Journal of the European Ceramic Society 20 (2000) 39–43

Phase compositions and microstructural characteristics of solidified Al_2O_3-rich spinel solid solution/YAG composite

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Received 4 February 1999; accepted 13 March 1999

Abstract

The phase compositions and microstructures of an Al_2O_3-rich spinel solid solution (MA_{ss})–YAG composite were investigated by conventional solidification. A binary eutectic system of YAG–MA_{ss} exhibiting changed eutectic temperature was proven to exist in the YAG–spinel–alumina ternary phase region. A YAG–MA_{ss} eutectic-like composite was obtained by controlled cooling process. It was found that metastable phase, $YAlO_3$, was formed during rapid solidification of the YAG–MA_{ss} composite from an annealing temperature of 1795°C. When reheating the as-solidified $YAlO_3$–MA_{ss} composite at 1500°C, a YAG–MA_{ss} composite with fine-grained YAG phase was obtained. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Spinel; Yttrium aluminium garnet; Composites; Solidification; Microstructure-final

1. Introduction

Oxide/oxide composites have been recognized as promising candidates for high-temperature structural applications above 1500°C, considering the inherent chemical stability of oxide materials in oxidizing atmospheres.[1,2] The current work is focused on searching for novel methods to prepare oxide/oxide composites with improved high temperature mechanical properties such as creep resistance and fracture toughness. Unidirectionally solidified YAG–Al_2O_3 eutectic composites appear to meet the design guidelines for creep rates in turbine blades at 1530°C.[3] However, the eutectic creeps are faster than sapphire (α-Al_2O_3) at slow strain rates,[4] although it has greater flow resistance at high strain rates. This result may be related to the properties of the eutectic interfaces in the composite,[5] in which the possible interfacial thermal mismatch caused by the anisotropic thermal expansion coefficient of the α-Al_2O_3 phase should be considered.

Another complex cubic crystal, magnesium–aluminum spinel ($MgAl_2O_4$) can retain some strength at temperatures approaching 2000°C[1] and displays an even larger high-temperature hardness than α-Al_2O_3.[2] Both YAG and spinel have cubic symmetry and it is reported that the cubic complex crystals exhibit increased fracture toughness with increasing temperature.[6,7] Based on these considerations, the authors suggest that YAG-spinel cubic system composites may have better high-temperature mechanical behaviour in which the thermally introduced interface stresses should be uniform and isotropic in comparison to the YAG-alumina system. Further improvement may be made by solid-solution strengthening and precipitation strengthening through formation of spinel solid solution.[8]

Recently, the authors examined microstructures in the solidified YAG-spinel system and found that this system exhibits a binary eutectic phase,[9] which could be maintained with the formation of an Al_2O_3-rich spinel solid solution (MA_{ss}).[10] It suggests that a binary eutectic phase region YAG–MA_{ss} may exist in the YAG–spinel–alumina ternary system. In this work, a composite with a composition situated in the YAG–MA_{ss} phase region was prepared to verify the phase relation and to investigate the changes in phase composition and microstructure in the as solidified and annealed specimens.

2. Experimental procedures

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

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PII: S0955-2219(99)00073-4

(99.9%, Shin-Etsu Chemical Co., Ltd.) powders were used as starting materials to prepare the sample with composition C_M (62 mol% Al_2O_3 + 30 mol% MgO + 8 mol% Y_2O_3), as shown in Fig. 1. The powder mixture was prepared by ball-milling with plastic-coated steel balls in ethanol for 24 h. The slurry was dried using an evaporator and subsequently oven-dried at 110°C before calcination at 700°C for 1 h in air. Solid state reaction and densification of the samples were conducted simultaneously by hot-pressing at 1600°C for 1 h in vacuum in graphite dies lined with graphite foil. No reaction was observed between the hot-pressed sample and the dies. The hot-pressed disc (16 mm in diameter and 2–3 mm in thickness) was cut into four equal-volume parts for the subsequent annealing treatments.

