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Ceramics International 35 (2009) 391–396

CERAMICS INTERNATIONAL

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Effect of yttria on crystallization and microstructure of an alumina–YAG fiber prepared by aqueous sol–gel process

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Received 22 January 2007; received in revised form 14 September 2007; accepted 17 November 2007
Available online 8 April 2008

Abstract

Continuous fiber development is needed for high performance and high temperature composites. Various methods have been used to make ceramic fibers. In this research, composite fibers (yttrium aluminum garnet (YAG)/Al_2O_3) were prepared by a sol–gel method using aqueous solution. They were synthesized from aluminum salt, aluminum metal, yttrium oxide and water used as solvent. Transparent gel fibers were obtained by immersing a thin wire into the viscous sol, then pulling it out by hand. The obtained fibers contained very fine grains with diameter ranging from 10 to 80 μm after heat treatment. When yttria content was increased, the crystallization of YAG shifted to a lower temperature, whereas the transformation temperature to α-Al_2O_3 shifted to a higher temperature. Nevertheless, the fibers with different amounts of yttria contained alumina and YAG after heat treatment at 1400 °C. The composite fibers had vermicular structure and were denser than alumina fibers. The yttria percent concerning the limits of this study ($\leq$10 wt%) effected on fiber diameter. As the yttria content was increased, the fiber diameter increased, whereas grain size and densification of the composite fibers decreased.

Keywords: Sol–gel processing; YAG/Al_2O_3 composite fibers; Microstructure; Crystallization

1. Introduction

Continuous fiber-reinforced ceramic composites (CFCCs) show improved toughness and great potential for high temperature applications. Fibers used in these composites are required to exhibit good thermal and mechanical properties in high temperature oxidizing environments [1–4]. Commercially available oxide fibers are alumina fibers. However, the applications of these fibers are limited by the degradation in fracture strength and creep properties above 1000 °C [5].

Numerous cation impurities including Mg, Ca, Si, Ti, Y and Zr play a major role in modifying the microstructure and related properties of sintered polycrystalline α-Al_2O_3. The first quantitative investigation of yttrium segregation behavior showed that as the grain size increased, the yttrium level at the boundary increased monotonically and the saturated at the certain level. At this level yttrium aluminum garnet (YAG) precipitates start to form and further increases in yttrium doping resulted in an increased amount of precipitates [6].

The second phase particles affect the deformation rate of a polycrystal. In addition, the second phase particles may affect grain growth, microstructure and creep rate by grain growth boundary pinning [7–9]. Yttrium aluminum garnet is believed to be a very suitable candidate for reinforcing Al_2O_3 due to its excellent creep resistance, similar coefficient of thermal expansion and no reaction with alumina [10,11]. On the other hand, yttrium has a deleterious effect on alumina sintering by reducing the densification rate [12]. Yttrium was known to have a very low solubility limit in α-Al_2O_3 and segregate strongly to grain boundaries.

It was show that as yttrium segregation in Mg-codoped samples delayed densification when the yttrium was at a level below the saturation limit as well as when the yttrium level was high enough to induce significant YAG precipitation [6].

If the Al_2O_3 and Y_2O_3 mixed powder was used as starting materials to fabricate α-Al_2O_3/YAG composites, it was very difficult to get well dispersion of the particles. If the solution including Y and Al elements was used to produce oxides (α-

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doi:10.1016/j.ceramint.2007.11.010

Al_2O_3 and YAG) after heat treatment, a homogenous microstructure would be hopeful to obtain [11,13].

In the present study, an α-Al_2O_3–YAG fiber was synthesized through an aqueous sol–gel method. The effect of yttria on phase transformation, morphology and microstructure was investigated. No organic additives have been used to stabilize the sol because of their deleterious effects on product properties.

