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Metastable precipitation in isothermally solidified YAG-alumina composites with off-eutectic composition

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YAG-alumina composites with Al_2O_3-rich and YAG-rich compositions were prepared by annealing the hot-pressed composites at the eutectic temperature (1820 °C) for 1 h followed by cooling down at 10 or 100 °C/min in argon atmosphere. Microstructural observations of the solidified composites identified that metastable phase δ-Al_2O_3 precipitated in the Al_2O_3-rich specimens cooled down at both the cooling rates. For the solidified YAG-rich specimens, however, equilibrium phase α-Al_2O_3 could not be reprecipitated, moreover, metastable $YAlO_3$ phase was formed at cooling rate of 100 °C/min. Formation of the metastable phases in the solidified composites was attributed to the decreased melting temperature caused by the divorced eutectic precipitation and the metastable decomposition of YAG component in YAG-alumina eutectic melt during rapid solidification.

1. Introduction

It has been identified that the unidirectionally solidified YAG ($Y_3Al_5O_{12}$)-Al_2O_3 eutectic composites can exhibit excellent high-temperature flexural strength, creep resistance and structural stability [1–3]. It is known that low-energy eutectic interfaces exhibiting specific orientation relationships are usually present in the eutectic composites [2, 4, 5], which may be responsible to some extent for the specific performances possessed by the eutectic composites. Developing the eutectic composites, however, is restricted to the particular processing (unidirectional solidification) and the fixed eutectic composition, which does not apply to the fabrication of other advanced ceramic composites with changeable compositions.

Recently, the authors investigated the isothermally solidified microstructures of YAG-spinel ($MgAl_2O_4$) system, in which intergranular precipitates with YAG and spinel compositions were observed in the solidified microstructures with spinel-rich and YAG-rich compositions [6], respectively. The formation of the intergranular YAG or spinel precipitates was attributed to the divorced eutectic precipitation caused by the metastable growth of the primary phase during solidification [7]. It was further identified by a solidified spinel-YAG composite with spinel-rich composition [8] that intergranular YAG precipitates were formed with nanosized structures, moreover, some specific orientation relationships at the interfaces between the YAG precipitates and the spinel primary phase were revealed. It was suggested that the isothermal solidification and the divorced eutectic precipitation could be employed to develop novel high-temperature structural oxide/oxide composites with nano-sized second phase and low-energy interfaces.

However, according to the principle of divorced eutectic precipitation [7], the crystal growth of primary phase may occur prior to eutectic nucleation during solidification and consequently result in metastable change in composition of the supercooled eutectic melt towards rich in composition of the secondary phase accompanying with the decrease in the melting temperature. Therefore, it was thought that the divorced eutectic precipitates might be formed as a metastable phase due to significantly decreased nucleation temperature. In this work, the YAG-Al_2O_3 composites with Al_2O_3-rich and YAG-rich compositions were prepared by isothermal solidification and the solidified microstructures were examined to verify the possible metastable precipitation.

2. Experimental

High purity Al_2O_3 (99.99%, TM-100, Taimei Chem. Co. Ltd.) and Y_2O_3 (99.98%, Ube Ind. Ltd.) powders

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were used to prepare two kinds of powder mixtures with compositions of 3.5mol%Y_2O_3 + 96.5mol%Al_2O_3 (3.5Y-A) and 34mol%Y_2O_3 + 66mol% Al_2O_3 (34Y-A) by ball milling for 24 h in plastic pot charged by plastic-coated steel balls and ethanol. After drying, the powder mixtures were calcined at 700 °C for 1 h in air, then densified by hot pressing with graphite dies at 1500 °C for 1 h under pressure of 33 MPa in an argon atmosphere, during which $Y_3Al_5O_{12}$ (YAG) phase was formed. The hot-pressed disks with 16 mm diam. and 2 mm thick were then cut into 3 × 3 × 2 mm pieces for the subsequent annealing treatments which were carried out at 1820 °C, the eutectic temperature of Al_2O_3-YAG system [9], for 1 h in argon atmosphere and cooled down at 10 or 100 °C/min. A graphite cylinder was used as the supporter of the annealed specimens. The microstructures of the annealed specimens were characterized by means of EPMA and XRD.

