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Structure of interface in directionally solidified oxide eutectic systems

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Abstract

The morphology and orientation relationships between two phases was investigated in directionally solidified oxide eutectics of ZrO_2–MgO, Al_2O_3–$ZrO_2(Y_2O_3)$ and YIG–Fe_3O_4 systems using the high-resolution transmission electron microscopic technique. The growth morphology was determined by the volume fraction of the minor phase, the misfit between the two phases, and the growth direction of the eutectics. The interface included misfit dislocations and steps with an atomic height to accommodate the misfit at the interface.

Keywords: Interfaces; Composites; Electron microscopy; Oxide eutectics

1. Introduction

In the past decades, directionally solidified eutectics have received considerable attention both as structural materials and for use in electronic devices.[1,2] Because of their high melting points, high strength to weight ratios at high temperatures, and resistance to oxidation, many ceramic eutectics are of interest as potential high temperature structural materials.[3–5] Since directionally solidified ceramic eutectics are free from transverse grain boundaries, they exhibit high rupture strength at high temperatures in comparison with sintered polycrystalline or single crystal material. Recently, Waku et al. found a peculiar microstructure resulting from directional solidification, in which a YAG single crystal forms a network involving a single sapphire crystal.[6] This microstructure is quite different from that formed by directional solidification showing a fibrous or lamellar microstructure. Although the mechanical properties of a eutectic depend on the microstructure, an understanding of the crystallographic relationship and the interface structure between the phases is important to fundamental understanding as well as to realization of a good performance of the mechanical properties at high temperatures.

The present paper examines the crystallography and microstructure of directionally solidified oxide eutectics of ZrO_2–MgO, Al_2O_3–$ZrO_2(Y_2O_3)$ and YIG–Fe_3O_4 systems. The interface structure was intensively observed using high-resolution electron microscopy.

2. Experimental procedure

The directional solidification of an oxide eutectic was accomplished by the Bridgman method using Mo crucibles. The growth rates used in the present experiments were 5–100 mm/h. Some sapphire base eutectics were directionally solidified at the growth rate of 10–90 mm/h by the floating melting method using a single ellipsoid image furnace. The directionally solidified eutectic was cut and polished perpendicular and parallel to the growth direction. Thin foils were prepared by sectioning the directionally solidified eutectics. After being ground down to 0.1 mm with a diamond polisher, the section was ion-beam thinned in argon. The resulting foil was examined by JEOL-200CX and JEOL-ARM1250 transmission electron microscopes.

3. Results and discussion

3.1. Growth morphology

The basic growth morphology of oxide eutectics can be generalized from the relative interfacial surface area per unit volume for the fibrous and lamellar structures. Fig. 1 shows a schematic of the volume fraction dependence of interfacial area per unit volume.[7] Assuming an isotropic surface energy, to minimize the interfacial surface area in the development of a lamellar or fibrous microstructure, a hexagonal array

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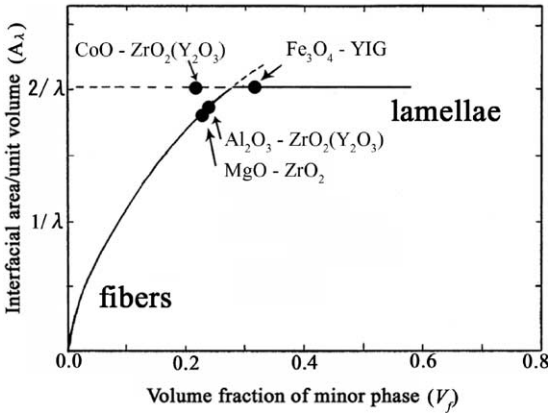

Fig. 1. Schematic of volume fraction dependence of interfacial area per unit volume.

of fibers is favored when the volume percent of the minor phase is less than 28%. If the volume fraction of the minor phase is greater than 28%, the morphology is lamellar. This situation is represented in Fig. 1. If substantial anisotropy in the surface energy exists, the lamellar structure can be stable at all volume fractions. In the present paper, mainly MgO–ZrO_2, Al_2O_3–$ZrO_2(Y_2O_3)$ and YIG–Fe_3O_4 eutectics were mainly investigated. These eutectics are located close to the transition point from fibrous to lamellar morphology.