The annealing processes proceeded in an argon atmosphere using the identical hot-pressing equipment with graphite heating elements. The hot-pressed specimen, supported by a graphite holder, was heated at 10°C min^{-1} to the temperature at which the specimen melted substantially. At each annealing temperature, the specimen was held for 1 h and then cooled down at 100°C min^{-1} or 0.5°C min^{-1}. 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 over the whole temperature range. In addition, part of the solidified specimens were reheated in a corundum crucible at 1500°C for 2 h in air to examine the changes in microstructure and phase composition.

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

3. Results and Discussion

The presence of an equilibrium phase relation between YAG and MA_{ss} was verified by XRD [Fig. 2(a)] of the sample hot-pressed at 1600°C. The microstructure of the hot-pressed specimen is shown in Fig. 3(a) where the bright contrast phase is YAG and the dark contrast phase is spinel solid solution (MA_{ss}). Subsequently, the melting point or eutectic temperature of this system was examined through the annealing processes at higher temperatures. It was identified that the hot-pressed specimen melted significantly at 1795°C, a spherical shape being exhibited for the solidified specimen.

Moreover, it was identified from XRD analysis [Fig. 2(b)] that the phase compositions of the specimen quenched from 1795°C at 100°C min^{-1} were changed; the initial YAG phase disappeared and instead the metastable $YAlO_3$ phase was formed. Figure 3(b) shows the typical microstructure of this solidified specimen. It is observed from Fig. 3(b) that the solidified microstructure consists of large and faceted spinel solid solution (MA_{ss}) grains which were bounded with a $YAlO_3$ and spinel eutectic-like phase. EPMA quantitative analysis demonstrated that the average composition of the eutectic-like phase was 64 ± 1 mol% Al_2O_3, 17 ± 3 mol% MgO and 19 ± 3 mol% Y_2O_3, as shown by E_M in Fig. 1.

The decreased melting temperature of the YAG–MA_{ss} system in comparison with the YAG–MA system (about 1830°C)[9] indicates that the eutectic temperature of the YAG–MA_{ss} system decreases with an increase in Al_2O_3/MgO molar ratios in the spinel solid solution phase. The dependence of Al_2O_3 solubility in spinel on temperature is demonstrated in the phase diagram of the MgO–Al_2O_3 binary system. In addition, it is known

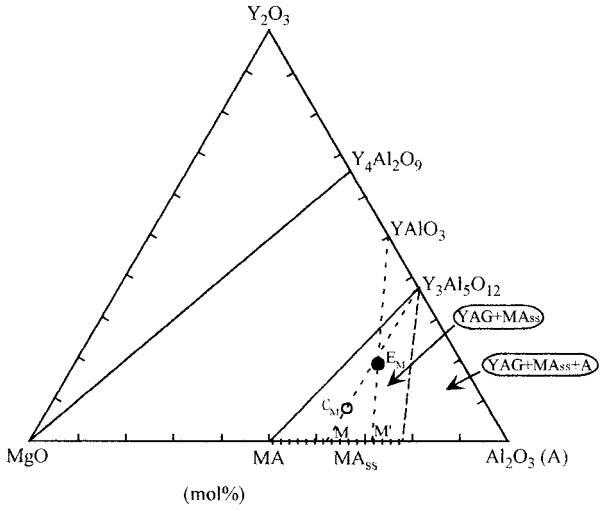

Fig. 1. Diagram of partial phase relations in MgO–Al_2O_3–Y_2O_3 ternary system, subsolidus.

