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Metastable precipitation of $YAlO_3$ in isothermally solidified YAG/(Al_2O_3-rich) spinel composites

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Phase composition and microstructure of isothermally solidified YAG/spinel (or Al_2O_3-rich solid solution) composites were investigated. It was verified that an equilibrium binary eutectic phase region consisting of YAG and Al_2O_3-rich spinel solid solution exists in the YAG-spinel-Alumina ternary system. Moreover, it was identified that a metastable system, $YAlO_3$ and Al_2O_3-rich spinel solid solution, could be formed during rapid cooling from the eutectic temperature. © *1998 Kluwer Academic Publishers*

1. Introduction

It was reported that the metastable eutectic system $YAlO_3$ (Yttrium Aluminate Perovskite, YAP) and alumina with eutectic temperature of about 1700 °C could be formed during solidification of the melts in the equilibrium YAG-alumina eutectic system [1–3]. However, it was pointed out that the non-equilibrium YAP/alumina eutectic could only precipitate from the melt with temperature at least higher than the melting point of YAG (1940 °C). Moreover, it was identified that heat treatment of the metastable eutectic above 1418 °C could cause solid state reaction between YAP and alumina leading to the formation of equilibrium phase YAG while maintaining the rod/lamellae morphology [2, 3].

Recently, the authors investigated the phase compositions and microstructures of the YAG-spinel and YAG-alumina systems with off-eutectic compositions [4, 5]. It was found that metastable YAP phase could precipitate in both the YAG-rich specimens solidified from the eutectic temperatures (1830 °C and 1820 °C, respectively) at cooling rate of 100 °C/min, moreover, it was shown that the secondary phase, spinel or alumina, appeared to precipitate as an amorphous phase during the solidification process. The formation of the metastable phases in the solidified composites was explained based on the divorced eutectic precipitation caused by metastable primary growth below equilibrium eutectic temperature.

In this work, the presence of a binary eutectic phase region between YAG and Al_2O_3-rich spinel solid solution within YAG-spinel-alumina ternary system, as predicted in the study of YAG-spinel eutectic precipitates [6], was verified using composite samples. Then, the solidification behaviors of this binary system were investigated with emphasis on phase composition and microstructure. Experimental results indicated that the metastable YAP phase could precipitate in the YAG-spinel (or Al_2O_3-rich solid solution) composites from temperature below 1800 °C. In this paper, the microstructures of the equilibrium YAG/spinel and non-equilibrium YAP/spinel solid solution eutectic precipitates are characterized, and the formation process of the metastable YAP precipitates is discussed.

2. Experimental

High purity Al_2O_3 (99.99%, TM-100, Taimei Chem. Co., Ltd.), MgO (99.98%, Ube Ind. Ltd.) and Y_2O_3 (99.9%, Shin-Etsu Chemical Co., Ltd.) powders were used as starting materials to prepare the samples with compositions designated by C_{M1} (52.3 mol % $Al_2O_3 + 40.9$ mol % $MgO + 6.8$ mol % Y_2O_3 or 10 mol % $Y_3Al_5O_{12} + 90$ mol % $MgAl_2O_4$) and C_{M2} (62 mol % $Al_2O_3 + 30$ mol % $MgO + 8$ mol % Y_2O_3), as shown in Fig. 1. The powder mixtures were prepared by ball-milling with plastic-coated steel balls in ethanol for 24 h. The slurries were dried by means of evaporator and oven, and then the dried mixtures were calcined at 700 °C for 1 h in air. Solid state reaction and densification of the samples were conducted simultaneously through hot pressing with graphite dies at 1700 °C for C_{M1} and 1600 °C for C_{M2} in vacuum for 1 h, respectively. The as hot pressed samples with diameter 16 mm and thickness 2–3 mm were cut into several smaller pieces to prepare for the subsequent annealing treatments.