3. Results and discussion

3.1. Metastable precipitation in solidified Al_2O_3-rich sample

The solidified microstructures of the Al_2O_3-rich samples (3.5Y-A) were first examined. Fig. 1 shows the XRD patterns of the specimens annealed at 1820 °C for 1 h followed by cooling down at 10 and 100 °C/min, respectively, together with the specimen hot pressed at 1500 °C for 1 h. It is found from the XRD patterns (Fig. 1) that δ-Al_2O_3 phase was formed in the two annealed specimens with different cooling rates. Fig. 2 shows a typical SEM micrograph of the specimen cooled down at 10 °C/min. EPMA qualitative analysis identified that the bright phase regions possessed YAG composition, while the dark phases are Al_2O_3, in which two kind phase regoins are involved, the α-Al_2O_3 primary phase and the intergranular phase which is denoted by arrows (Fig. 2). The intergranular Al_2O_3 phase may be the δ-Al_2O_3 phase, as evidenced by XRD analysis (Fig. 1).

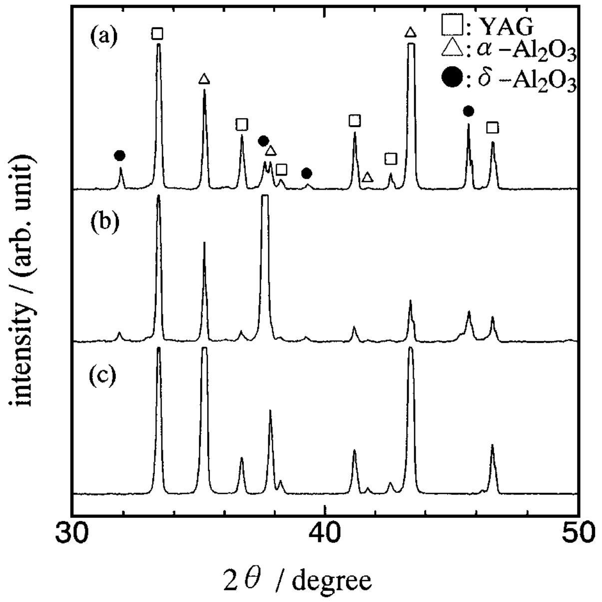

Figure 1 XRD patterns of the specimens (3.5Y-A) annealed at 1820 °C for 1 h followed by cooling at (a) 100 °C/min and (b) 10 °C/min in comparison with (c) the specimen as hot pressed at 1500 °C for 1 h in Ar.

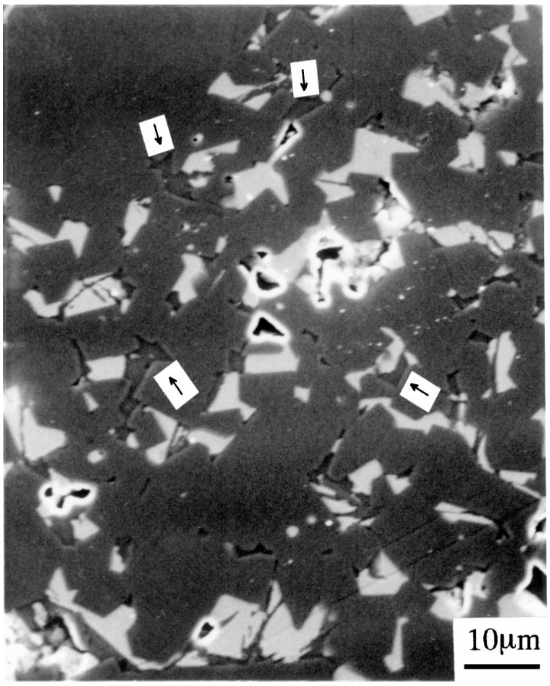

Figure 2 Typical SEM picture showing phases distribution in specimen (3.5Y-A) annealed at 1820 °C for 1 h and cooled down at 10 °C/min in Ar, in which the bright phase is YAG, the grain-like dark phase is primary phase α-Al_2O_3 and the intergranular dark phase marked by arrows may correspond to the metastable δ-Al_2O_3 phase, as identified by XRD (Fig. 1).

