_2O_3$  and YAG coexist (Fig. 4). So crystallization of  $\alpha$ - $Al_2O_3$  and YAG is responsible for the exothermic effect at temperature 1231°C (Fig. 2).

In Table 2 results of density, Vickers hardness and fracture toughness measurements are shown. The latter two could be assessed only in case of dense samples. An essential difference of density between sintered samples derived from the powders seeded with  $\alpha$ - $Al_2O_3$  and un-seeded ones should be pointed out.

Densification results correspond well with the SEM micrographs of the samples (Fig. 5). We notice that material derived from the un-seeded powder shows not only open porosity (Table 2) but also intra-grain pores. It suggests that during sintering discontinuous grain growth occurs in this material. What is more we observe YAG inclusions intra-alumina grains. Both microstructural features do not exist in the material derived from the powder seeded with 5 wt.%  $\alpha$ - $Al_2O_3$  particles. Alumina and YAG grain sizes of the materials derived from the seeded and un-seeded powders sintered at 1500°C are shown in Table 3. Grain sizes of pure  $\alpha$ - $Al_2O_3$  (TM DAR TaiMai Chemicals, Japan) also sintered at 1500°C are introduced to these data. Striking difference between pure alumina and material with YAG inclusions is evident. We conclude that YAG inclusions limit grain growth of alumina matrix.

**Table 3.** Grain sizes of  $Al_2O_3$  and YAG grains in samples sintered at 1500°C

Material	$Al_2O_3$ [ $\mu$ m]	YAG [ $\mu$ m]
TM DAR	2070	-
AY	616	289
AY+ $\alpha$ ,	530	297

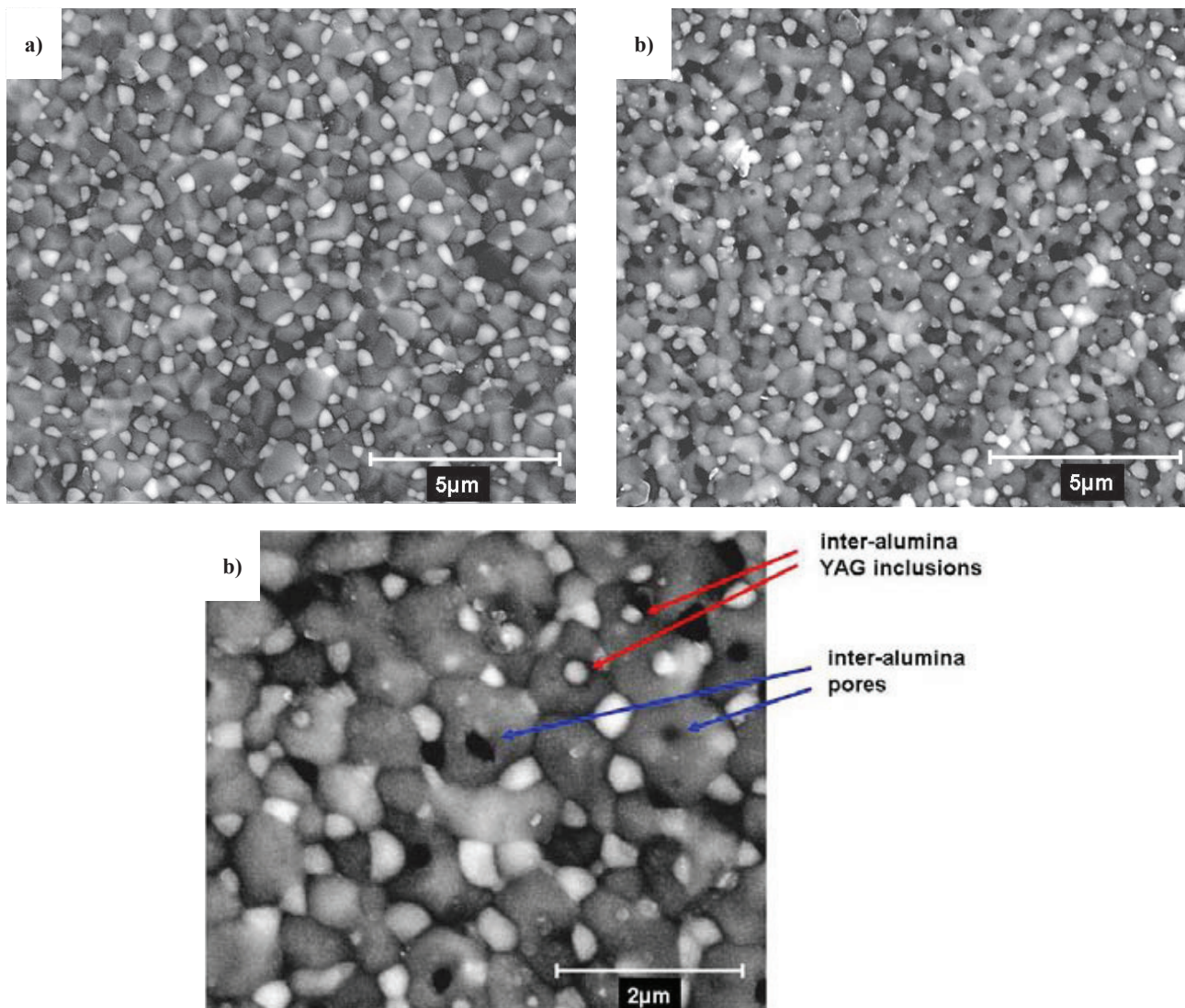


Figure 5. SEM micrographs of materials sintered at 1500°C: a) 5 wt.% seeded  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and b) unseeded.

Hardness of dense materials is higher than observed in case of pure alumina polycrystals (16.55 GPa) [12]. Also it is higher than observed in materials derived from the co-precipitated with ammonia from nitrate solution powders of YAG content of 25 vol% hot pressed at 1400°C (16.15 GPa) [1]. Fracture toughness, although not too bad, is lower than observed by us in the material prepared by the alternative method [12]. This problem should be further investigated.

#### IV. Conclusions

Composition of Al/Y ratio corresponding to composite Al<sub>2</sub>O<sub>3</sub> + 20 vol% YAG was co-precipitated with (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. The process results in ammonia dawsonite ((NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>) with yttrium incorporated in the dawsonite structure. At elevated temperature this compound decomposes to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and at still higher temperatures to  $\delta$ -Al<sub>2</sub>O<sub>3</sub> and  $\theta$ -Al<sub>2</sub>O<sub>3</sub> again with no traces of yttrium containing phase. The latter appears at 1198°C as YAH and YAP together with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and at still higher temperatures transforms to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> + YAG.

The starting precipitate calcined at 600°C was used for sintering experiments. It was found that such powder does not lead to dense composite polycrystals. However, seeding of this powder with 5 wt.%  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder results at temperatures 1500°C and 1600°C in dense materials of high hardness.

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