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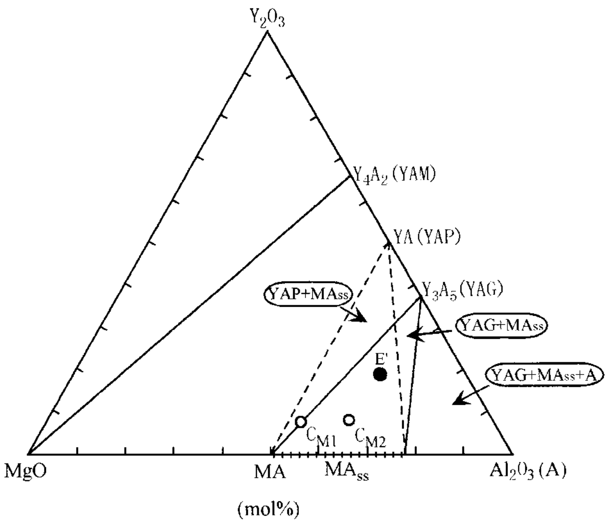


Figure 1 Diagram of partial phase relations in MgO-Al_2O_3-Y_2O_3 ternary system, subsolidus.

The annealing processes proceeded in argon atmosphere through heating the specimens at 10 °C/min up to the temperature at which the specimens were melted substantially. At each annealing temperature, the specimens were held for 1 h and then cooled down at 100 °C/min or 0.5 °C/min. The temperature measurement was carried out by optical pyrometer (IR-Q2C, Chino Works, Ltd.) and calibrated by Pt-30Ph/Pt-6Rh thermocouple. The mean error of the calibrated temperatures was about ±5 °C in the whole temperature range.

In addition, part of the solidified specimens were re-annealed at 1500 °C for 2 h to examine the change in microstructure and phase composition.

The microstructures and phase compositions of the specimens before and after the annealing treatments were characterized by SEM, EPMA and XRD.

3. Results and discussion

3.1. Phase relationships and metastable precipitation of $YAlO_3$

Fig. 2 shows the phase distributions of the hot pressed samples C_{M1} and C_{M2}. It was known from XRD analysis (Fig. 3) that both the samples were composed of two phases, YAG and spinel. However, it was noted that the diffraction intensities corresponding to spinel in sample C_{M2} shifted towards large angles (Fig. 3b), indicating that Al_2O_3-rich spinel solid solution was formed. EPMA analysis exhibited that the bright-contrast phases were YAG and the dark-contrast phases were spinel in C_{M1} and Al_2O_3-rich spinel solid solution in C_{M2} (Fig. 2).

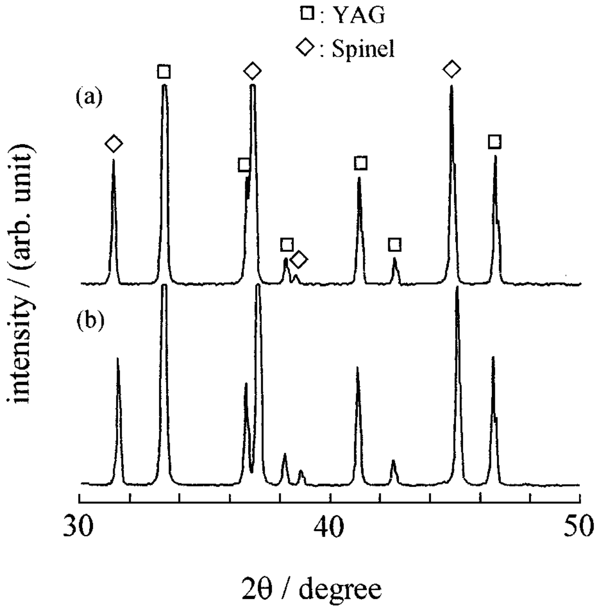


Figure 3 XRD patterns of the hot pressed samples, (a) C_{M1} at 1700 °C for 1 h and (b) C_{M2} at 1600 °C for 1 h in vacuum.