2. Experimental procedure

The precursor solutions for α-Al_2O_3/YAG composite fibers were prepared by sol–gel method using $AlCl_3{\cdot}6H_2O$ (Merck), aluminum powder (M.A. University), yttrium oxide powder (Sigma–Aldrich) and HCl. Yttrium oxide powder was first dissolved in aqueous HCl. The solutions were prepared by dissolving aluminum chloride hexahydrate, aluminum powder and yttrium oxide solution into the distilled water. Addition of aluminum powder to the solution was carried out with 0.78 g/min rate. The amount of yttrium oxide was 0, 2, 4, 6, 8 wt% of premixed raw materials. The precursor solution was then continuously stirred with 400 l/min rate at 98 °C for 2–6 h to completely dissolve the starting materials and was aged at 25 °C. The gel fibers were prepared by immersing a thin stainless steel wire into the condensed precursor sol and pulling it out slowly by hand. The fibers drawing speed was about 3–4 cm/s and the fibers could be drawn in condition of about 50% relative humidity at room temperature. The gel fibers were dried at room temperature for 24 h and further dried at 45–50 °C for 24 h in an oven. They were then put in an alumina plate and heat treated in air with a three step-heating schedule as follows:

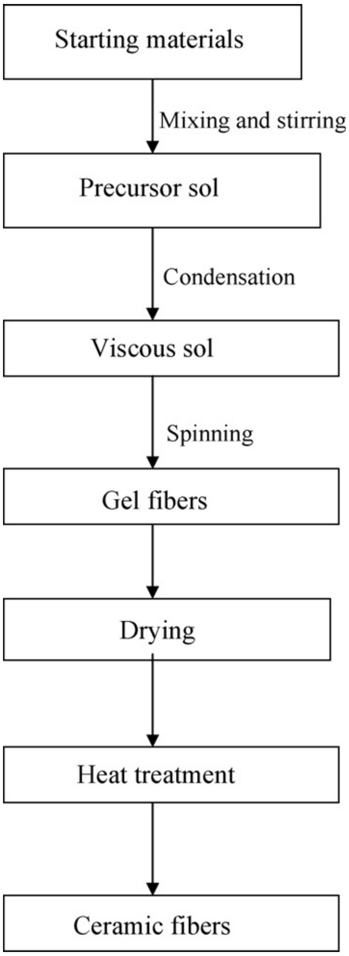

Fig. 1. Flowchart of the preparation of fibers.

Step 1: from room temperature to 200 °C with a rate of 10 °C/min and heating at 200 °C for 1 h,
Step 2: from 200 to 600 °C with a rate of 5 °C/min and heating at 600 °C for 2 h,
Step 3: from 600 °C to various temperatures above 900 °C with a rate of 5 °C/min and heating for 4 h.

The fibers were cooled in the furnace after heat treatment. The flowchart of the fiber preparation is shown in Fig. 1. In order to study the effect of aging on the fibers, the gel fibers were aged at room temperature for several weeks. They were then heat treated at 1300 °C for 4 h.

X-ray diffraction was carried out for phase analysis of the fibers using Philips Xpert model with Cu Kα radiation. Differential thermal analysis (DTA) and thermogravimetry (TG) were used in the range of 25–1360 °C with a rate of 10 °C/min with the STA 429 equipment (Netzoch, Germany). Morphological and microstructural features of the fibers were investigated using Philips XL30 scanning electron microscope.

3. Results and discussion

3.1. The effect of yttria on phase transformation of the fibers

The XRD patterns of the dried gel fibers without yttria are shown in Fig. 2. As can be seen, θ-Al_2O_3 or γ-Al_2O_3 was detected in the gel fibers heat treated at 900 °C. By increasing the heat treatment temperature up to 1000 °C, α-Al_2O_3 was also appeared. Transformation of the transitional alumina phases, θ-

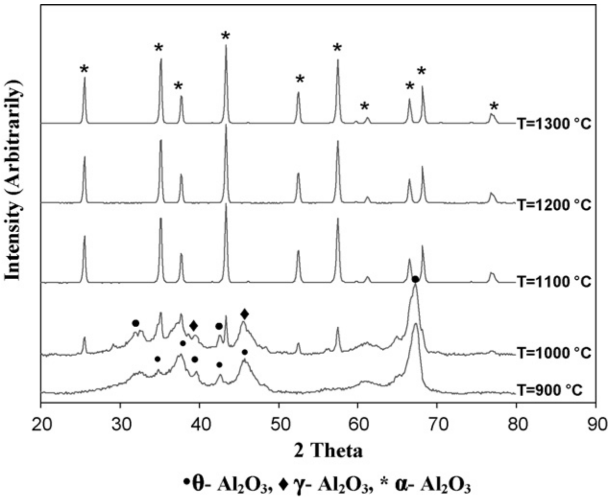

Fig. 2. XRD patterns of alumina (0 wt% YAG) fibers heat treated at different temperatures for 4 h.