Fig. 2 shows microstructures of transverse and longitudinal sections of a directionally solidified MgO–ZrO_2 eutectic.[8,9] This indicates that the directional solidification of the MgO–ZrO_2 eutectic forms a finely oriented microstructure of two phases with lamellar as well as the fibrous morphology. As seen from Fig. 1, the MgO–ZrO_2 eutectic, in which the volume fraction of the MgO phase is 26%, should have a fibrous morphology, if the surface energy is assumed to be isotropic. There are two reasons why the both morphologies are observed in one sample, namely, the anisotropic interfacial energy and the growth direction. Fig. 3 shows the electron diffraction pattern of the area of the directionally solidified MgO–ZrO_2 showing the fibrous morphology (a) and that of the area showing the lamellar microstructure (b). This figure revealed growth directions [0 1 1]z//[0 1 1]m and interfaces (*hkl*)z//(*hkl*)m for the fibrous morphology and growth

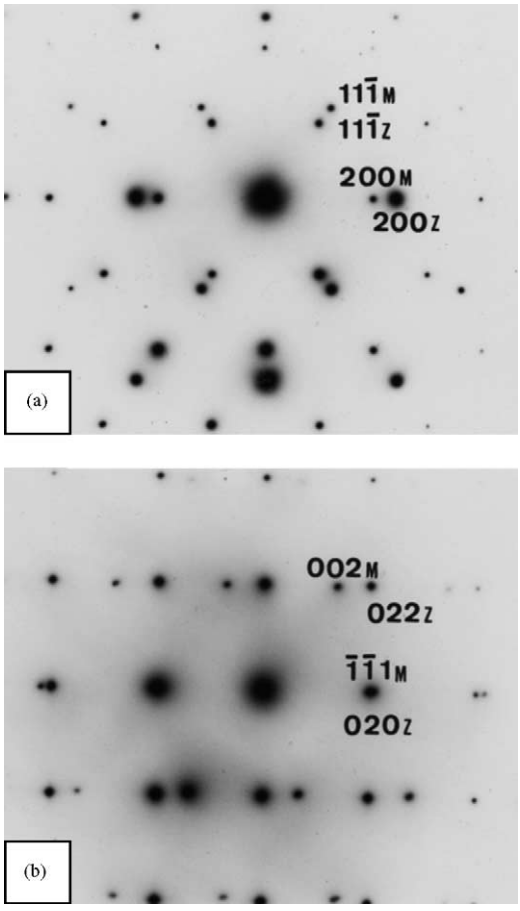

Fig. 3. Electron diffraction pattern of the area showing the fibrous morphology (a) and the area showing the lamellar morphology (b) of directionally solidified MgO–ZrO_2.

directions [0 0 1]z//[0 1 1]m and interface (0 1 0)z//(1 1 1)m for the lamellar morphology, where m and z indicate MgO and cubic ZrO_2 phases, respectively. That the orientation relationships between the two phases are different for the different morphologies suggests that a low energy interface exists for the particular interface of (0 1 0)z//(1 1 1)m. The lamellar morphology is observed only when the growth direction includes the low energy interface of (0 1 0)z//(1 1 1)m. When the growth direction is different from the above condition, the

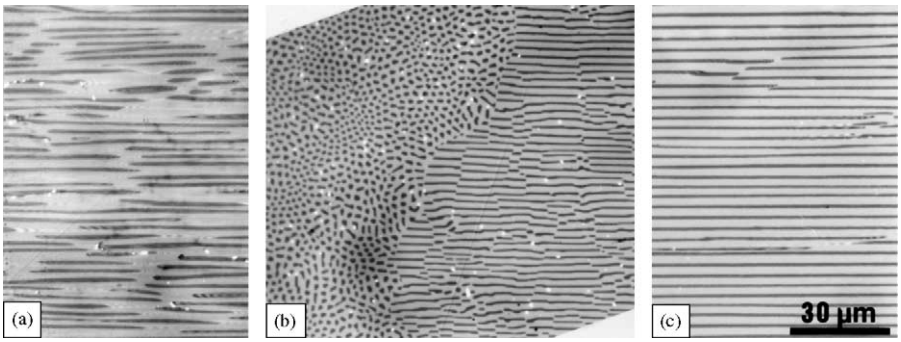

Fig. 2. Microstructures of transverse and longitudinal sections of directionally solidified MgO–ZrO_2 eutectic.