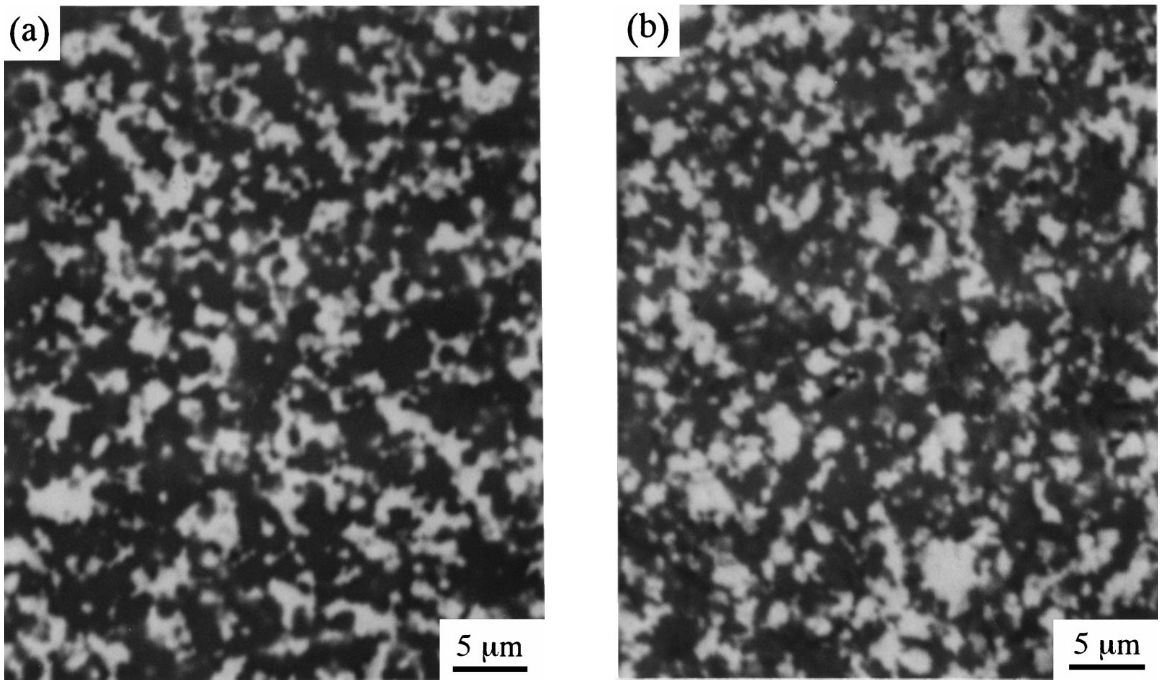


Figure 2 Back scattering electron (BSE) micrographs of samples C_{M1} (a) and C_{M2} (b) hot pressed at 1700 °C and 1600 °C, respectively, for 1 h in vacuum.