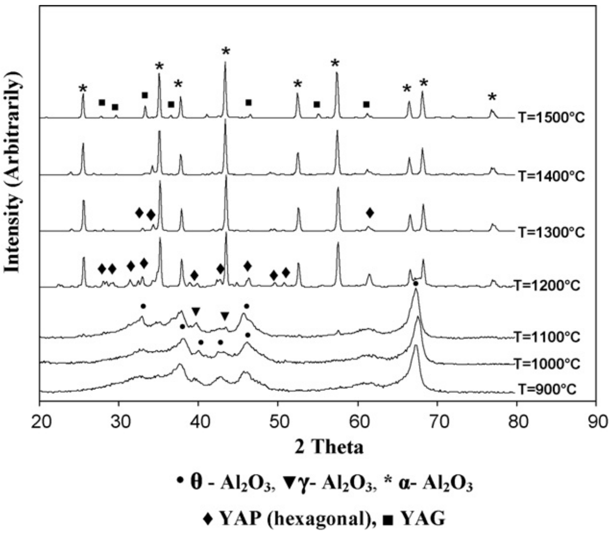

Fig. 3. XRD patterns of alumina/YAG (7 wt% YAG) fibers heat treated at different temperatures for 4 h.

Al_2O_3 and/or γ-Al_2O_3, to the final stable α-Al_2O_3 took place approximately at about 1100 °C.

Fig. 3 shows the XRD patterns of the alumina composite fibers consisting of 2 wt% yttria. As it is shown, θ-Al_2O_3 was detected in the gel fibers heat treated in temperature ranging from 900 to 1000 °C. By increasing the heat treatment temperature α-Al_2O_3 and γ-Al_2O_3 were detected at 1100 °C. The first transition phase of YAG (hexagonal $YAlO_3$, YAP: yttrirum aluminum perovskite) was formed at 1200 °C. Hexagonal $YAlO_3$ was transformed to YAG at 1400 °C.

The XRD patterns of the composite fibers consisting of 4, 6, 8 wt% yttria are shown in Figs. 4–6. These fibers showed a similar transformation behavior. Crystallization of YAG appears to involve the formation of hexagonal and orthorhombic YAP as intermediate phases. It seems that yttrium reacted with Al_2O_3 as the heat treatment temperature was increased, to produce a hexagonal $YAlO_3$ above 1000 °C. At the same time, crystallization of YAG was started at 1000 °C. Hexagonal YAP was then transformed to orthorhombic YAP at 1200 °C. Increasing the heat treatment temperature resulted in an increase in the content of YAG and α-Al_2O_3, whereas it resulted in disappearance of YAP phases. The transitional phases in fibers were completely transformed to α-Al_2O_3 and YAG at 1400 °C.

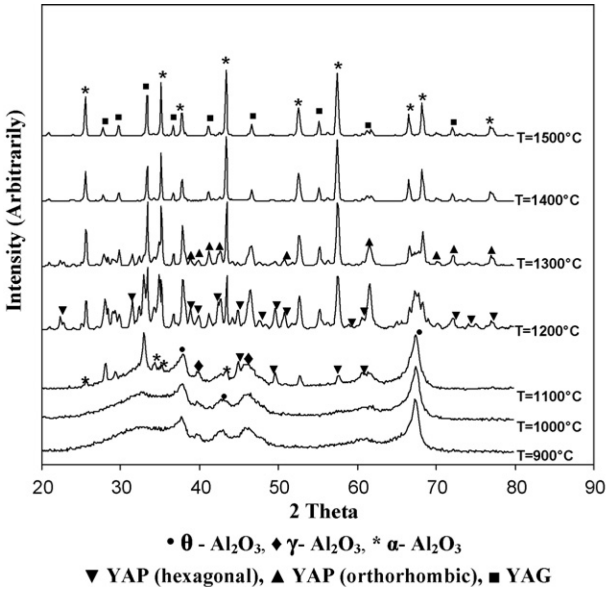

Fig. 4. XRD patterns of alumina/YAG (14 wt% YAG) fibers heat treated at different temperatures for 4 h.

