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Eutectic $Al_2O_3/Y_3Al_5O_{12}$ fibers modified by the substitution of Sc_2O_3, Fe_2O_3 or Cr_2O_3

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Abstract

A variety of corundum/garnet eutectic fiber samples were produced by the micro-pulling-down (μ-PD) method in an Ar atmosphere and the substitution of Cr_2O_3, Fe_2O_3 or Sc_2O_3 for Al_2O_3 in the eutectic fiber sample $0.81Al_2O_30.19Y_2O_3$ was studied by a scanning electron microscope (SEM) and electron backscattering (EBSP) together with the X-ray diffraction (XRD). Although the chemical substitution resulted in the formation of a colony structure consisting of a fine ordered "Chinese-script" structure of corundum and garnet surrounded by a thick boundary region, a fundamental crystallographic relationship ⟨0 0 1⟩ corundum//⟨1 1 2⟩ garnet was found to be perpendicular to the solidification direction was readily observed. Cr_2O_3 is distributed in corundum and garnet structures, Sc_2O_3, however, preferred the garnet structure. The EDX and XRD analyses showed that the presumably reduced FeO contributes to the formation of hercynite $FeAl_2O_4$.

Keyword: Eutectic fiber

1. Introduction

Much attention has been paid to Al_2O_3 based directionally solidified eutectic composites because of their excellent mechanical properties at high temperatures.[1–4] Among a variety of single crystal oxides eutectics, a directionally solidified $Al_2O_3/Y_3Al_5O_{12}$ eutectic has been demonstrated as one of the most promising materials by indicating the high strength together with the creep resistance superior to a conventionally sintered composite with the similar chemical composition.[4–9] The microstructure of such $Al_2O_3/Y_3Al_5O_{12}$ eutectic is composed of three-dimensionally entangled α-Al_2O_3 (corundum) and $Y_3Al_5O_{12}$ (garnet). This characteristic "Chinese script" microstructure is suggested to be one of the important factors for providing its excellent mechanical properties at high temperatures. Nevertheless, an ordinary fiber eutectic sample frequently exhibits inhomogeneous area at different length scale from grains to colonies and the controlling parameter of the mechanical strength appears to be the coarse size of the colony area. This makes the real mechanical strength much lower than expected from the characteristic microstructure or lamella size. Therefore, the investigation of the eutectic morphologies in this corundum/garnet system remains of primary importance, and the effect of the process parameters together with the parent chemical composition has been studied so as to obtain the reliable process parameters, which allow us to maintain the homogeneous "Chinese script" microstructure.[6,9–17]

On the other hand, solid solution effect has been known in metal to improve tensile strength by deterring the movement of dislocations in metals, as an example. Coherence of the constituent phases, which is greatly affected by the chemical compositions of constituents, is also counted as a factor influencing the mechanical strength. Recently, several research groups have studied the role of elemental modifiers on the eutectic microstructure.[18,19] As an example, the CeO_2-doped and Pr_2O_3-doped corundum/garnet eutectic composites were grown by the EFG technique and the

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deflection of the propagating crack along the interface structure was suggested in the CeO_2-doped eutectic sample.[18]

The present study has prepared a variety of corundum/garnet eutectic fibers by the micro-pulling down (μ-PD) method,[10,11,15] and the substitution of Sc_2O_3, Fe_2O_3 or Cr_2O_3 for Al_2O_3 was studied with a special emphasis on the microstructure together with the crystallographic orientation relationship developed in the fiber samples. These three dopants were chosen because the variety of ionic radii was presumed to produce distinct results.

Table 1
Chemical composition of the present fiber samples ($M_2O_3 = Cr_2O_3$, Fe_2O_3 or Sc_2O_3)

	Al_2O_3 (mol%)	Y_2O_3 (mol%)	M_2O_3 (mol%)
Cr03%	78.6	19.0	2.4 Cr_2O_3
Cr05%	77.0	19.0	4.0 Cr_2O_3
Fe03%	78.6	19.0	2.4 Fe_2O_3
Fe05%	77.0	19.0	4.0 Fe_2O_3
Sc03%	78.6	19.0	2.4 Sc_2O_3
Sc05%	77.0	19.0	4.0 Sc_2O_3
Reference	81.0	19.0	–

