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Phase and microstructural evolution of yttrium-doped nanocrystalline alumina: A contribution of advanced microscopy techniques

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Abstract

Well-dispersed nano-crystalline transition alumina suspensions were mixed with yttrium chloride aqueous solutions, with the aim of producing Al_2O_3–$Y_3Al_5O_{12}$ (YAG) composite powders. DTA analysis allowed to highlight the role of yttrium on the α-phase crystallization path. Systematic XRD and HRTEM analyses were carried out in parallel on powders calcined in a wide temperature range (600–1300 °C) in order to follow phase and microstructural evolution. A thin, homogeneous yttrium-rich layer was yielded on the alumina particles surface; yttrium diffusion into the alumina matrix was negligible up to 1150 °C whereas, starting from 1200 °C, aggregates of partially sintered alumina particles appeared, stuck together by yttrium-rich thin films. Moreover, in the yttrium-richer zones, such as alumina grain boundaries and triple joints, yttrium-aluminates precipitated at alumina particles surface. Finally, at 1300 °C, alumina–YAG composite powders were produced, in which YAG was homogenously distributed among the alumina grains.

Keywords: Al_2O_3; Yttrium-doping; Powders-solid state reaction; Electron microscopy; Microstructure-prefiring

1. Introduction

Several oxide impurities, including MgO, CaO, SiO_2, TiO_2, ZrO_2, La_2O_3 and Y_2O_3 play a major role in modifying the microstructure and related properties of sintered polycrystalline α-alumina.[1–3] In addition, small contents (in the range 100–1000 ppm) of various metal cations can lead to an increase of alumina creep temperature and stress limits. Among them, the most effective ones seem to be the trivalent cations, such as yttrium: in fact, due to their ionic radius larger than the aluminium one, they segregate at alumina grain boundary and reduce the intergranular diffusion.[4–6] Moreover, if yttrium content increases up to saturation,[7] $Y_3Al_5O_{12}$ (YAG) precipitation at alumina grain boundaries occurs and dramatically improves both room and high-temperature mechanical properties of the matrix.[8–12]

By keeping in mind the several beneficial effects of YAG on the fired microstructure and on the overall mechanical behavior of alumina, in some previous works[13,14] we have set-up an innovative and easy process for the production of alumina–YAG nanocomposites. Briefly, it consists on the alumina surface modification with an inorganic yttrium salt; upon heating, a highly pure alumina–YAG composite powder is successfully yielded through a solid-state reaction between the yttrium-rich precursor layer and alumina. By strictly controlling all the processing parameters, completely homogenous and fully dense alumina–5 vol.% YAG composite materials were finally obtained. However, a suitable microstructural tailoring of the dense composites can be achieved only through an effective control of the powder features and of the role of its thermal pre-treatment prior forming and sintering.

This paper is therefore aimed to deepen the role of such yttrium-rich precursor on the phase and microstructural development of a nanocrystalline transition alumina powder, upon thermal treatment. In particular, we used advanced microscopy techniques (such as HRTEM and HAADF) to follow the whole path from the starting alumina surface doping to the final development of the composite powder. In fact, to the best of the

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Author's knowledge, a similar systematic investigation was never reported in literature, even for alumina–YAG composite materials yielded by quite similar doping process.[2,9,15]

A deeper understanding of the crystallization mechanism and microstructural evolution phenomena involved is the second goal which aims this work. In fact, if achieved, it can supply some general guidelines of this quite innovative processing route, leading to its more conscious exploitation toward the production of a wide range of micro/nanocomposites materials, having controlled and homogeneous microstructures.

2. Experimental

A commercial, nano-crystalline alumina (Nanotek®, supplied by Nanophase Technologies Corporation, Darien, IL, USA), produced by a physical vapour synthesis (PVS) process, was used as starting material. The powder has a spherical morphology, is highly pure (99.95%) with an average crystallites size of 45 nm and a specific surface area of 35 $m^2 g^{-1}$. It is composed by γ/δ-transition alumina phases, as declared by the supplier,[16] even if the δ*-Al_2O_3 phase [ICDDP file no. 46-1215] was also detected, as described in a previous paper.[17] From literature,[18] the δ*-Al_2O_3 phase is formed during the phase transformation from γ to α-alumina in plasma treated materials.