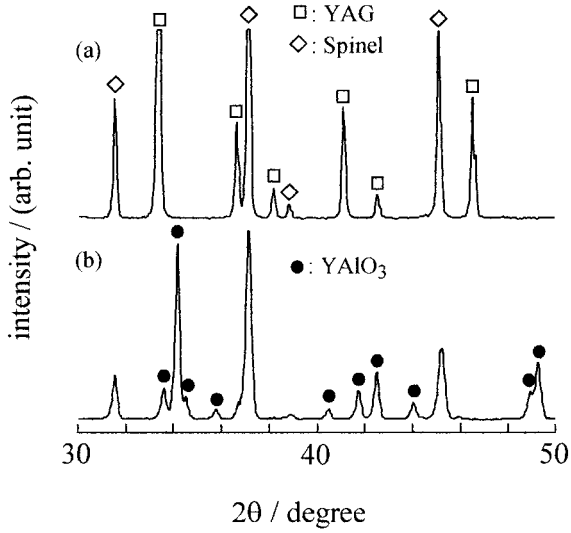

Fig. 2. XRD patterns of samples C_M: (a) hot-pressed at 1600°C for 1 h in vacuum and (b) annealed at 1795°C for 1 h followed by cooling down at 100°C min^{-1} in argon atmosphere.

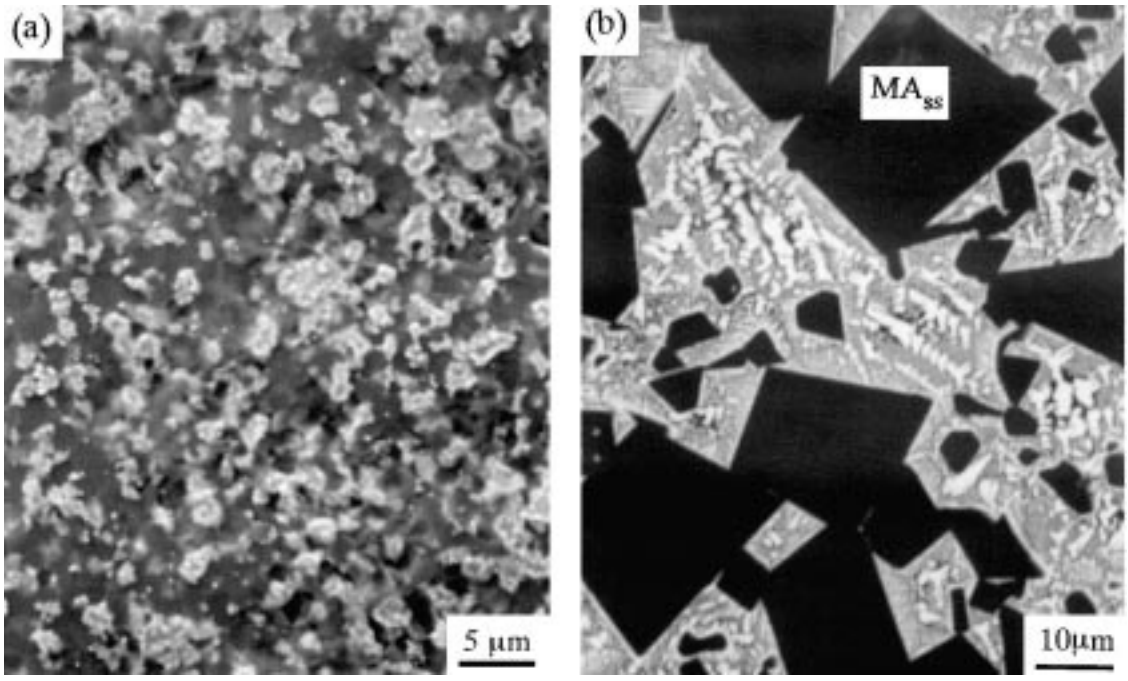

Fig. 3. SEM micrographs of samples C_M: (a) hot-pressed at 1600°C for 1 h in vacuum and (b) annealed at 1795°C for 1 h followed by cooling down at 100°C min^{-1} in argon atmosphere.

from comparing the compositions between C_M and E_M (Fig. 1) that the spinel solid solution (MA_{ss}) should behave as the primary phase or the pro-eutectic phase. In other words, the MA_{ss} phase co-existed with the YAG–MA_{ss} eutectic melt at the annealing temperature of 1795°C.