Generally, metastable phases of alumina (γ-Al_2O_3, δ-Al_2O_3 and θ-Al_2O_3) are formed in the alumina prepared by flame [10] and plasma [11] melting of powders, and by condensation of vapor from arcs [12], etc. The studies of transformation of vapour-deposited amorphous alumina to α-Al_2O_3 [13] indicate that γ-Al_2O_3 and δ-Al_2O_3 are the principal intermediate forms. Although the details of the crystal structures of the metastable forms are not completely clear, it was detected that γ, δ and θ-Al_2O_3 are based on a more or less distorted cubic close packing of oxygen ions with different ordering of the Al ions in the available octahedral and tetrahedral sites [14, 15]. Dragoo and Diamond [13] suggest that δ-Al_2O_3 is formed from γ-Al_2O_3 in the temperature range of 800–1200 °C. The available data suggest that γ-Al_2O_3 will form by homogeneous nucleation in liquid alumina, basically because of its lower liquid-solid interfacial energy. Because the interfacial energy reflects the difference in structure between the crystalline phase and the liquid, and the nucleus would be expected to be the phase with structure most nearly approaching that of the liquid [16]. From this point of view, Plummer's suggestion [10] that the metastable phase observed has a structure closer to that of the liquid would seem correct. Consequently, the δ-Al_2O_3 precipitate obtained in the present work may be attributed to the phase transformation from γ-Al_2O_3 which formed initially during the solidification of the supercooled melt in the YAG-Al_2O_3 system. According to the estimation of critical free energies for nucleation of α- and γ-alumina as a function of temperature [15], α-Al_2O_3 could not nucleate at temperatures lower than 1740 °C. Because any metastable precipitation was not found in the unidirectionally solidified eutectic composites, the δ-Al_2O_3 phase identified in this work (Fig. 1) may be attributed to the divorced eutectic precipitation caused by the metastable grain growth of the α-Al_2O_3 primary phase during solidification, which would result in the change in composition of the eutectic melt towards richer in YAG accompanying with the decrease in melting temperature of the supercooled melt. As described above, if the eutectic temperature was metastably decreased to lower than 1740 °C, the Al_2O_3 component in the supercooled melt would not nucleate as equilibrium phase α-Al_2O_3. Therefore, it is presumed that the primary growth of α-Al_2O_3 phase occurred prior to the nucleation of characteristic eutectics during the cooling processes of the Al_2O_3-rich sample, resulting in the precipitation of YAG as the divorced eutectic precipitates, while the residual Al_2O_3 component in the supercooled melt nucleated finally as a metastable phase (e.g. δ-Al_2O_3) because of the decreased nucleation temperature.

3.2. Metastable precipitation in YAG-rich sample

Fig. 3 shows the XRD patterns of the YAG-rich sample (34Y-A) annealed at 1820 °C for 1 h followed by cooling down at 10 and 100 °C/min, respectively, together with the specimen hot pressed at 1500 °C for 1 h. It is found from Fig. 3 that after the annealing treatments, α-Al_2O_3 phase disappeared in both the solidified specimens, moreover, $YAlO_3$ phase was formed in the specimen cooled down at 100 °C/min. Fig. 4 shows a typical SEM micrograph and the corresponding back scattering electron image of the specimen cooled down at 100 °C/min, in which four different phases are displayed. EPMA quantitative analysis (Table I) indicates that the phases (a), (b) and (c) exhibit the compositions close to Al_2O_3, $YAlO_3$ and YAG, respectively, while the composition of the needle-like phase (d) could not be detected by the EPMA due to the smaller phase sizes. In contrast, only two phases, YAG primary phase and intergranular Al_2O_3 phase, were observed by EPMA for the specimen cooled down at 10 °C/min, as shown in Fig. 5, although only primary phase YAG was displayed in the XRD patterns (Fig. 3b).

