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Divorced eutectic and interface characteristics in a solidified YAG-spinel composite with spinel-rich composition

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Solidified microstructures of YAG ($Y_3Al_5O_{12}$)-spinel ($MgAl_2O_4$) composite with spinel-rich composition (YAG : spinel = 1 : 30 molar ratio) were investigated. Intergranular YAG divorced eutectic exhibiting fine-grained structures was observed in the solidified composite. Formation of the divorced eutectic was attributed to the metastable growth of primary phase spinel during solidification, which was verified by the presence of *in situ* spinel precipitates. TEM-SAD technique and crystal structure analysis reveal that a set of specific crystallographic orientation relationships are present between {640} plane of YAG and {111} plane of spinel crystals. The presence of low-energy YAG/spinel interfaces is believed to be responsible for the transgranular fracture characteristics exhibited for the solidified composite.

1. Introduction

The nature of interfaces between matrix and reinforcements has increasingly been recognized to be one of the key factors influencing mechanical properties of both metallic and ceramic matrix composites [1–3]. For high-temperature alloys, strong grain boundaries with low grain-boundary energy, e.g., low-angle boundaries, are identified to exhibit excellent resistance to intergranular fracture [4]. Similarly, it is reported that the creep resistance and high-temperature toughness of multiphase ceramic composites can be improved by formation of low-energy interfaces [5, 6]. It is known that low-energy interfaces exhibiting particular orientation relationships (ORs) are usually present in oxide eutectic composites [7–9], which can exhibit much more excellent high-temperature strength and creep resistance than sintered materials with identical compositions [10, 11].

Generally, the oxide eutectic composites are prepared through unidirectional (UD) solidification of eutectic melts. Due to the particular processing and the limitation in composition (eutectic point), the UD method has not been applied to prepare general ceramic composites with various compositions. For a eutectic system with off-eutectic composition, however, the interfaces in the solidified composites would involve not only eutectic interfaces but also the interfaces between the intergranular eutectic and the primary phase. It is found that in the solidified microstructures of eutectic composites with off-eutectic compositions, the primary phases are frequently not contacted directly with the characteristic eutectic precipitates, instead, a layered precipitate with composition rich in the secondary phase is formed between the primary phase and the characteristic eutectic precipitates [12, 13]. The layered precipitate may be regarded as the "divorced eutectic", as named by Chalmers [14]. It was illustrated that the formation of the divorced eutectic originated from metastable primary growth below eutectic temperature. However, the crystallographic morphology of the divorced eutectic and the interfacial characteristics between the divorced eutectic and the primary phase were little reported.

Recently, the authors investigated YAG ($Y_3Al_5O_{12}$)-spinel ($MgAl_2O_4$) system using conventional solidification method. The divorced eutectic-like microstructures were obtained using a solidified YAG/spinel diffusion couple sample [15]. A eutectic phase relationship between YAG and spinel was proven by a solidified composite sample [16]. It was identified that the YAG/spinel eutectic could be maintained with formation of Al_2O_3-rich spinel solid solution [17]. A divorced eutectic with composition rich in spinel solid solution was observed in between YAG dendrites in a solidified microstructure [17]. In this work, the solidified microstructure of a YAG-spinel composite with excess spinel composition was studied with emphasis on the characterization of the crystallographic morphology of the divorced eutectic and interface characteristics between the divorced eutectic and the primary phase. It is expected that the formation of the divorced eutectic may be employed to prepare novel composites with *in situ* controlled low-energy interfaces by conventional

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sintering processes containing intergranular eutectic liquid phase.

2. Experimental procedure

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 sample with composition of YAG : spinel = 1 : 30 molar ratio. The powder mixture was prepared by ball-milling for 24 h in plastic pots charged with plastic-coated steel balls and ethanol. Solid state reaction and densification of the powder mixtures were carried out by hot pressing at 1700°C for 1 h under 33 MPa in an argon atmosphere in graphite dies lined by graphite sheet. The hot pressed sample with 16 mm in diameter and 2–3 mm in thickness was then cut into one-fourth pieces for subsequent annealing treatments at the eutectic temperature about 1830°C [16] for 1 h and cooled down at 100°C/min in the hot pressing furnace, in which a graphite column was used as the supporter of the annealed specimens. The temperature measurement was conducted by two-color type optical pyrometer (IR-Q2C, Chino Works, Ltd.) and calibrated by Pt-30Rh/Pt-6Rh thermocouple. The mean error of the calibrated temperatures was about ±5°C over the whole temperature range.