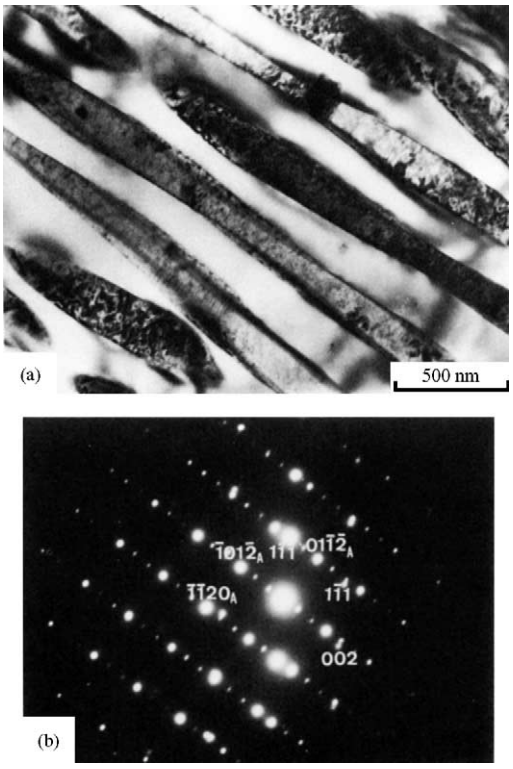

Fig. 4. Electron micrograph of directionally solidified Al_2O_3–ZrO_2 (3 mol% Y_2O_3) grown on a (1 0 2) sapphire single crystal.

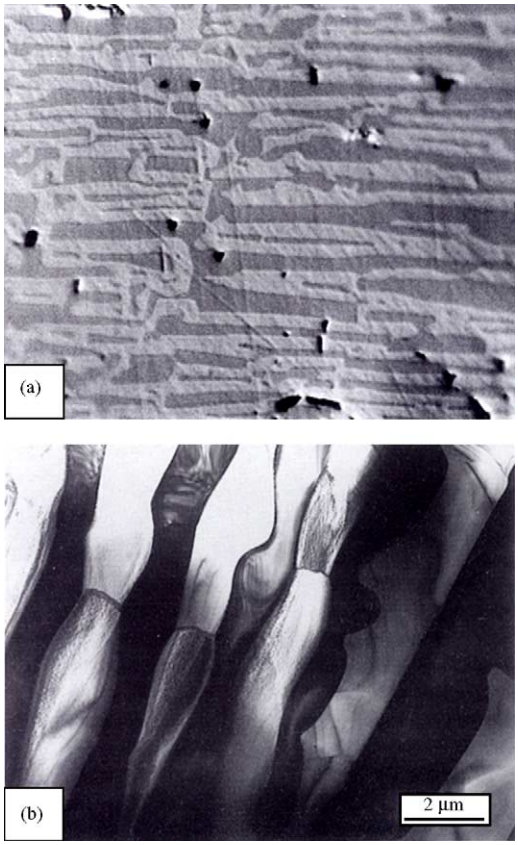

Fig. 5. Optical micrograph (a) and electron micrograph (b) of directionally solidified Fe_3O_4–YIG($Y_3Fe_5O_{12}$) eutectic.

growth morphology should be fibrous. It should be pointed out that the growth directions of lamellar and fibrous morphologies were different, i.e., the directionally solidified eutectic is a polycrystalline including grain boundaries even though it did not form a cell structure. Only lamellar morphology could be observed in the sample of the directionally solidified CoO–ZrO_2 and CoO–ZrO_2(Y_2O_3) eutectics, even when the volume fraction of the minor phase was 23%.[10,11] This is a typical example of the growth direction including a low energy interface of (0 1 0)z//(1 1 1)c.

Fig. 4 is an electron micrograph of directionally solidified Al_2O_3–ZrO_2 (3 mol% Y_2O_3) grown on a (1 0 2) sapphire single crystal.[12] The morphology is fibrous and the orientation relationship is as follows: growth direction perpendicular to (1 0 2)a//(0 0 1)z and (1 1 0)a//(0 1 0)z, (0 1 2)a//(1 1 0)z.

The microstructure has a wavy interface and the minor phase of the tetragonal/cubic ZrO_2 is not well aligned. The growth morphology of Al_2O_3–ZrO_2 eutectic grown on a (0 0 0 1) sapphire single crystal was indicated to have a fibrous structure with cells.[13,14] The orientation relationship was fundamentally (0 0 1)a//(0 0 1)z, (1 0 0)a//(0 1 0)z, and (1 1 0)a//(1 0 0)z, though the plane perpendicular to the growth direction of [0 0 1]z was distributed from (0 0 1) to (1 0 1)a.