The formation of the $YAlO_3$ phase may be attributed to the metastable decomposition of YAG into two immiscible liquids, $YAlO_3$ and Al_2O_3.[11] In the present study, due to the presence of the MA_{ss} component in the eutectic melt, a spinel solid solution phase with richer content of Al_2O_3 may be formed in the solidified microstructure, accompanied with the solidification of the metastable $YAlO_3$ phase. Thus, two spinel solid solution phases having compositions M (primary phase) and M′ (intergranular eutectic phase), respectively (as shown in Fig. 1) may co-exist metastably in the solidified specimen. It appears that the spinel phase lowers the melting point of YAG through the formation of an Al_2O_3-rich spinel solid solution. This may be the reason that the metastable $YAlO_3$–MA_{ss} eutectic could be obtained at a lower annealing temperature (1795°C) than the formation of the metastable $YAlO_3$-alumina eutectic which needs an annealing temperature at least higher than the melting point of YAG (1940°C).[11–13]

Further experiments indicated that the phase compositions of the solidified composites could be changed with the cooling rates. For example, when the specimen was cooled from 1795°C to about 1770°C for solidification with a cooling rate of 0.5°C min^{-1} and then cooled at 100°C min^{-1} to lower temperatures, the $YAlO_3$ phase did not form; rather the equilibrium YAG phase was formed [Fig. 4(a)], the corresponding solidified microstructure being shown in Fig. 5(a). It is observed from Fig. 5(a) that the YAG phase is present continuously between primary phase MA_{ss} grains which exhibit dendritic growth. This result indicates that the formation of the $YAlO_3$–MA_{ss} metastable eutectics could be controlled

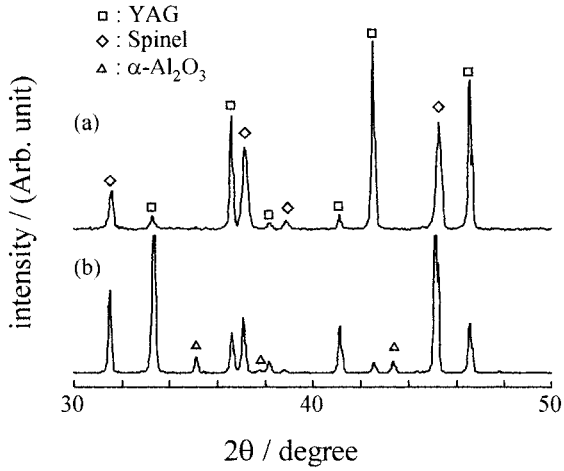

Fig. 4. XRD patterns of sample C_M: (a) annealed at 1795°C for 1 h and then cooled down at initially 0.5 min^{-1} to 1770°C and then quickly at 100°C min^{-1}, in argon and (b) annealed at 1795°C for 1 h and cooled down at 100°C min^{-1} in argon and then re-heated from room temperature to 1500°C, keeping for 2 h in air.