The hot pressed and the solidified bulk specimens with polished surfaces were characterized by means of x-ray diffraction (XRD), scanning electron microscope (SEM), and electron probe micro analyzer (EPMA, Shimadzu Mfg. Co., Ltd.). Further, transmission electron microscopy (TEM, JEM-2000EX) was used to observe the interface characteristics of the solidified composites by means of selected area diffraction (SAD) technique. The specimens used for the TEM analysis were prepared by crushing and grinding the solidified bulk sample into fine particles which were ultrasonically dispersed in ethanol before TEM observations. Chemical compositions of the observed particles were determined qualitatively by energy disperse X-ray spectroscopy (EDX, TN-2000) equipped in the TEM.

3. Results and discussion

Fig. 1 shows the microstructures of the specimens hot pressed at 1700°C (Fig. 1a) and annealed at 1830°C (Fig. 1b), in which the bright and dark phases are YAG and spinel, respectively. It is observed that the phase distributions in the YAG-spinel composite change significantly after the annealing process. It is found after thermally etching at 1400°C for 0.5 h in air that fine-grained structures appear in the intergranular YAG phase near the YAG/spinel interfaces, as shown in Fig. 2. High magnification observations (Fig. 3) identify that the grain sizes of the YAG stuck at the interfaces with the primary phase spinel are about 100–300 nm, while the YAG in the center regions exhibited very smooth surface feature. The intergranular YAG phase may be regarded as the divorced eutectic, as reported previously [15]. The formation of the divorced eutectic of YAG phase may be attributed to the metastable primary growth of spinel during solidification, resulting in the formation of a supercooled melt with YAG-rich composition. The microstructures shown in Figs 2 and 3 may indicate that the YAG component in the supercooled melt nucleated preferentially at the interfaces with the primary phase spinel, whereas the YAG far from the interfaces may have finer grain size or lower crystallinity due to the decreased nucleation temperature.

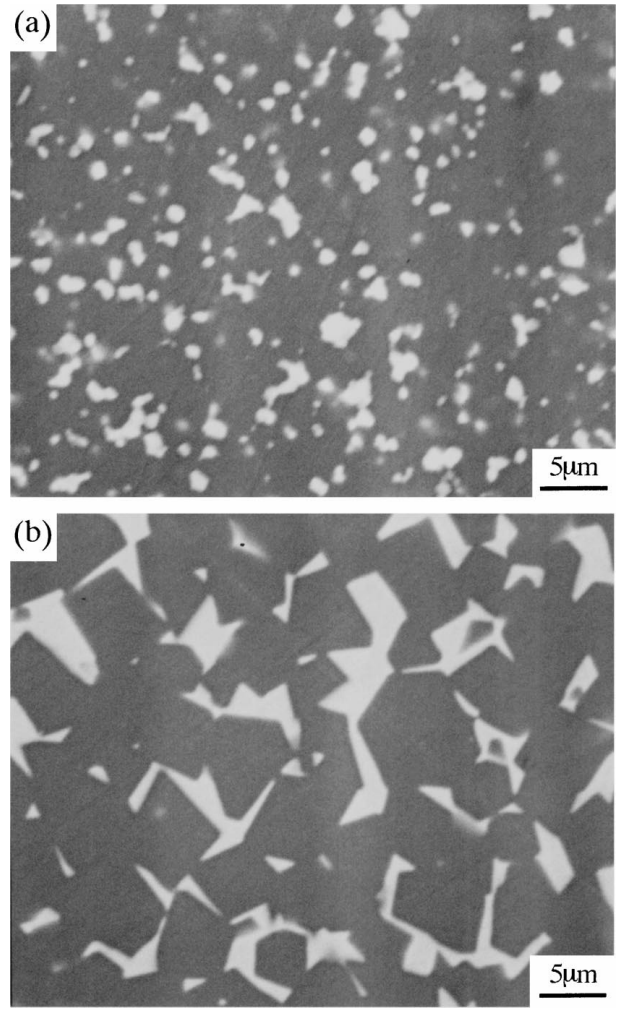

Figure 1 SEM micrographs of the samples (a) as-hot pressed at 1700°C for 1 h (a) and (b) annealed at 1828°C for 1 h followed by cooling down at 100°C/min in argon atmosphere.