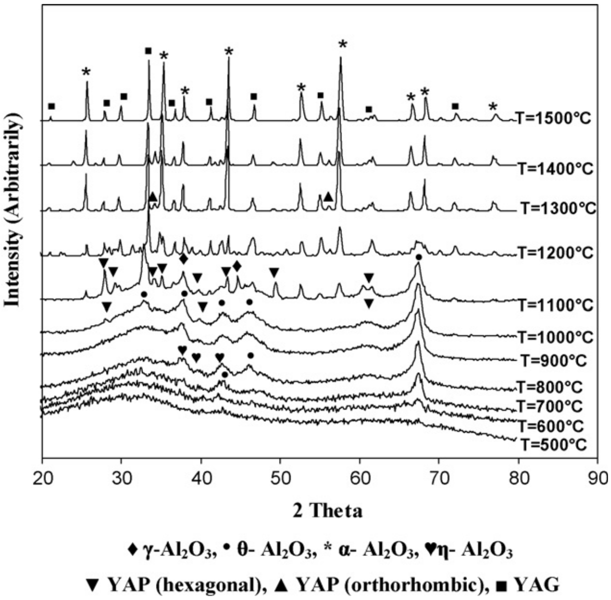

Fig. 5. XRD patterns of alumina/YAG (21 wt% YAG) fibers heat treated at different temperatures for 4 h.

Although, formation of YAG phase requires a higher temperature using conventional micron sized alumina and yttria powders [7], its crystallization temperature was lowered in the present work. This is because diffusion

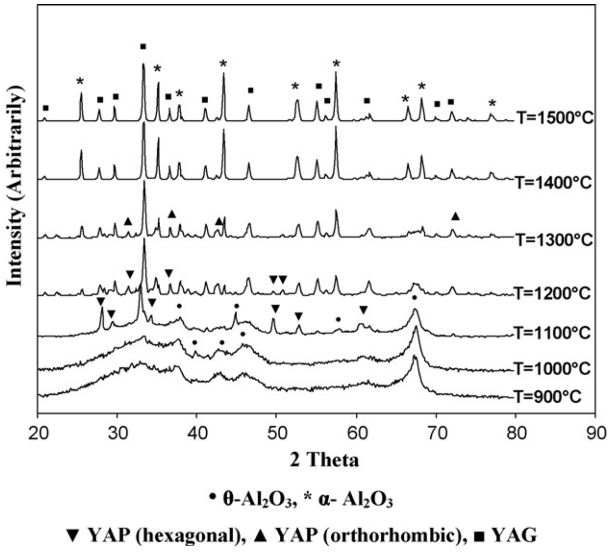

Fig. 6. XRD patterns of alumina/YAG (28 wt% YAG) fibers heat treated at different temperatures for 4 h.

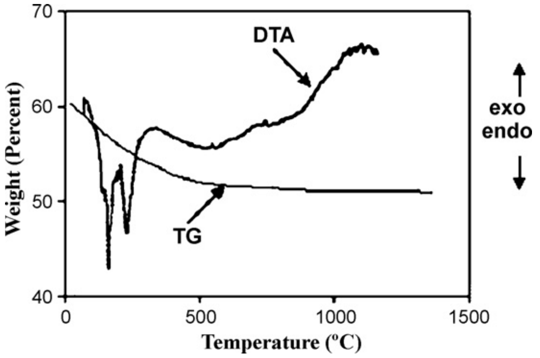

Fig. 7. TG and DTA curves of YAG/alumina (YAG: 21 wt%) fibers.

occurs much more readily in gels than in conventional mixtures due to the more intimate mixture and shorter diffusion distances.

Furthermore, the crystallization of YAG was also dependent on yttria content. It shifted to a lower temperature with increasing the yttria content.

It is seen from XRD patterns in Figs. 2–6 also shown that the presence of yttria postponed the formation of α-Al_2O_3. According to the literature, the lattice constant of the alumina fibers heat treated at 1200 °C for 4 h, was 4.7582 Å, whereas it was 4.7591 Å in the composite fibers heat treated at the same temperature. The larger lattice constant of the composite fibers was indicative of yttrium substitution in the α-Al_2O_3 crystal structure that increases the lattice constant of alumina [7]. It can be proposed that some yttrium ions were dissolved into the α-Al_2O_3 and expanded the diffusion path in the composite fibers. Therefore, it resulted in increased the crystallization temperature of α-Al_2O_3.