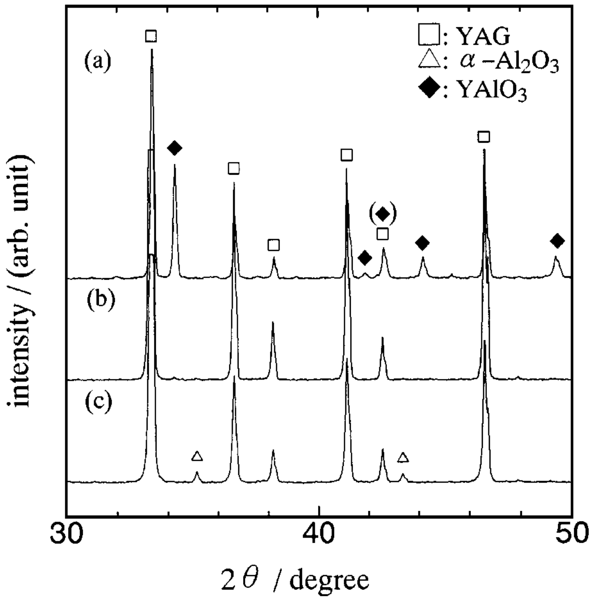

Figure 3 XRD patterns of the specimens (34Y-A) annealed at 1820 °C for 1 h followed by cooling at (a) 100 °C/min and (b) 10 °C/min in comparison with (c) the specimen as hot pressed at 1500 °C for 1 h in Ar.

TABLE I EPMA quantitative analysis of the phases (a), (b) and (c) in the specimen (34Y-A) annealed at 1820 °C for 1 h and cooled down at 100 °C/min in Ar, as shown in Fig. 4

Position	Al_2O_3 (mol%)	Y_2O_3 (mol%)
Phase region (a)	98 ± 1.3	2 ± 1.3
Phase region (b)	48 ± 0.1	52 ± 0.1
Phase region (c)	60 ± 0.1	40 ± 0.1

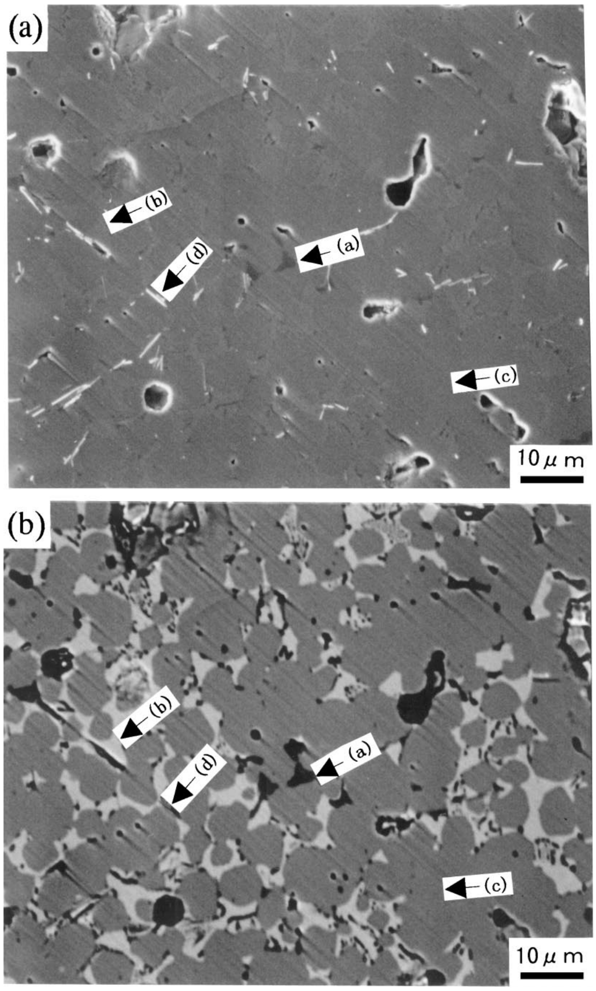

Figure 4 A typical SEM micrograph (a) and corresponding back scattering electron (BSE) image (b) of specimen (34Y-A) annealed at 1820 °C for 1 h and cooled down at 100 °C/min in Ar, showing four different phases, (a) Al_2O_3, (b) $YAlO_3$, (c) YAG and (d) needle-like precipitates.