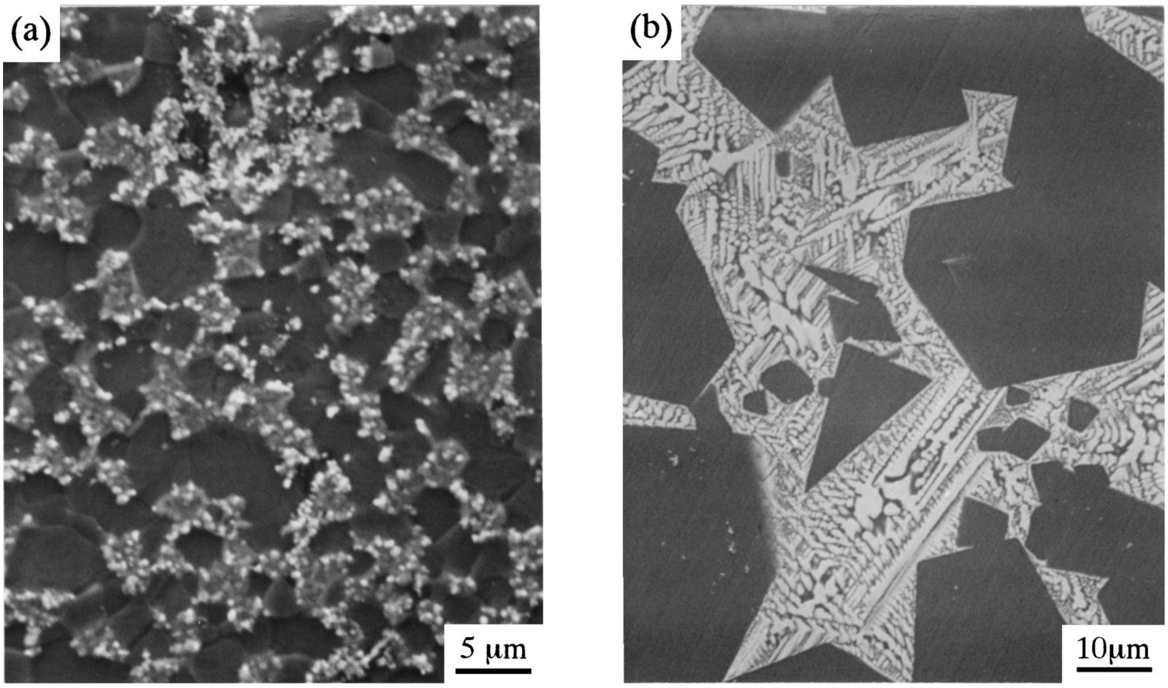


Figure 4 Typical SEM microstructures of the sample C_{M1} annealed at (a) 1828 °C for 1 h and (b) 1843 °C for 1 h, cooled down at 100 °C/min in Ar.

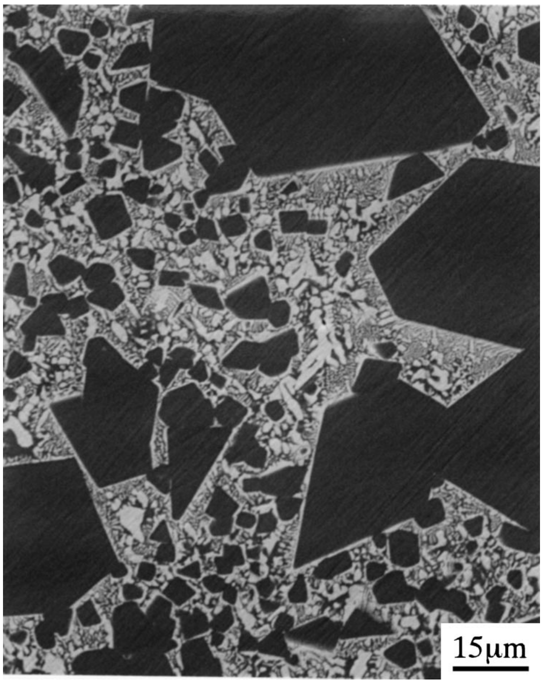


Figure 5 A typical SEM picture of sample C_{M2} annealed at 1795 °C for 1 h and cooled down at 100 °C/min in Ar.