It was found that the solidified composite exhibit transgranular fracture mode. Fig. 4 shows a representative microstructure of room-temperature fracture surfaces of the solidified composite. It is noticed that the transgranular fracture occurs also within the YAG intergranular phase which contains fine-grained structures (Fig. 3). Moreover, some acicular precipitates seemed to be present near the interfaces. Fig. 5 shows a typical micrograph of the *in situ* precipitates appeared on the fracture surface. It was identified by TEM analyses that these precipitates are spinel single crystals. Obviously, the formation of the *in situ* spinel precipitates could be related to the metastable primary growth of spinel during the cooling process.

It is assumed that the intergranular YAG phase or divorced eutectic in the solidified composite is formed

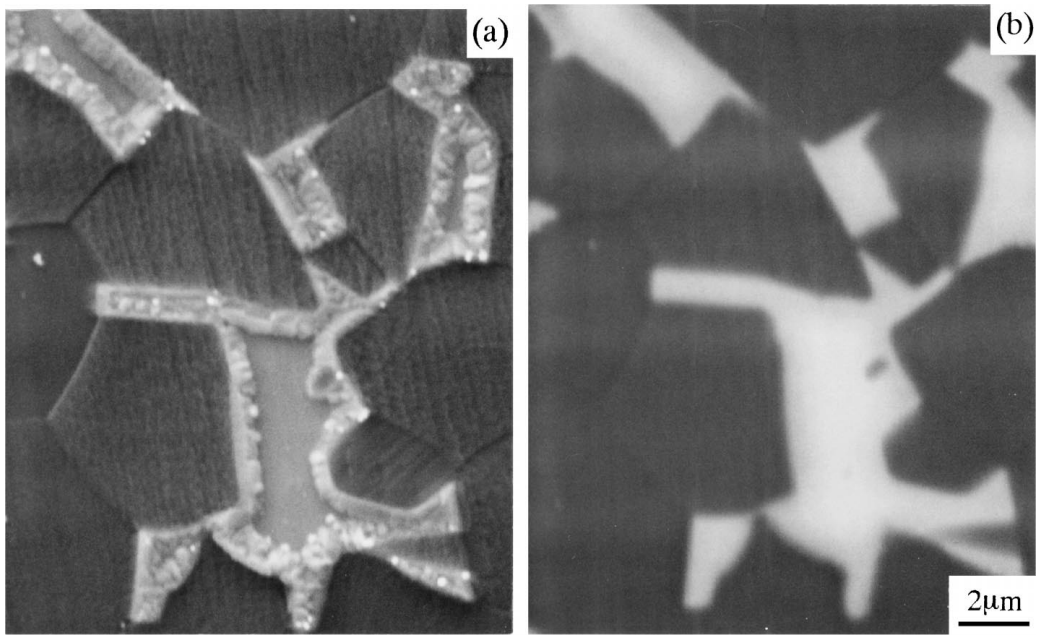

Figure 2 SEM (a) and corresponding back scattering electron (b) micrographs of the solidified specimen shown in Fig. 1b after thermally etching at 1400°C for 30 min in air.