Nanotek® powder was dispersed in distilled water under magnetic stirring for 120 h, reaching an average particle agglomerate size of about 0.5 μm.[17]

Aqueous solutions of $YCl_3{\cdot}6H_2O$ (Aldrich, 99.99% purity) were employed as yttrium precursor for developing alumina–$Y_3Al_5O_{12}$ (YAG) composites, containing 5 (AY-5), 10 (AY-10) and 20 (AY-20) vol.% YAG. Further details on this process can be found elsewhere.[13,14] The yttrium-doped slurries were kept under magnetic stirring for two additional hours and then dried in an oven at 105 °C.

The doped powders were characterized as follows:

- DTA–TG analysis (Netzsch STA 409C), performed on powdered samples of about 150 mg, up to 1450 °C in static air, at a heating rate of 10 °C/min. On the ground of thermogravimetric results, powders were calcined at 600 °C for 6 min, at 900 °C, 1150°, 1200 °C, 1300 °C and 1500 °C for 30 min, at a heating and cooling rate of 10 °C/min, in air.
- X-ray diffraction (XRD) analysis (Philips PW 1710), performed on the same calcined powders. Cu Kα radiation (1.541874 Å) was used; spectra were acquired in the range 5–70° 2θ, with a step size of 0.05° 2θ and an acquisition time per step of 5 s. Diffraction patterns were indexed by using the Powder Data File database (P.D.F. 2000, International Centre of Diffraction Data, Pennsylvania).
- High resolution transmission electron microscopy (HRTEM) observations performed by a JEOL 2010 FEG instrument operating at 200 kV; elemental analyses were performed by energy dispersive X-ray spectroscopy (EDX INCA system) under a nano-probe condition (beam size in the range 2–5 nm). Some micrographs were also obtained using a chemical information mode with an high angle annular dark field detector (HAADF), sensitive to the atomic number variations (Z contrast). The analyses were carried out on the doped powders just dried at 105 °C or calcined in the 600–1300 °C temperature range. Powders were ultrasonically dispersed into absolute ethanol; the suspensions were deposited on a holey carbon film and then let to dry at ambient conditions.

3. Results

3.1. DTA–TG analysis

TG analyses of the three doped materials evidenced that the by-products (mainly chlorides) decomposition was almost accomplished at about 450 °C. Upon heating, AY-5, AY-10 and AY-20 underwent to total mass loss of 6.6, 14.7 and 20.8%, respectively.

DTA curves allowed to evidence the metastable (precisely, the θ-phase[19]) to α-Al_2O_3 transformation temperature; this value is reported in Fig. 1 as a function of the YAG volume fraction, showing an exponential increase of such temperature by increasing the yttrium content. For sake of comparison, the α-Al_2O_3 crystallization temperature in raw Nanotek® was also evaluated, showing the lowest value.

In AY-20, two additional DTA signals at about 900 °C and 1075 °C were also detected: as discussed in the following, the former exothermic peak can be imputed to the crystallization of the monoclinic $Al_2Y_4O_9$ (YAM), the latter to its conversion into aluminium-richer phases, such as YAG and/or hexagonal $YAlO_3$ (h-$YAlO_3$). In contrast, AY-5 and AY-10 DTA curves showed only the α-alumina exothermal crystallization, whereas yttrium-aluminates signals were not visible due to their lower yttrium content.

3.2. XRD analysis

The three doped powders showed different crystallization paths as a function of the calcination temperature: the crystalline phases detected are collected in Table 1.

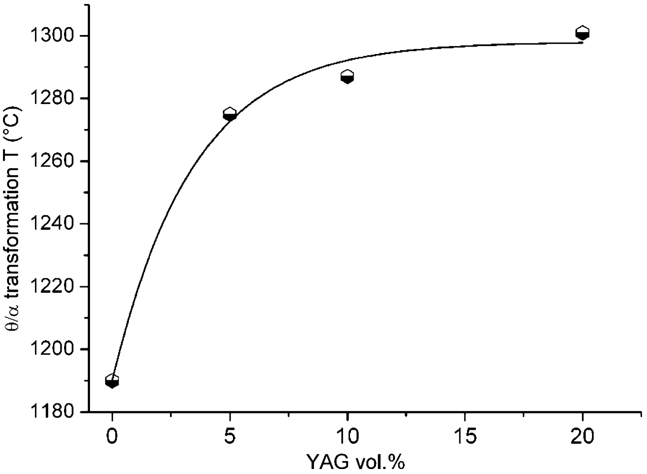

Fig. 1. Metastable to α-Al_2O_3 phase transformation temperature as a function of YAG volume percentage in the composite powders.