2. Experimental

The μ-PD method involves pulling down of a fiber sample through a capillary hole of about 300 μm in diameter centered at the bottom of a conical crucible.[10,11,15] The ordinary starting mixture used for a corundum/garnet eutectic fiber sample is 81 mol% Al_2O_3 (4N High-Purity Chemicals Co. Ltd.)/19 mol% Y_2O_3 (4N Nippon Yttrium Co., Ltd). Therefore, the chemical compositions for present samples were selected so as to exchange 3 or 5 mol% of Al_2O_3 in the parent composition $Al_2O_3/Y_2O_3 = 81/19$ by the corresponding amount of Fe_2O_3 (3N, Wako Pure Chemical Industries, Ltd.), Cr_2O_3 (3N, Wako Pure Chemical Industries, Ltd.) or Sc_2O_3 (3N, Nippon Yttrium Co., Ltd.) as listed in Table 1. Each prepared powder mixture was melted in the iridium crucible by a RF induction heating module. The iridium crucible together

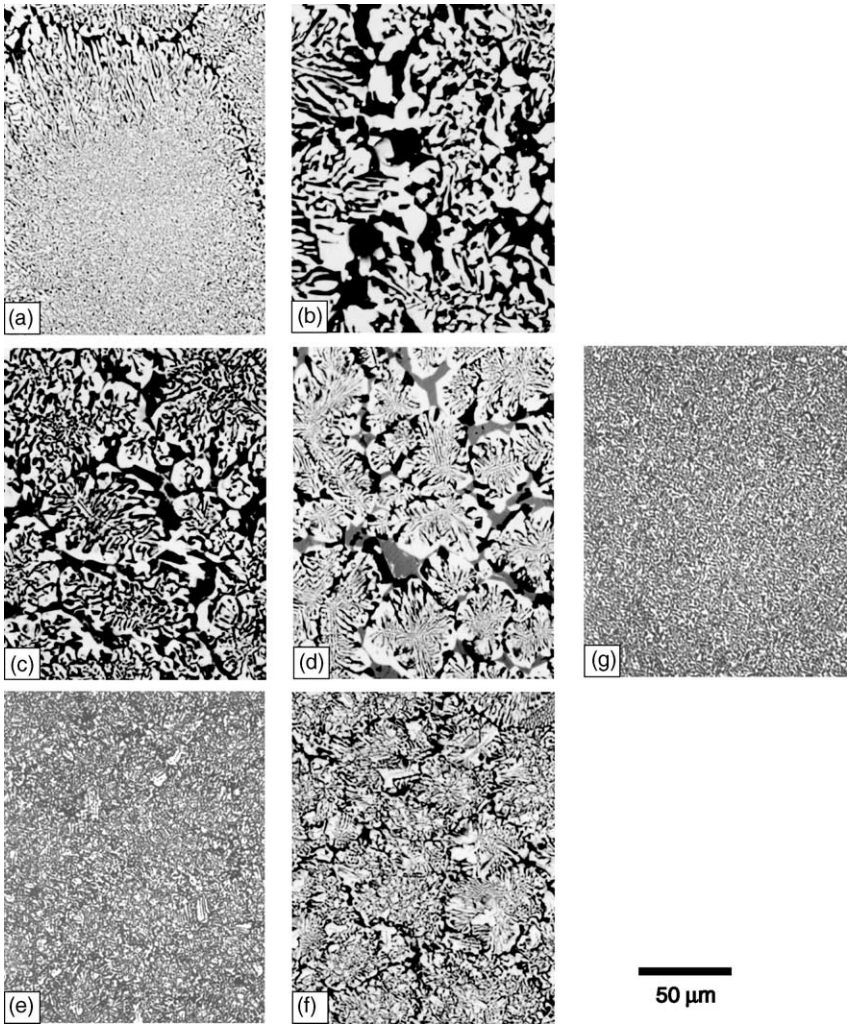

Fig. 1. SEM images of cross sections for the fiber samples (a) Cr03%, (b) Cr05%, (c) Fe03%, (d) Fe05%, (e) Sc03% and (f) Sc05% together with the reference sample (g).

with the starting powder mixture was sealed by a tight SiO_2 glass tube and the atmosphere was controlled by the flowing of Ar gas at the rate of about 1 l/min. An appropriate length of a corundum/garnet eutectic fiber sample was positioned at the capillary hole by using an *x*–*y* stage, and the fiber sample was pulled down at the rate of about 10 mm/min over a maximum length of 500 mm. For the convenience of discussion, a reference corundum/garnet eutectic fiber sample with the chemical composition $Al_2O_3/Y_2O_3 = 81/19$, was prepared by applying the similar growth rate and studied in the present study.