Fig. 7 presents TG and DTA curves of the dried gel fibers containing 6 wt% yttria. As it is shown, weight loss of the gel fibers heat treated from 25 to 580 °C was about 15.34%. The highest weight loss (8.9%) occurred between 25 and 260 °C. Corresponding two endothermic peaks were appeared in DTA curve. These peaks were due to dehydration of the residual water and decomposition of hydroxides in the dried gel fibers. A weight loss of about 6.44 wt% occurred in the temperature ranging from 260 to 580 °C due to the decomposition of residual chlorides in the gel fibers [14]. A broad exothermic peak corresponding to the formation of α-Al_2O_3 and YAG phases was observed in DTA curve between 600 and 1360 °C. As previously shown in Fig. 5, transformation of transitional alumina and yttrium aluminate phases to α-Al_2O_3 and YAG occurred respectively in this temperature range.

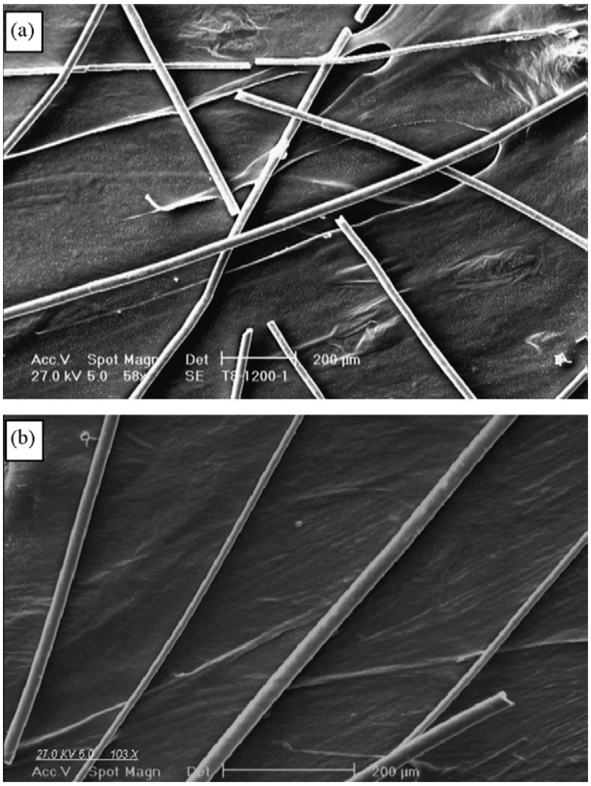

Fig. 8. SEM picture of the fibers heated at 1400 °C for 4 h: (a) YAG: 21 wt% and (b) YAG: 28 wt%.

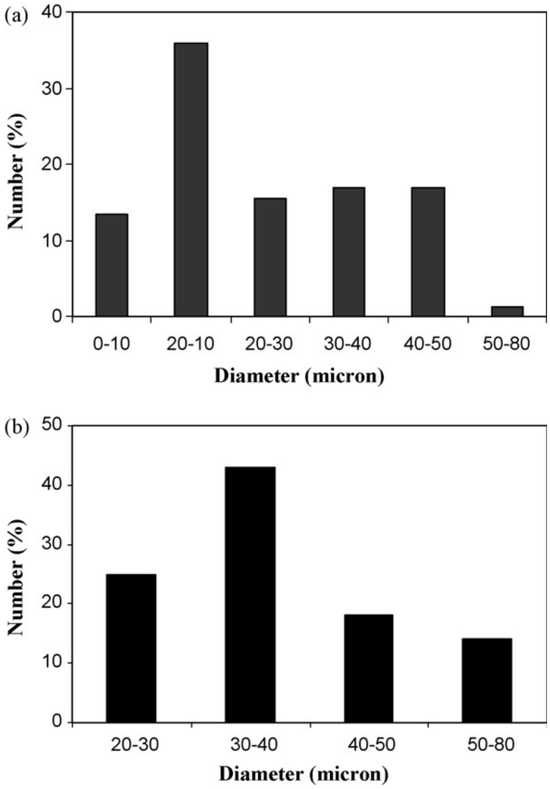

Fig. 9. Diameter distribution of the fibers heated at 1400 °C for 4 h: (a) YAG: 21 wt% and (b) YAG: 28 wt%.