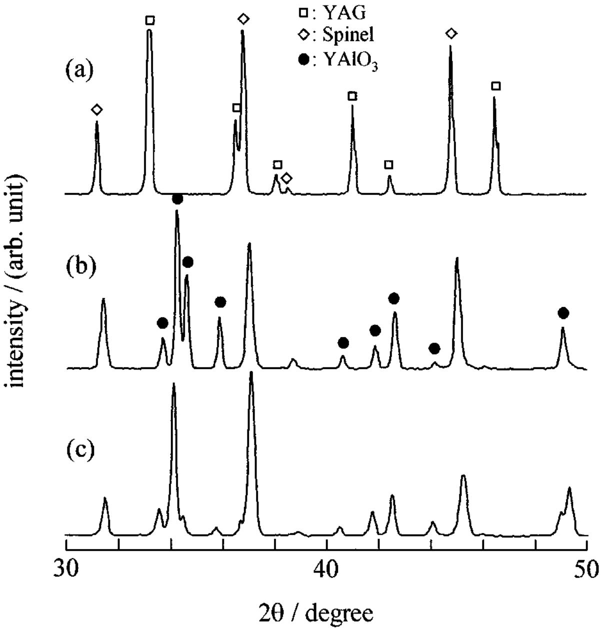


Figure 6 XRD patterns of samples C_{M1} annealed at (a) 1828 °C for 1 h and (b) 1843 °C for 1 h, and sample C_{M2} annealed at 1795 °C for 1 h (c), cooled down at 100 °C/min in Ar.

Furthermore, annealing treatments indicated that sample C_{M1} exhibited higher melting temperature than sample C_{M2}. For instance, at 1828 °C, the annealed sample C_{M1} was little deformed, whose microstructure is shown in Fig. 4a. When increasing the annealing temperature to 1843 °C, however, sample C_{M1} was melted significantly, in which large amount of needle or platelet-like precipitates were formed in the solidified microstructure, as shown in Fig. 4b. In contrast, the annealed sample C_{M2} was melted substantially at 1795 °C, whose solidified microstructure being shown in Fig. 5, in which the composition E′ (Al_2O_3: 64 ± 1 mol %, MgO: 17 ± 3 mol %, Y_2O_3: 19 ± 3 mol %) of the intergranular precipitates, determined by EPMA, was shown in Fig. 1. It was identified by XRD analyses of the observed surfaces that the equilibrium phases were maintained in the sample C_{M1} annealed at 1828 °C (Fig. 6a), whereas YAG phase disappeared, instead, $YAlO_3$ (YAP) phase precipitated in the samples C_{M1} and C_{M2} solidified from 1843 °C and 1795 °C, respectively, accompanied with the shift of the lines corresponding to spinel phase towards larger angles (Fig. 6b and c). The difference in the diffraction intensities corresponding to YAP in Fig. 6b and c may be related to the preferred orientations of the YAP precipitates formed during the cooling processes, which is to be clarified in further work. In addition, it may be noted from Fig. 6c that a weak line at about 36.8 °, which might correspond to the strongest line of spinel. The possible coexistence of the spinel phase and the Al_2O_3-rich spinel solid solution (primary phase) is suggested combining with the precipitation process of YAP, as described below.

The above results revealed that an equilibrium binary eutectic system, Al_2O_3-rich spinel solid solution(MA_{ss})-YAG, should exist in YAG-spinel (MA)-alumina(A) ternary system, indicating that the solid solution characteristic of spinel in MgO-Al_2O_3 binary system is still present in the ternary system. Thus, according to the dependence of the solubility of Al_2O_3 in spinel on temperature (phase diagram of MgO-Al_2O_3 system [7]), the YAG-MA-A ternary phase region could be divided into two parts, YAG-MA_{ss} and YAG-MA_{ss}-A phase regions, as illustrated in Fig. 1. For the YAG-MA_{ss} binary system, eutectic feature has been identified in the previous work [6]. Comparing the results of the annealed samples C_{M1} and C_{M2} indicates that the equilibrium eutectic temperatures in the YAG-MA_{ss} system decrease with increase in content of Al_2O_3 in the spinel solid solution.