In order to identify component phases for the present fiber samples, powder X-ray diffraction analysis (Rigaku RINT-Ultima) was carried out by using Cu Kα radiation with a pyrolitic graphite monochromator in the diffraction beam path. The cell parameters for corundum and garnet phases were determined by the whole powder pattern decomposition (WPPD) method[20] with an internal standard of NBS Si (640B). Microstructure of present fiber samples was examined by means of back-scattered electron (BSE) imaging. X-ray energy-dispersive spectral (EDS) analysis was also carried out in order to study the elemental distribution found in the present fiber samples (SEM JEOL JSM-5900LV). Electron probe micro analysis (EPMA JEOL 6900) was also performed so as to determine the chemical compositions for constituent phases. The crystallographic orientation relationship was also studied by using an electron backscattering pattern (EBSP) observed by a Phase IP EBSP system (NORAN Instruments Inc.) and detailed analytical processing has been described elsewhere.[21]

3. Results and discussion

Fig. 1(a)–(g) show representative SEM images of the cross-sections perpendicular to the solidification direction for the $Al_2O_3/Y_3Al_5O_{12}$ and the effect of substitutions. The abbreviations Cr03% and Cr05% in Fig. 1(a) and (b) stands for a sample with 3% and 5% of total Al_2O_3 replaced by Cr_2O_3, respectively. EDS analysis clearly supports the distribution of Cr in both corundum and garnet phases, which agrees well with the previous results.[18] Although fundamental feature in the microstructure of Cr03% and Cr05% samples is rather similar to the reference sample of the non-substituted $Al_2O_3/Y_3Al_5O_{12}$ eutectic fiber in Fig. 1(g), the substitution of Cr_2O_3 appears to encourage the development of the colony texture in the parent "Chinese script" structure. The appearance of such colony texture was also observed in the eutectic samples prepared by the relatively rapid growth rate.[22] Therefore, the substitution of Cr_2O_3 into the binary $Al_2O_3/Y_3Al_5O_{12}$ system is suggested to bring about the effect similar to the rapid solidification of eutectic samples. The weight fraction of Cr_2O_3 in corundum and garnet structure were almost consistent to those expected from the parent chemical composition of the Cr05% sample and no remarkable evaporation of Cr_2O_3 appeared to be occurred. Nevertheless, the further trial for producing a Cr10% sample with the similar technique resulted in the evaporation of about a half of the substituted Cr_2O_3. Fig. 1(c) and (d) indicate SEM images for Fe03% and Fe05% samples, respectively. In particular, the SEM image of Fig. 1(d) for Fe05% clearly indicates three different phases with black, gray and white contrasts. The EDS analysis readily confirmed the distribution of Fe in the small gray area only, by suggesting that corundum and garnet phases reject the incorporation of Fe. It should be noted that the colony texture was developed by the substitution of Fe_2O_3 similar to those found in Cr03% and Cr05% samples. Fig. 1(e) and (f) show SEM images for Sc03% and Sc05% samples, respectively. Although the SEM image for Sc03% indicates the microstructure, more or less, similar to those for the reference sample, the SEM image for Sc05% shows the obvious development of the colony texture similar to the cases of Cr03% and Cr05%. The EDS analysis shows the distribution of Sc in the garnet phase, only.

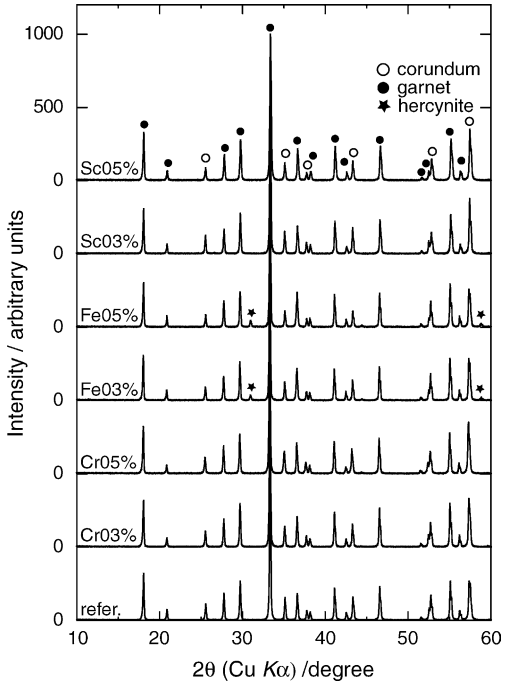

Fig. 2. XRD patterns for the fiber samples prepared by the substitution of Cr_2O_3, Fe_2O_3 or Sc_2O_3. Hercynite is readily detected in the Fe03% and Fe05% samples. The cell constants of corundum and garnet phases were analyzed by the WPPF method.[20]