3.2. The effect of yttria on morphology and microstructure of the fibers

Fig. 8 shows the scanning electron microscopy of the composite fiber with different amounts of yttria. It showed that the fibers had a uniform diameter after heat treatment. As shown in Fig. 9, diameter of the fibers increased with increasing the amount of yttria. As yttria content was increased, precursor

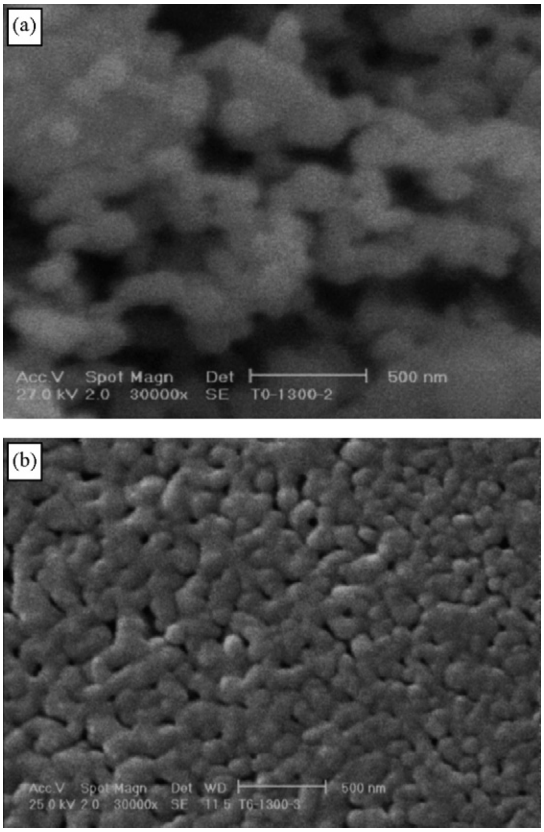

Fig. 10. Cross-section of the fibers heated at 1300 °C for 4 h: (a) YAG: 0 wt% and (b) YAG: 21 wt%.

sols were drawn at higher viscosity. Hence, it resulted in thicker gel fibers.

Fig. 10 shows cross-section of the alumina and composite fibers. The composite fibers had vermicular structure and were denser than the alumina fibers. This may be due to better sinterability of the composite fibers. It is because according to binary phase diagram of Y_2O_3–Al_2O_3 shown in Fig. 11 [15], the

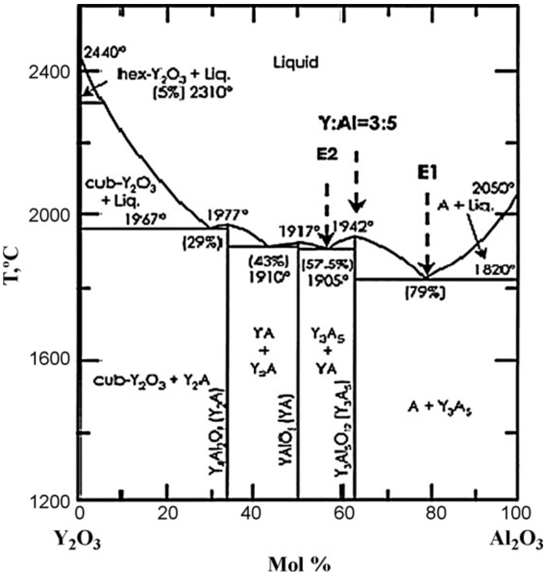

Fig. 11. Phase diagram of Y_2O_3–Al_2O_3 system [15].

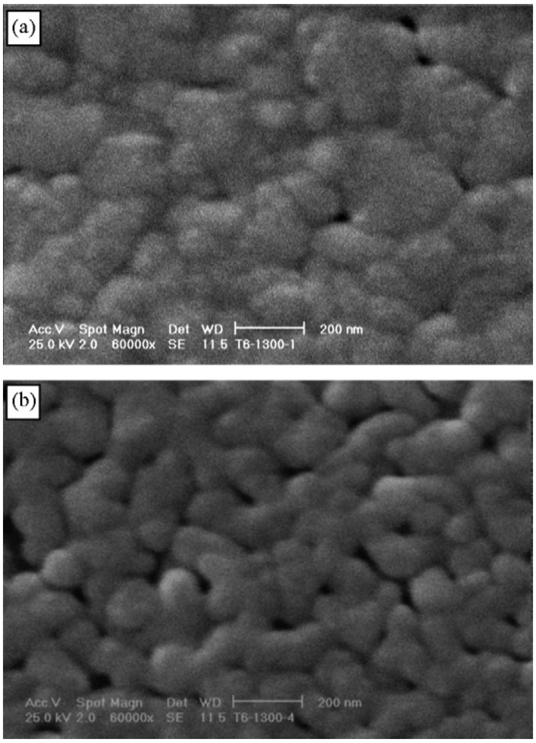

Fig. 12. Cross-section of the composite fibers heated at 1300 °C for 4 h: (a) YAG: 21 wt% and (b) YAG: 35 wt%.