Fig. 5(a) and (b) show an optical micrograph and an electron micrograph of a directionally solidified Fe_3O_4–YIG($Y_3Fe_5O_{12}$) eutectic.[15] Since the volume fraction of the minor phase in the system is more than 30%, the growth morphology is a plate structure, i.e., a structure with broken and deformed lamellae. This structure is known as the Chinese script morphology, such morphology being formed by the connection of the plates with each other. The electron micrograph indicates a wavy interface. The orientation relationship between the two phases was obtained by electron diffraction patterns and determined as being (1 1 1)f//(1 2 1)y and (0 1 1)f//(5 1 3)y and (2 1 1)f//(3 1 1)y, where f and y indicate Fe_3O_4 and YIG phases, respectively, as shown in Fig. 6. The two phases of the eutectics showed the same orientation relationship for any growth direction throughout the present experiment. Fig. 6 reveals that reflections of the second layer are completely coincident with each other. Since the lattice spacing which gives rise to the coincident reflections is almost the same throughout the specimen, the planes with small misfits exist perpendicular to the growth direction. This is one of the reasons that the interface plane was wavy in this system.

3.2. Interface structure

Fig. 7 shows a high-resolution electron micrograph of the fibrous interface in the directionally solidified MgO–ZrO_2 eutectic.[16] The interface was faceted and formed by (1 0 0), (1 1 0) and (1 1 1) planes. Because of the large misfit of 17% between cubic ZrO_2 and MgO in the case of the cube/cube relationship, the misfit dislocations were introduced period-

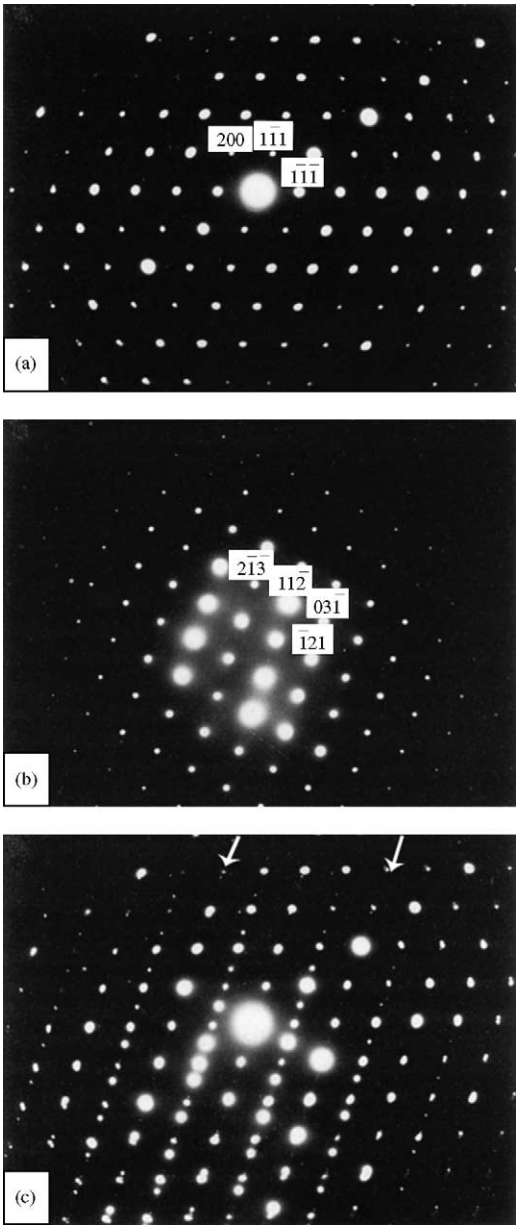

Fig. 6. Electron diffraction patterns of directionally solidified Fe_3O_4–YIG eutectic: (a) Fe_3O_4, (b) YIG phase and (c) an interface.

ically at intervals of 1.7 nm. The lamellar interface, which was formed by (0 0 1)z//(1 1 1)m planes, has an extremely good atomic fit. The sequence of the atomic plane parallel to the interface is metal/oxygen/metal/oxygen/metal/oxygen stacking across the interface as shown schematically in Figs. 8 and 9 shows a high-resolution electron micrograph of the lamellar interface observed in the directionally solidified MgO–ZrO_2 eutectic. Careful observation reveals a stepped structure at the interface. The height of a step is one atomic layer of 0.25 nm and the spacing between steps is 3.75 nm. Fig. 10 shows the superimposed oxygen lattices of MgO and cubic ZrO_2 phases seen from the growth direction. This indicates that atomic steps are responsible for the increase of the area of good fit. This means that a misfit of about 1.9%