Fig. 2 indicates the powder XRD patterns for the fiber samples of Cr03%, Cr05%, Fe03%, Fe05%, Sc03% and Sc05% together with the reference sample. The diffraction patterns for the samples prepared by the substitution of Cr_2O_3 or Sc_2O_3 indicate no significant change in constituent phases with that of the reference sample, and the diffraction patterns can be readily explained by means of corundum and garnet structures. On the other hand, the sample prepared by the substitution of Fe_2O_3 prompts the formation of hercynite $FeAl_2O_4$ as indicated by stars, and this is natural when

considering that Fe_2O_3 is not stable at high temperatures applied in the present synthesis and that divalent Fe^{2+} is large enough to be rejected by the tetrahedral and octahedral sites of the garnet structure as well as the octahedral sites of the corundum structure.

Table 2 summarizes the cell constants for corundum and garnet phases found in the present fiber samples. The cell constants of corundum and garnet for the Cr03% and Cr05% samples increase as the increment of Cr_2O_3 substitution by suggesting the distribution of Cr into both structures. On the other hand, the cell constants of corundum and garnet for the Fe03% and Fe05% samples indicate no significant change from those of the reference sample. The variation found in the samples prepared by the substitution of Cr_2O_3 and Fe_2O_3 (FeO) agrees well with the results of the EDS analysis described in the previous section. The substitution by Sc_2O_3 produces the slight decrease in the cell constant of garnet phase. This decrease in the cell constant of garnet strongly suggests the distribution of Sc at the expense of larger Y in the garnet structure. However, it may be contradicts to the fact