Comparing the specimens cooled down at 100 and 10 °C/min indicates that the formation of the $YAlO_3$ precipitates was closely related to the cooling rate. As identified by Caslavsky and Viechnicki [17], melting YAG would decompose into α-Al_2O_3 and $YAlO_3$ in quenching process from the temperatures higher than the melting point of YAG, accompanied with a metastable change in eutectic point from E to E′ along the metastable liquidus of α-Al_2O_3, as shown in Fig. 6. This result may imply that the metastable primary growth of YAG below eutectic temperature T_E

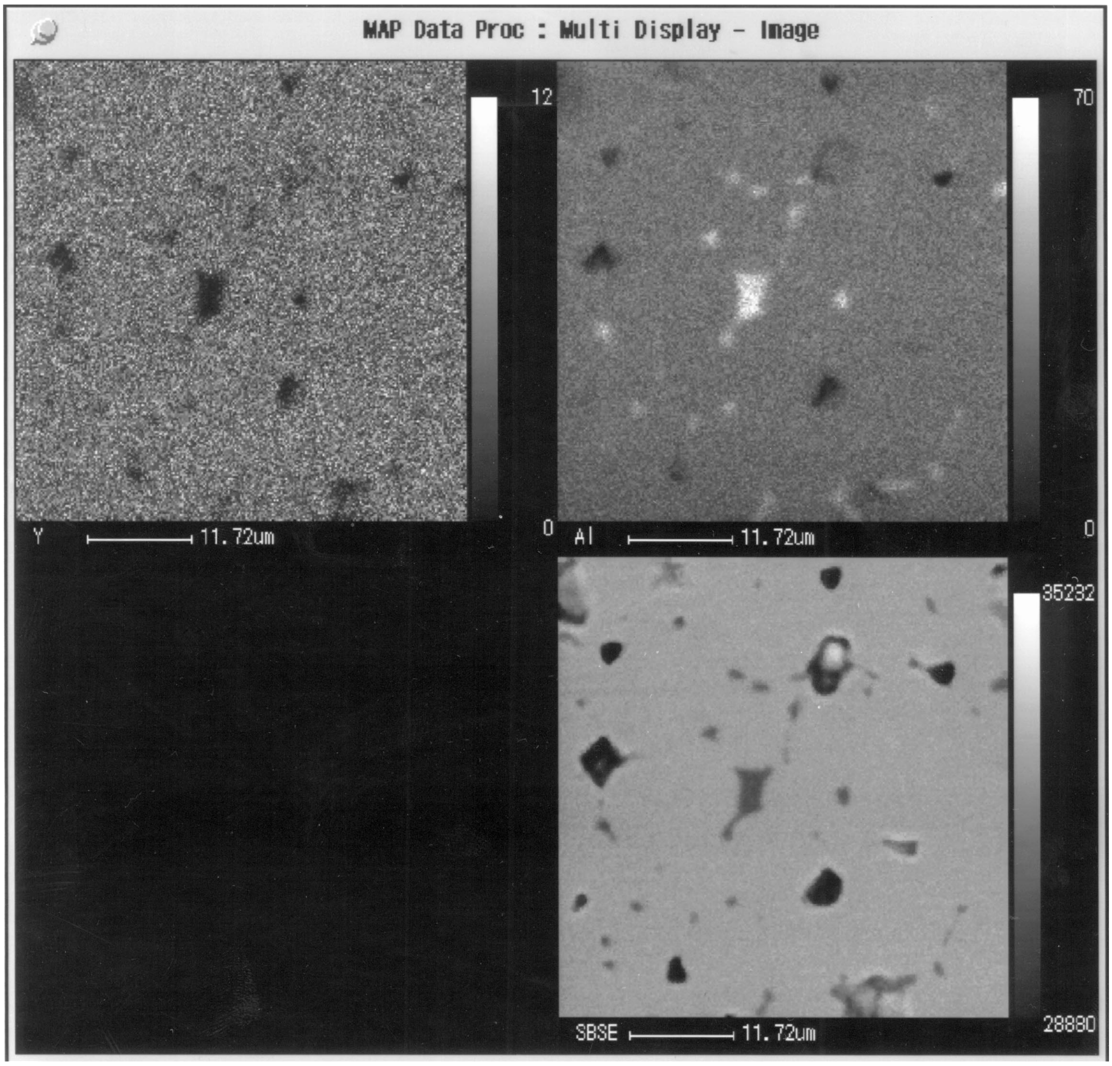

Figure 5 An EPMA qualitative analysis of specimen (34Y-A) annealed at 1820 °C for 1 h and cooled down at 10 °C/min in Ar, showing element distributions of Y (a) and Al (b) and BSE image (c) corresponding to primary phase YAG and intergranular Al_2O_3 phase.

was much more difficult than that of α-Al_2O_3 under rapid cooling process due to the large difference in crystal structures between the two phases. Therefore, it could be expected that the divorced eutectic precipitation would not occur in the rapidly solidified YAG-rich sample (34Y-A). Instead, when the temperature was decreased below T_E, the melting Al_2O_3 component in the supercooled eutectic melt would become a primary phase to precipitate accompanying the metastable change in eutectic composition from E to E′ (Fig. 6). Thus, the needles (phase (d)) exhibiting bright contrast in SEM image and dark contrast in back scattering electron (BSE) image (Fig. 4), are very possibly correspondent to the α-Al_2O_3 phase precipitated during the cooling process between temperatures T_E (1820 °C) and $T_{E'}$ (1700 °C) although it was not detected by XRD analysis (Fig. 3) due to probably smaller volume fraction of the α-Al_2O_3 needles precipitated in the solidified specimen.