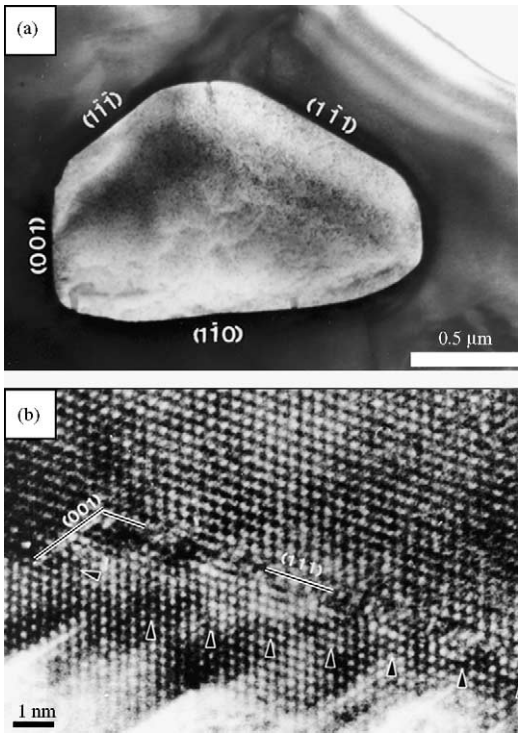

Fig. 7. High-resolution electron micrograph of the fibrous interface in the directionally solidified ZrO_2–MgO eutectic.

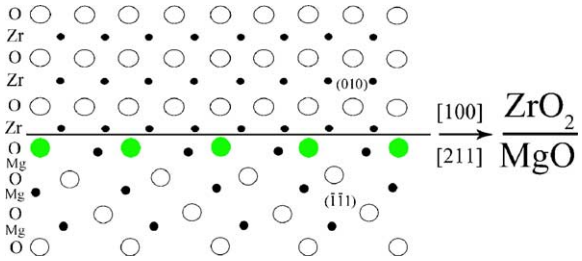

Fig. 8. Schematic drawing of lamellar interface, which was formed by (0 0 1)z//(1 1 1)m planes, showing the sequence of atomic plane parallel to the interface.

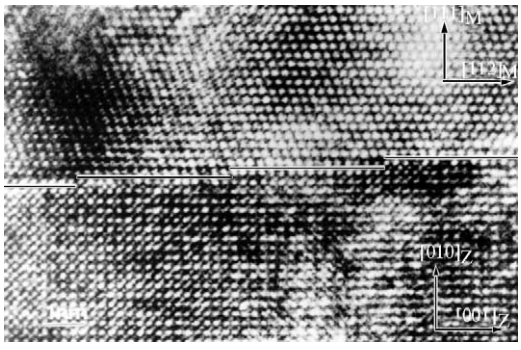

Fig. 9. High-resolution electron micrograph of the lamellar interface observed in the directionally solidified MgO–ZrO_2 eutectic.

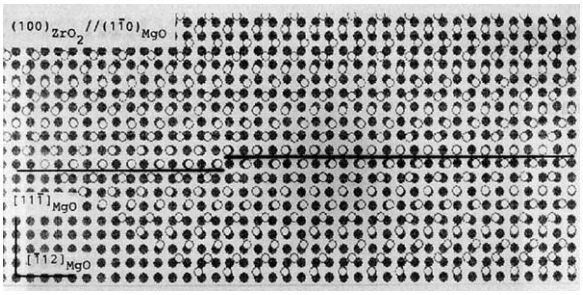

Fig. 10. Superimposed oxygen lattices of MgO and cubic ZrO_2 phases seen from the growth direction.

of atomic distance between the [2 1 1]m and [1 0 0]z directions, which is along the interface, is accommodated by steps with an atomic height of 1. The periodic introduction of steps leads to the declination of the interface plane from the exact (1 1 1)m and (1 0 0)z planes. The stepped structure at the interface was also observed in the lamellar interface of the directionally solidified CoO–ZrO_2(Y_2O_3) and NiO–Gd_2O_3 eutectics.[11,17] This stepped structure with an atomic height of 1 in the MgO–ZrO_2 eutectic is the first such observation in directionally solidified eutectics to accommodate a misfit at the interface. The misfit dislocations and steps may play important roles as sinks or sources of vacancies and as a nucleation site of dislocations in the case of high temperature deformation.