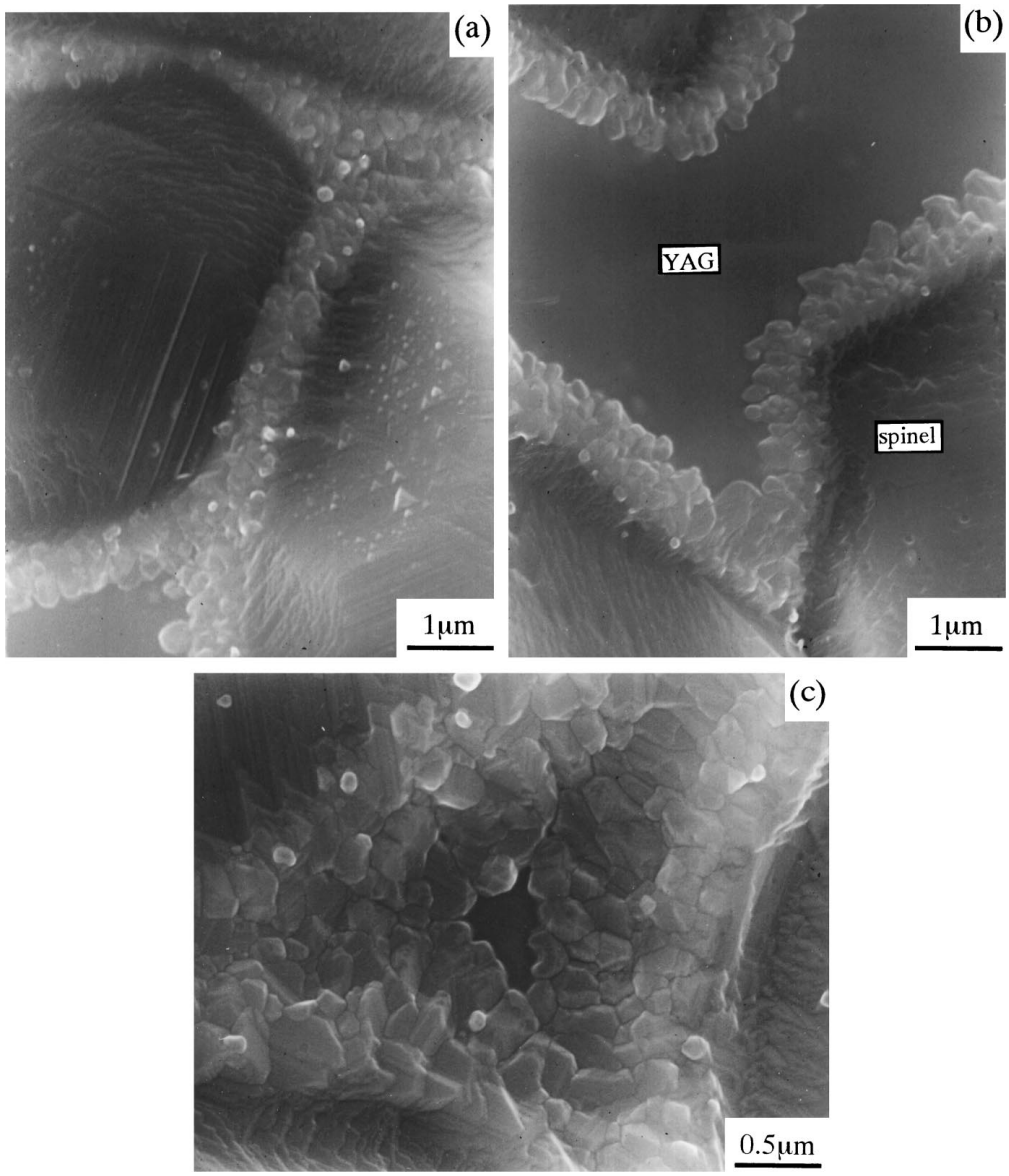

Figure 3 Typical morphologies of the intergranular YAG phases situated (a) at a narrow grain boundary, (b) at a wide grain boundary, and (c) at a three-grain junction in the solidified sample.

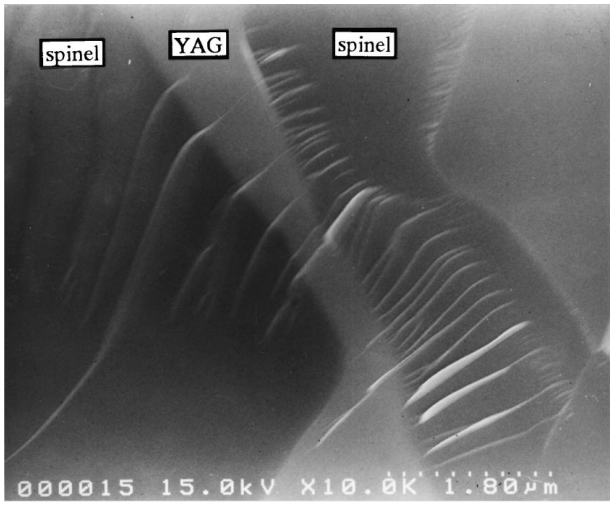

Figure 4 SEM micrograph showing a typical room-temperature fracture surface of the solidified specimen.

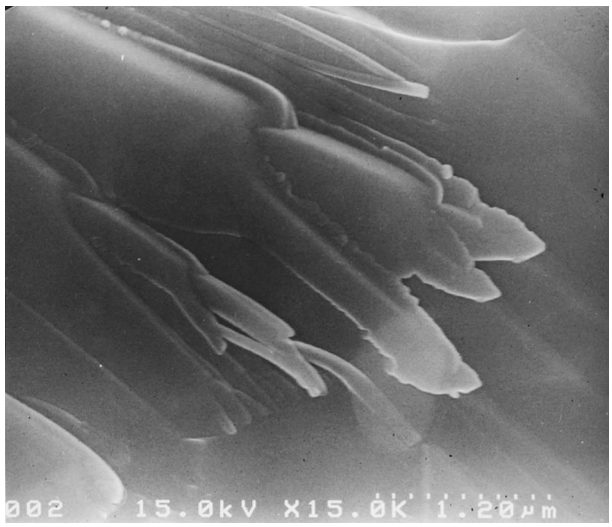

Figure 5 SEM micrograph showing the growth morphology of the *in situ* spinel precipitates observed on a fracture surface of the solidified YAG/spinel composite.