Furthermore, it might be thought from the metastable phase relation (Fig. 6) that when temperature was decreased below $T_{E'}$, $YAlO_3$-Al_2O_3 eutectic would precipitate from the metastable eutectic melt (E′). In this case, three phases, Al_2O_3, $YAlO_3$ and YAG, should be present in the solidified specimen, as identified by the three phases (a), (b) and (c) in the specimen cooled down at 100 °C/min (Fig. 4 and Table I), in which the Al_2O_3 phase might be present as an amorphous phase other than α-Al_2O_3 due to the low nucleation temperature below 1700 °C [15], as evidenced by XRD analysis (Fig. 3). In addition, it was evidenced by microstructural observation (Fig. 4) that the Al_2O_3 and $YAlO_3$ precipitates (phases (a) and (b)) were present separately around the primary phase YAG (phase (c)), indicating that eutectic nucleation did not occur in the rapidly solidified specimen.

In contrast, for the specimen slowly cooled at 10 °C/min, however, metastable primary growth of YAG might occur during solidification at the temperatures between T_E and $T_{E'}$, accompanied with the change in eutectic point E along the metastable liquidus of YAG until pure Al_2O_3 component was achieved at some temperature which might be too low to nucleate for α-Al_2O_3 phase, as illustrated in Fig. 6. The formation of the possible amorphous Al_2O_3 phase as the intergranular divorced eutectic precipitates was supported by the XRD analysis (Fig. 3b) and the EPMA qualitative analysis (Fig. 5).

On the other hand, the above results may indicate that the formation of the metastable Al_2O_3-$YAlO_3$ eutectic