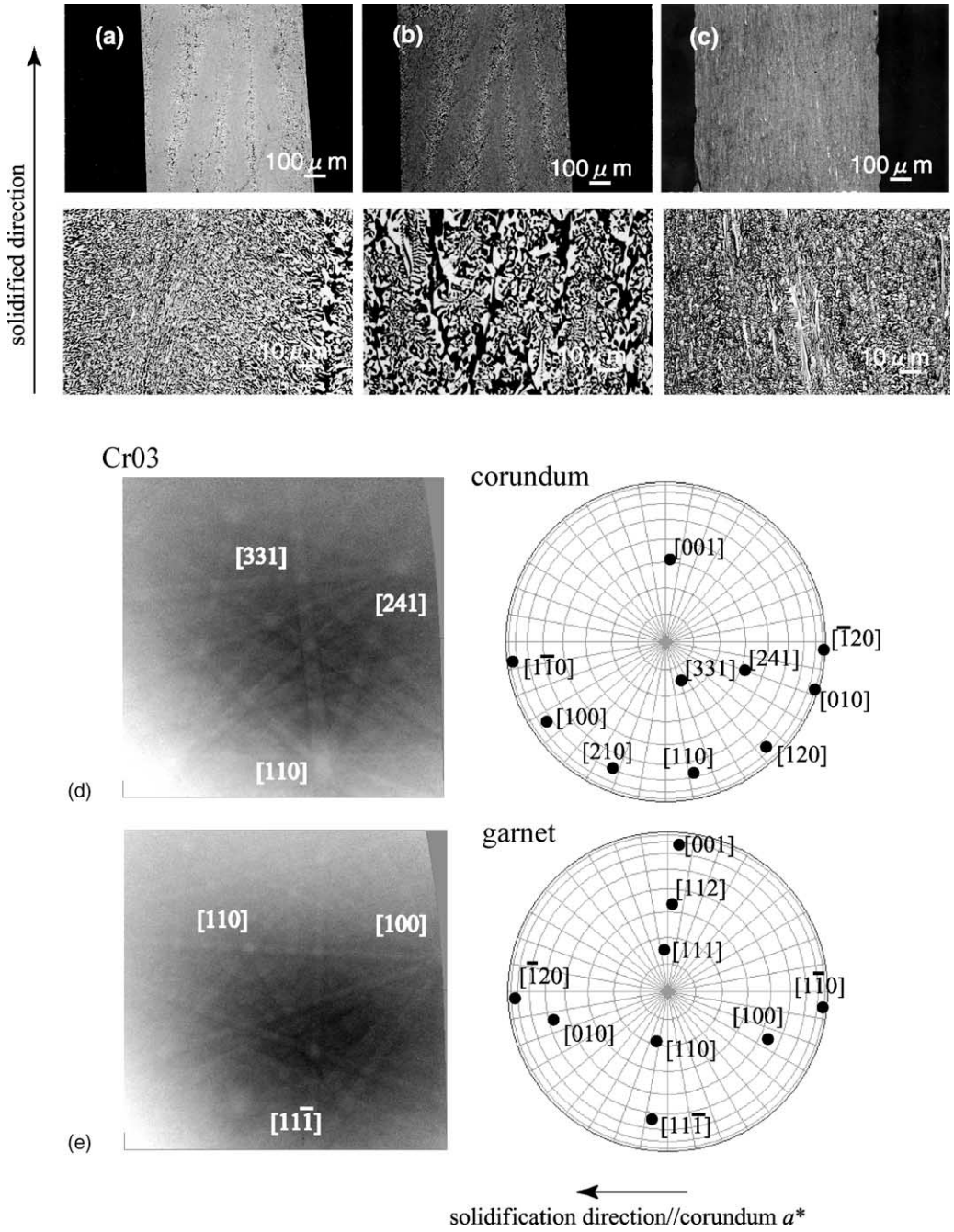

Fig. 3. SEM images of longitudinal sections for the (a) Cr03%, (b) Fe03% and (c) Sc03% samples. Typical EBSPs for the corundum (d) and garnet (e) in the fiber sample of Cr03% are given together with the corresponding stereographic projections.

Table 2
Cell parameters for the constituent corundum and garnet phases for the present fiber samples

	Corundum		Garnet	
	a (Å)	*c* (Å)	*a* (Å)	R_p (%)
Cr03%	4.7664(1)	13.0139(5)	12.0207(2)	8.1
Cr05%	4.7741(1)	13.0289(7)	12.0299(3)	8.1
Fe03%	4.7593(1)	12.9934(4)	12.0092(1)	6.6
Fe05%	4.7595(1)	12.9934(4)	12.0094(1)	6.3
Sc03%	4.7617(1)	13.0017(5)	11.9958(1)	7.6
Sc05%	4.7637(2)	13.0048(8)	11.9961(5)	6.5
Reference	4.7616(2)	13.0013(8)	12.0166(7)	5.8

The values of R_p (%) mean the converged reliable factors for the whole pattern profile fitting (WPPF) analysis.

that the common garnet structure indicates the Sc distribution at the small octahedral site.[23]

Fig. 3(a)–(c) show SEM images of the longitudinal sections for the Cr03%, Fe03% and Sc03% fiber samples parallel to the solidification direction together with the typical Electron Back-Scattered Pattern (EBSP) for the Cr03% fiber sample. These SEM images stressed that the present fiber samples are composed of a bundle of the smaller eutectic rods with the inhomogeneous coarse-grained boundary texture. Similar microstructural feature is frequently observed in the eutectic samples produced in the Al_2O_3–$ZrO_2(Y_2O_3)$ system, where ⟨0 0 1⟩ corundum is parallel to the solidification direction.[14–17] Nevertheless, the careful analysis of EBSP allowed to reproduce the nominal crystallographic orientation relationship ⟨0 0 1⟩ corundum//⟨1 1 2⟩ garnet perpendicular to the solidification direction, similarly to the cases of the directionally solidified $Al_2O_3/Y_3Al_5O_{12}$ eutectic samples without any substitution.[12,24,25] It may be noted that the microstructures in the smaller eutectic rods are elongated in the solidification direction by indicating good agreements with the previous reports.[6,12,13]

4. Conclusion

A variety of corundum/garnet eutectic fiber samples were prepared by the μ-PD method and effect of elemental substitution on the microstructure was studied. The substitution by Cr_2O_3, Fe_2O_3(FeO) or Sc_2O_3 encourages the enhancement of the colony texture in the typical "Chinese script" microstructure. The analysis of the EDS profile together with XRD patterns revealed that Cr^{3+} prefers corundum and garnet structures and that Sc^{3+} prefers garnet phase, only. On the other hand, Fe^{3+} was reduced into Fe^{2+} and the third phase of hercynite in an amoebic fashion was introduced in the parent eutectic microstructure. Present study demonstrates the fundamental crystallographic orientation relationship of ⟨0 0 1⟩ corundum//⟨1 1 2⟩ garnet perpendicular to the solidification direction irrespective of the substitution elements. However, more systematic microstructure analysis is strongly required in order to discuss the microstructure and corresponding mechanical properties as a function of the elemental substitution. The crystallographic orientation change induced by the further elemental substitution is also interesting.

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