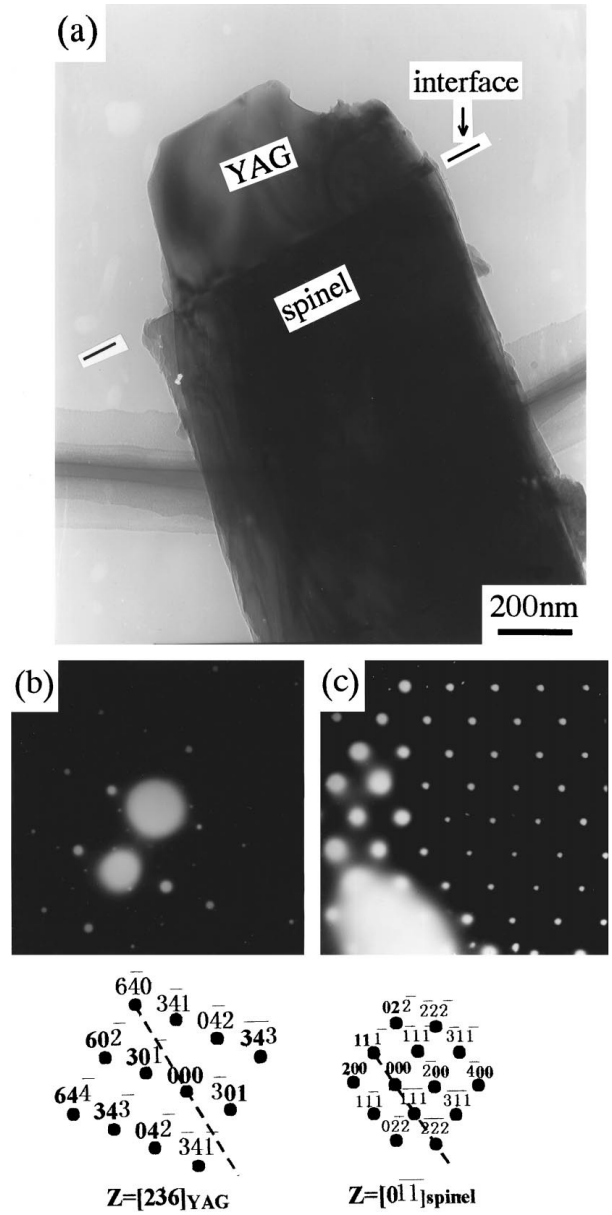

Figure 6 TEM-SAD analysis of a particle containing a YAG/spinel interface in the solidified specimen, (a) Bright-field (BF) image, (b) and (c) SAD patterns of the YAG and the spinel crystals, respectively.

initially through heterogeneous nucleation on spinel primary phase. Therefore, low-energy interfaces exhibiting coherent or semi-coherent characteristics, similar to eutectic interfaces, are expected to be present between the YAG and spinel phase. In order to verify the presence of the low-energy interfaces, crystallographic orientation relationships between YAG and spinel in the solidified sample were examined by TEM using the ground powder specimen. Fig. 6 shows a bright-field (BF) image and a set of SAD patterns of the YAG and spinel crystals bonded at an interface in the solidified specimen, from which an orientation relationship (1) is obtained. In the same way, a similar orientation relationship (2) was obtained at another particle containing a YAG/spinel interface in the identical solidified specimen.