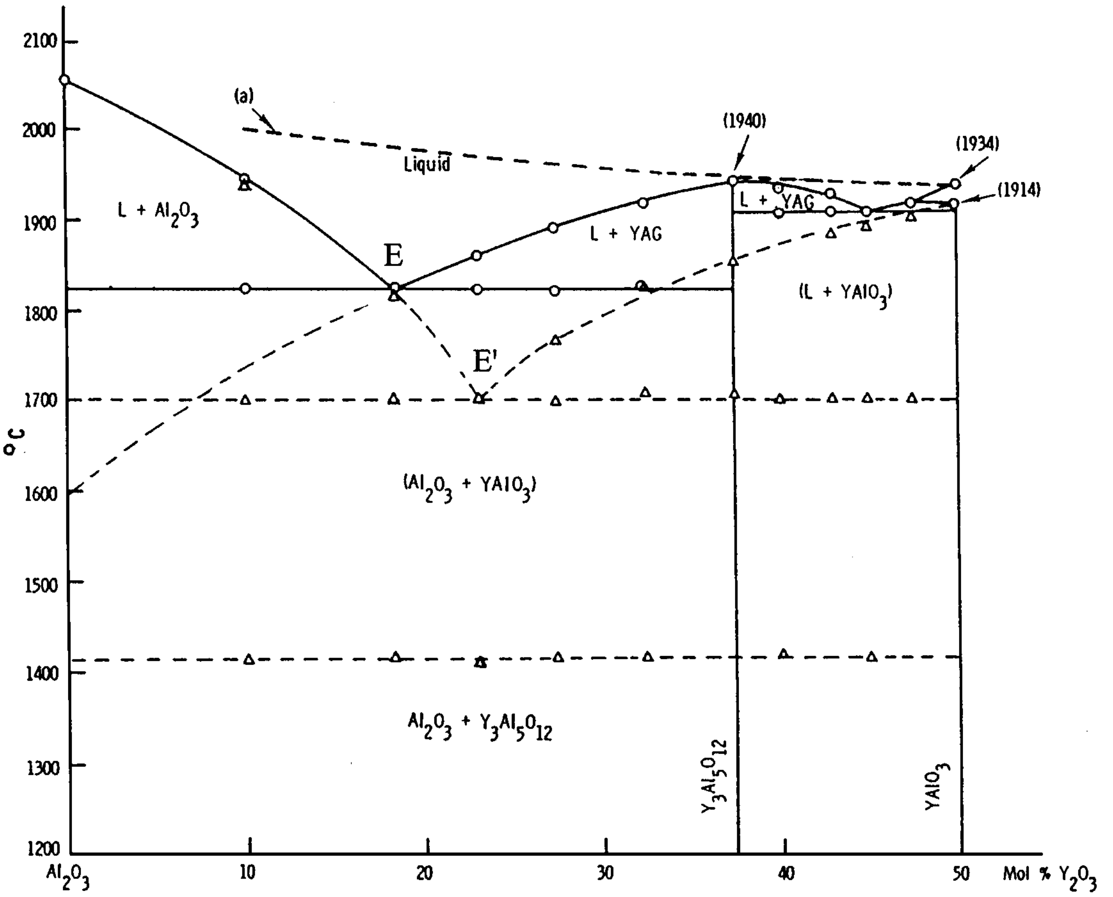

Figure 6 Phase diagram of the alumina-rich portion of Al_2O_3-Y_2O_3 system, in which the metastable phase diagram is superimposed with dashed lines and its pertinent phase fields are labelled with parentheses. Melts cooled down from temperature above the line (a) would follow metastable path of solidification [17]. The dashed line along YAG liquidus is suggested in this work to predict metastable primary growth of YAG during slow solidification of YAG-rich composition.

could be obtained during solidification of YAG-Al_2O_3 eutectic system from equilibrium eutectic temperature (1820 °C) other than the temperatures higher than the melting point of YAG (1940 °C), as suggested by Caslavsky and Viechnicki [17]. It is identified in this study that the divorced eutectic precipitation and the cooling rates are the controlling factors for the formation of the metastable Al_2O_3-$YAlO_3$ eutectic during solidification of YAG-Al_2O_3 equilibrium eutectic system.

4. Summary

Solidified microstructures of YAG-alumina composites with off-eutectic compositions were examined using Al_2O_3-rich (3.5Y-A) and YAG-rich (34Y-A) samples annealed at 1820 °C for 1 h in Ar followed by the cooling processes at 10 and 100 °C/min, respectively. It was identified that metastable δ-Al_2O_3 phase precipitated from the Al_2O_3-rich specimens cooled down at both the cooling rates. In contrast, for YAG-rich samples, amorphous Al_2O_3 phase seemed to be present in both the solidified specimens, moreover, metastable phase $YAlO_3$ precipitated in the specimen cooled down at 100 °C/min. The formation of the metastable phases in the solidified microstructures was attributed to the decreased melting temperature caused by the metastable primary growth and the metastable decomposition of melting YAG component in rapid solidification of YAG-alumina eutectic melt.

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