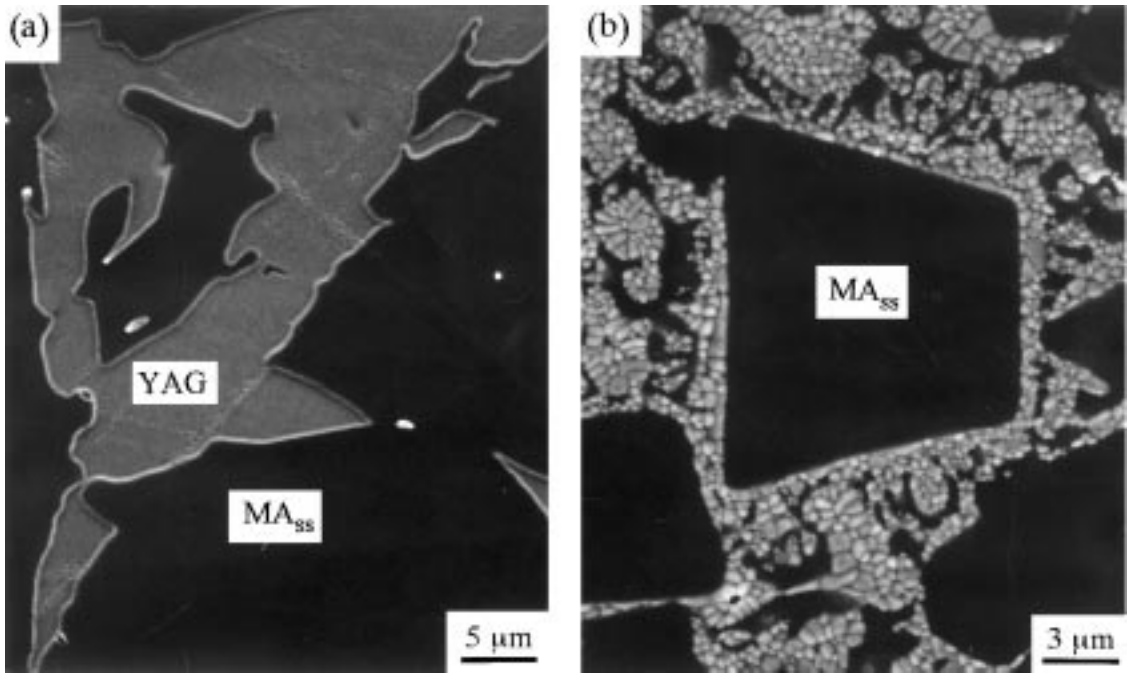

Fig. 5. SEM micrographs of sample C_M: (a) annealed at 1795°C for 1 h and then cooled down at initially 0.5°C min^{-1} to 1770°C and then quickly at 100°C min^{-1} in argon, thermally etched at 1500°C for 1 h in air and (b) annealed at 1795°C for 1 h and cooled down at 100°C min^{-1} in argon and then re-heated from room temperature to 1500°C, keeping for 2 h in air.

by cooling rate during solidification of the equilibrium YAG–spinel eutectic systems. As suggested by Caslavsky *et al.*[11] the metastability may be due to the fact that aluminum prefers the six co-ordination in the melt with the structure units of $YAlO_3$, alumina and spinel, whereas the growth rate of YAG is predominantly controlled by the rate of decrease in the aluminum co-ordination, which may be facilitated by slow cooling rates.

When the solidified specimen containing $YAlO_3$ was reheated at 1500°C for 2 h in air, the $YAlO_3$ phase transformed to YAG [Fig. 4(b)] which exhibits fine-grained structure [Fig. 5(b)]. This result may be related to the presence of the critical temperatures for the transformation from $YAlO_3$ to YAG in the presence of Al_2O_3[11,12] which precipitated from the spinel solid solution phases during the reheating process. The nucleation of the fine-grained YAG precipitates [Fig. 5(b)] may be similar to that in the reaction of directionally solidified eutectics of $YAlO_3$-alumina to YAG.[13]

4. Conclusions

A binary eutectic system of YAG–MA_{ss} exhibiting changed eutectic temperature with Al_2O_3 content in the spinel solid solution was proven to exist in the YAG-spinel-alumina ternary phase region. A YAG–MA_{ss} eutectic-like composite was obtained by controlled cooling process. During rapid solidification from an annealing temperature of 1795°C, however, metastable phase, $YAlO_3$, was formed, resulting in probably a metastable $YAlO_3$–MA_{ss} eutectic similar to the formation of the metastable $YAlO_3$–alumina eutectic in the YAG–alumina eutectic system. When reheating the as-solidified $YAlO_3$-MA_{ss} composite at 1500°C, a YAG–MA_{ss} composite with fine-grained YAG phase was obtained. It is implied that the YAG–MA_{ss} system could be used to develop either two-phase cubic eutectic composites or nanocomposites depending on the processing.

Acknowledgements

The authors are very grateful to Mr. F. Yamamoto for his contributions in this work.

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