$$(6\bar{4}0)[236]_{YAG}//(11\bar{1})[011]_{spinel} \quad (1)$$

$$(640)[\bar{2}32]_{YAG}//(\bar{1}\bar{1}1)[112]_{spinel} \quad (2)$$

In order to clarify the interrelation between the two specific orientation relationships, the lattice structures of {640} plane of YAG and {111} plane of spinel were examined. Fig. 7 illustrates the lattice arrays of cations on $(640)_{YAG}$ and on $(111)_{spinel}$, respectively. It is revealed that there are four kinds of independent crystallographic orientation relationships present between $(640)_{YAG}$ and $(111)_{spinel}$, as expressed in the following relationships (3), in which the

$$(640)[001][\bar{2}32][\bar{2}36][\bar{2}30]_{YAG}$$
$$//(111)[2\bar{1}\bar{1}][11\bar{2}][10\bar{1}][01\bar{1}]_{spinel} \quad (3)$$

orientation relationships (1) and (2) obtained by TEM are involved, considering the symmetry of cubic structures. In addition, it is noticed from Fig. 7 that an identical angle of 30° is present in between every two adjacent orientations. It is known from JCPDS card of

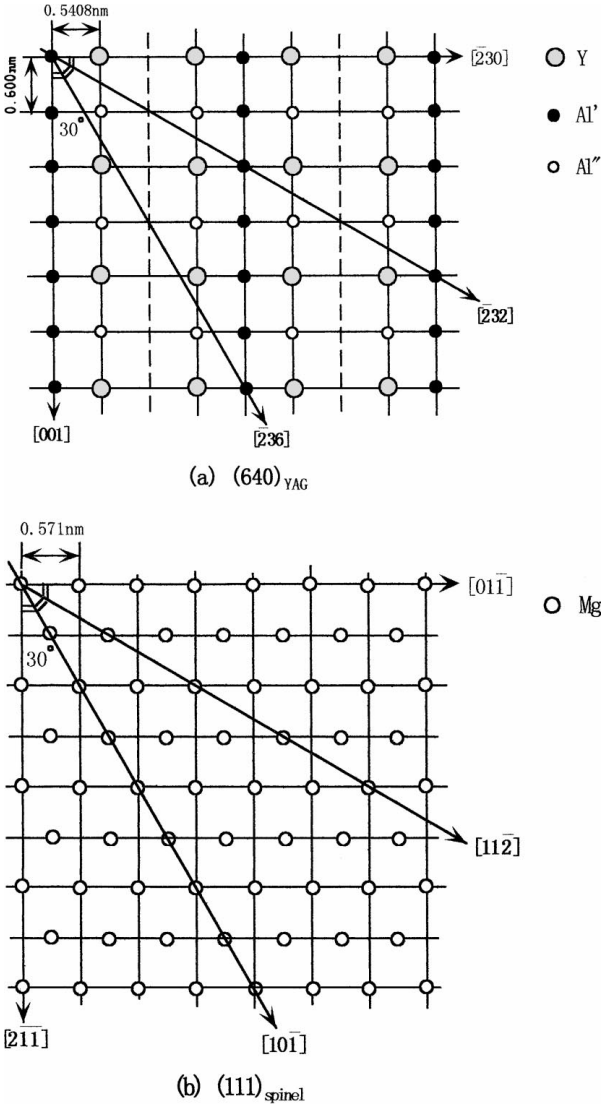

Figure 7 Schematic illustration of lattice arrays of cations on (a) (640) plane of YAG and (b) (111) plane of spinel, showing the specific orientation relationships on the two planes (Al′ and Al″ express the Al ions situated at octahedral and tetrahedral interstitials of oxygen ions, respectively).

YAG (No. 33–40) that the $(640)_{YAG}$ plane is the second high-intensity diffraction plane, i.e., $(640)_{YAG}$ plane possesses the feature of low-index planes having relatively higher lattice atom density or higher symmetry. The presence of the specific orientation relationships may imply that low-energy interfaces are formed between intergranular YAG divorced eutectic and primary phase spinel in the solidified composite. Because there are 24 and 8 kinds of equivalent planes for $(640)_{YAG}$ and $(111)_{spinel}$, respectively, the orientation relationships shown above may be formed in three-dimensional space. In other words, most of the YAG/spinel interfaces in the solidified composite may behave as low-energy interfaces similar to eutectic interfaces.

4. Conclusions

Divorced eutectic of YAG exhibiting fine-grained structures was formed in the YAG-spinel eutectic composite with spinel-rich composition. Formation of the divorced eutectic could be ascribed to the metastable growth of primary phase spinel during solidification, which was verified by the presence of *in situ* spinel precipitates in the solidified composite. It was identified by TEM-SAD technique and crystal structure analysis that a set of specific crystallographic orientation relationships are present at solidified YAG/spinel interfaces. The formation of low-energy interfaces may be responsible for the transgranular fracture characteristics exhibited for the solidified composite.

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