The precipitation of YAP phase accompanied with the formation of Al_2O_3-rich spinel solid solution(MA_{ss}) in annealed samples may imply that the following reaction,

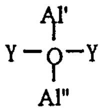
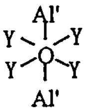
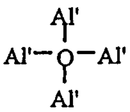
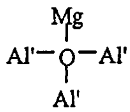
$$x\mathrm{Y_3Al_5O_{12}} + \mathrm{MgO}\cdot\mathrm{Al_2O_3} \rightarrow 3x\mathrm{YAlO_3} + \mathrm{MgO}\cdot(1+x)\mathrm{Al_2O_3} \qquad (1)$$

took place during the solidification process. It was known from the microstructures containing YAP precipitates (Figs 4b and 5) that spinel or MA_{ss} exhibited as primary phases. In other words, the initial YAG solid phase could be dissolved sufficiently into the eutectic melt during the annealing processes. Usually, it is believed that the structures of the nuclei formed initially from a melt, which may be stable or metastable phases under the existing equilibrium conditions, are similar to the short-range order structures of the melt because it is energetically favored to nucleation kinetics. YAG crystal was suggested to possess a higher nucleation energy than perovskite structure, but it could decompose into metastable $YAlO_3$ (YAP) and Al_2O_3 in melting state [2], as expressed by the following reaction.

$$\mathrm{Y_3Al_5O_{12}} = 3\mathrm{YAlO_3} + \mathrm{Al_2O_3} \qquad (2)$$

Therefore, it may be expected that the basic short-range order structures in the melt of YAG-spinel system involve $Y_3Al_5O_{12}$, $YAlO_3$, Al_2O_3, and $MgAl_2O_4$. On the other hand, the short-range order structures can be expressed by the basic structural units obtained through calculation of the coordination numbers of the crystal structures, as shown in Table I. It is known from the coordination numbers shown in Table I that the decomposition of YAG (Equation 2) would accompany with the increase in coordination numbers, which should be promoted with increase in temperature. In addition, it is known from Table I that the basic structural units of both α-Al_2O_3 and spinel possess Al-O octahedra and four-fold coordination of oxygen ions. Therefore, the formation of order structure of spinel solid solution between Al_2O_3 and spinel structural units in the melt is also energetically favorable unless the melting temperature was too low to nucleate. According to the estimation of critical free energies for nucleation of melting Al_2O_3 as a function of temperature [8], the nucleation of α-Al_2O_3 would be replaced by other metastable phases of alumina such as γ-, δ-, θ-Al_2O_3, and even amorphous phase when the nucleation temperature was lower than 1740 °C. In this case, MA_{ss} might not be formed from the melt, instead, partially spinel (MA) precipitated, as presumed by the weak line near 36.8° (Fig. 6c) which might correspond to the strongest line of spinel. It can be expected that the liquidus temperature of the metastable system YAP and MA_{ss} would be lower than that of the equilibrium YAG-spinel system, similar to the metastable system Al_2O_3-YAP (melting temperature $\approx$ 1700 °C), as appeared in YAG-alumina system [2]. The possible formation of amorphous phase of alumina and even spinel accompanied with the metastable precipitation of YAP was also found in YAG-alumina system with off-eutectic composition [5] and YAG-spinel system with YAG-rich composition [4].

TABLE I Coordination numbers and basic structural units of the related oxides

Oxides	$Y_3Al_5O_{12}$	$YAlO_3$	Al_2O_3	$MgAl_2O_4$
Al′	6	6	6	6
Al″	4			
Y	8	12		
Mg				4
O	4	6	4	4
Structural units				

Al′ – octahedral coordination, Al″ – tetrahedral coordination.