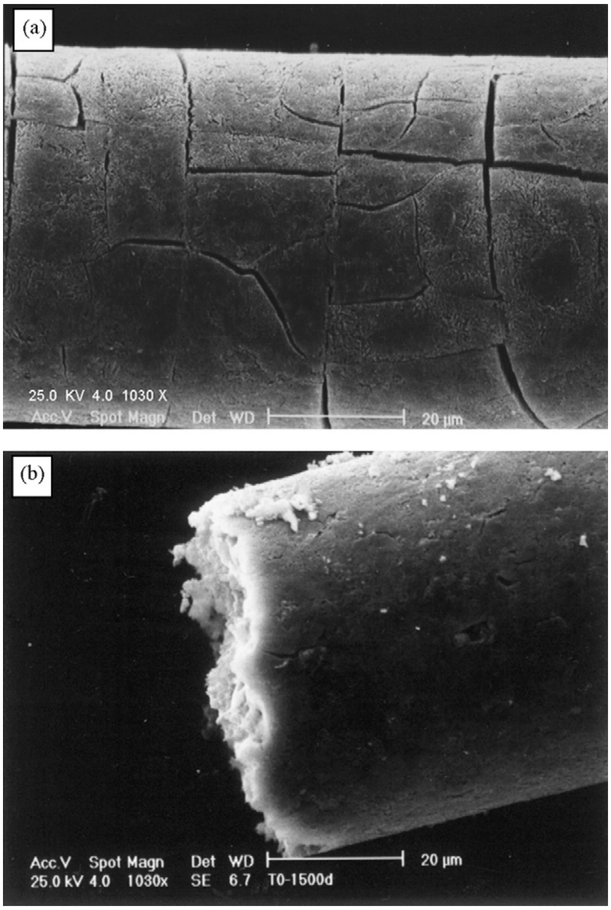

Fig. 13. SEM micrograph of (a) an aged fiber and (b) a non-aged fiber heated at 1300 °C for 4 h.

YAG phase has a lower melting point than that of alumina. As a result, it caused to form a neck between the particles and made a vermicular structure in the composite fibers. Moreover, transformation of transitional compositions, $YAlO_3$ (hexagonal and orthorhombic), to α-Al_2O_3 and YAG occurs by 11% volume expansion [5], that resulted in dense composite fibers.

The effect of yttria on microstructure of the fibers is shown in Fig. 12. As it is shown, grain size and densification of the fibers were decreased with increasing the amount of yttria. Cinibulk et al. showed that YAG segregated to the grain boundaries of alumina resulting in decreased grain boundary diffusivity and the corresponding rates of grain growth [16].

Fig. 13 shows the surface of an aged and a non-aged fiber after heat treatment. The surface of aged gel fiber was cracked, whereas that of non-aged gel fiber was smooth. The gel fiber was very flexible after drawing. It then became brittle after aging for a long time (8 weeks). This was attributed to the further hydrolysis–condensation reactions in room humidity with time. Thereby, concentration of the linear chains increased and entanglement of the chains gave a more complex structure in the fiber. Therefore, the volatile components were hardly removed during the heat treatment increasing the drying stresses in the fiber.

4. Conclusion

To prepare the composite (YAG/Al_2O_3) fibers, aluminum chloride hexahydrate ($Al/AlCl_3{\cdot}6H_2O$), aluminum and yttrium oxide powders were used in aqueous solution by sol–gel method. The obtained results are as follows:

1. The diameter of composite fibers was ranging from 10 to 80 μm.
2. The diameter of composite fibers increased with the increasing of yttrium oxide content.
3. Yttrium oxide played important role in the crystallization of α-alumina and delayed it, whereas promoted YAG formation.
4. The composite fibers were more denser than the alumina fibers and had a vermicular structure.
5. Grain size and densification of the composite fibers were decreased with YAG content.

Acknowledgements

The authors are thankful to Dr. Rezaie and Mrs. Faeghi-Niya and Mr. Sedaghat for their kind interest on this work.

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