3.2. Annealing processes and phase compositions

The experimental results on the samples solidified at 100 °C/min were given above. Further experiments indicated that the phase compositions of the solidified composites could be changed with cooling rates. For example, when sample C_{M2} solidified from 1795 °C at initially 0.5 °C/min to about 1770 °C and then at 100 °C/min to lower temperatures, YAP phase did not precipitate, while the equilibrium YAG phase was maintained, as verified by XRD analysis (Fig. 7a). Microstructural observation (Fig. 8a) showed that the YAG phase (bright contrast) was present as intergranular precipitates, and the interfaces between YAG and spinel (dark contrast) exhibited creasing-like characteristic. Furthermore, comparing Fig. 7a with Fig. 3b indicates that the relative diffraction intensities corresponding to YAG phase in the solidified sample are obviously inconsistent with those in the hot pressed sample. Assuming that the XRD patterns of the hot pressed sample (Fig. 3b) corresponding to the fine-grained structure (Fig. 2b) are similar to the patterns of its powder specimens, it could be expected that some possible preferred orientation occurred during the crystal growth of the YAG phase in annealed sample (Fig. 8a). On the other hand, when the solidified sample C_{M2} containing YAP precipitates (Fig. 5) was reheated at 1500 °C for 2 h in air, YAP phase was transformed into YAG again (Fig. 7b), the correspondent microstructure being shown in Fig. 8b. Similarly, the difference in the relative diffraction intensities corresponding especially to the YAG phases in Fig. 7a and b could be ascribed to the difference in the orientation and distribution of the phases. It was revealed that the YAG phases shown in Fig. 8a and b exhibited a continuous phase structure like a eutectic phase and a fine-grained structure, respectively [9].

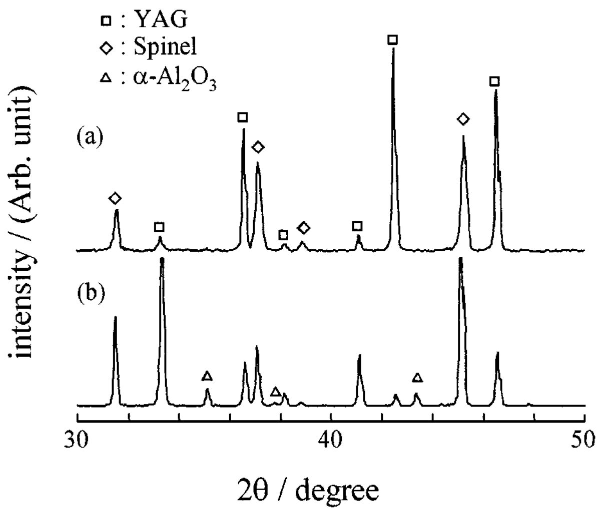


Figure 7 XRD patterns of sample C_{M2}, (a) annealed at 1795 °C for 1 h and cooled down slowly at initially 0.5 °C/min to 1770 °C and then quickly at 100 °C/min in Ar and (b) annealed at 1795 °C for 1 h and cooled down at 100 °C/min in Ar and reheated from room temperature to 1500 °C, keeping for 2 h in air.

As analyzed above, the precipitation of YAP and Al_2O_3-rich spinel solid solution in the rapid solidification process indicated that short-range order structures of YAP, spinel solid solution were present in the eutectic melt at the beginning of the solidification. However, due to the decreased solubility of Al_2O_3 in spinel with decrease in temperature, Al_2O_3 would precipitate gradually from the spinel solid solution under certain degree of supercooling. Therefore, it may be suggested that during slow cooling process, the basic structural units of Al_2O_3 exist throughout the supercooled melt, and at the same time, short-range orderness of YAG may be reestablished through the reverse reaction of Equation 2 at relatively higher temperature. The interface characteristics of the specimen shown in Fig. 8a may imply that the eutectic nucleation of YAG and spinel occurred at the solid/liquid interfaces during the slow solidification process.

Similarly, for the sample reheated at 1500 °C (Fig. 8b), large amount of Al_2O_3 should be precipitated from the initial spinel solid solution, which, then reacted with YAP to produce YAG. Evidently, the YAG/spinel interfaces formed at 1500 °C should be different from those formed through eutectic nucleation. It was noted that faceted primary phase was maintained (Fig. 8b).

In addition, the above experimental results have indicated that metastable phase YAP can be precipitated from the melt with temperature much lower than the melting point of YAG (1940 °C), which was believed to be impossible in YAG-alumina system [2, 3]. The reason may be ascribed to not only the sufficient dissolution and decomposition of YAG component in the melt but also to the rapid cooling rates which would depress significantly the reprecipitation of YAG due to its complex unit structure.

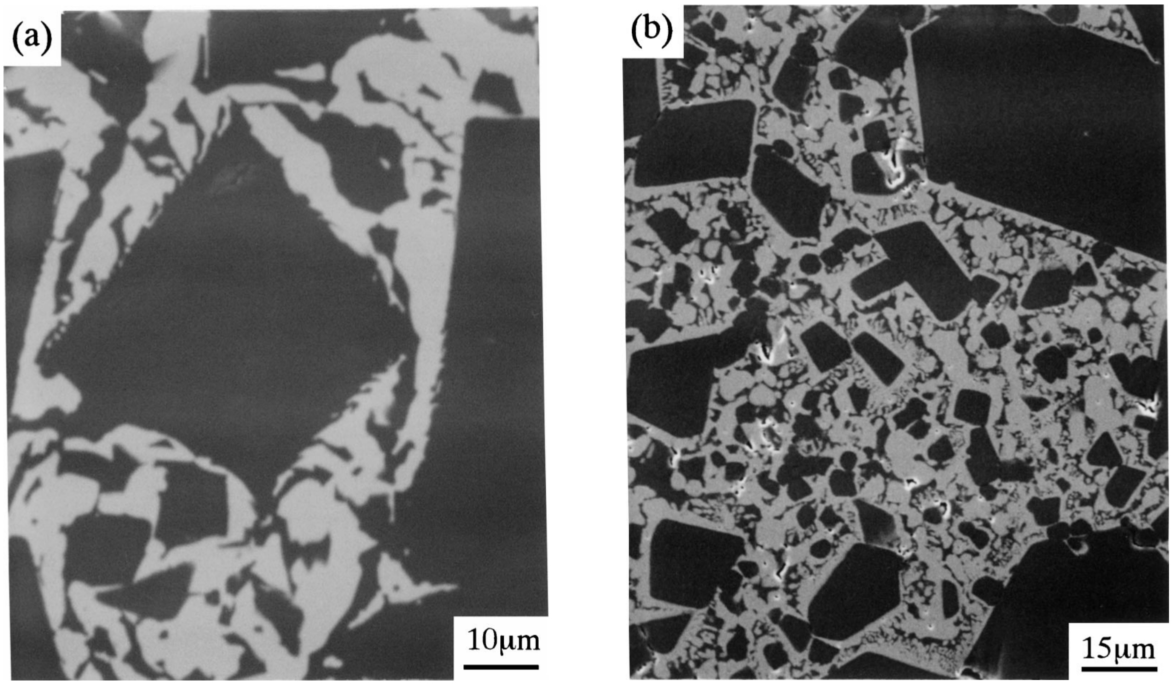


Figure 8 Typical phase distributions of sample C_{M2}, (a) annealed at 1795 °C for 1 h and cooled down slowly at initially 0.5 °C/min to 1770 °C and then quickly at 100 °C/min in Ar, (b) annealed at 1795 °C for 1 h and cooled down at 100 °C/min in Ar and then reheated from room temperature to 1500 °C, keeping for 2 h in air.

4. Conclusions

In this study, the phase relationship and solidification behaviors of YAG/Al_2O_3-rich spinel system are investigated. It is concluded that YAG-spinel-alumina ternary system consists of two sections, YAG-MA_{ss} binary eutectic system and YAG-MA_{ss}-alumina ternary system. The eutectic temperature in YAG-MA_{ss} system decreases with increase in content of Al_2O_3 in the spinel solid solution.

Metastable phase $YAlO_3$ (YAP) will precipitate from YAG-spinel (or Al_2O_3-rich solid solution) composites during rapid solidification processes from liquidus temperatures, which can be attributed not only to the decomposition of YAG structure unit in the eutectic melt but also to the rapid cooling rates.

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