Fig. 11 shows a high-resolution lattice image of the interface of Fe_3O_4–YIG eutectic seen from the [0 1 1]f//[1 3 5]y directions. The interface was wavy and consisted of low indexed planes of (1 1 1) and (3 1 1) Fe_3O_4 planes. The continuity of the lattice planes across the interface was extremely good. Fig. 11 shows a high-resolution electron micrograph of the directionally solidified eutectic. The beam direction, i.e., the growth direction, is [1 1 2]f//[1 1 3]y and (1 1 1)f is parallel to (1 1 2)y. This relationship is coincident with the relationship mentioned above, which means that the orientation relationships between Fe_3O_4 and YIG were retained even when the growth direction changed. The lattice fringe image of both phases was clear and well defined from grain to interface as seen in Fig. 11. On the other hand, as shown in Fig. 12, the lattice fringe image showing the ordered structure of YIG became diffuse near the interface within two to three atomic layers when an interface was not formed from the low-index plane. Because the ordered YIG structure has a complicated atomic arrangement with a large unit cell, disorder of the ordered structure seems to occur during solidification. The misfit between (1 1 1)f and (1 1 2)y planes is 4.2%.

3.3. Possibility of the application of eutectics to devices

The $BaTiO_3$–$CoFe_2O_4$ eutectic system is an interesting system because $BaTiO_3$ and $CoFe_2O_4$ are materials with large electric striction and magneto striction.[18] Application of this system can be achieved by the combination of magnetic and electric properties through strain. The interface in the directionally solidified $BaTiO_3$–$CoFe_2O_4$ eutectic was bonded directly, but the electrical resistivity of the eutectic was too small to apply to a device due to the dissolution of a small amount of solute. If the eutectic system is to be applied to devices, it will be necessary to select properties which

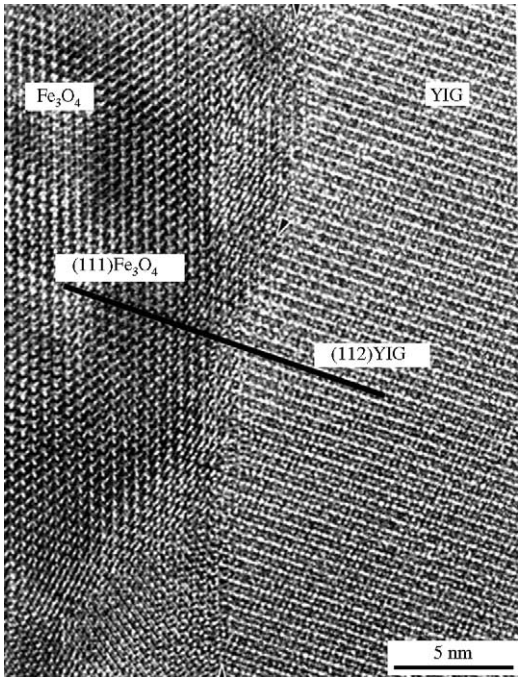

Fig. 11. High-resolution electron micrograph of the directionally solidified Fe_3O_4–YIG eutectic.

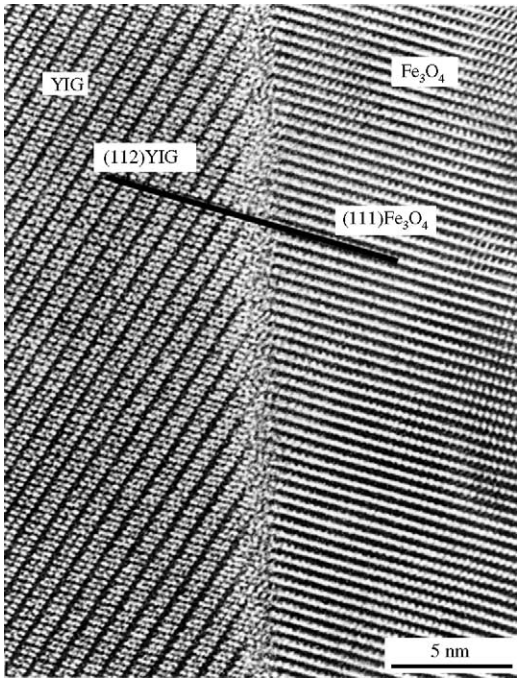

Fig. 12. Lattice fringe image of the directionally solidified Fe_3O_4–YIG eutectic showing diffuseness of atomic ordering of YIG near the interface. Growth direction was [1 1 2]f//[1 1 3]y.

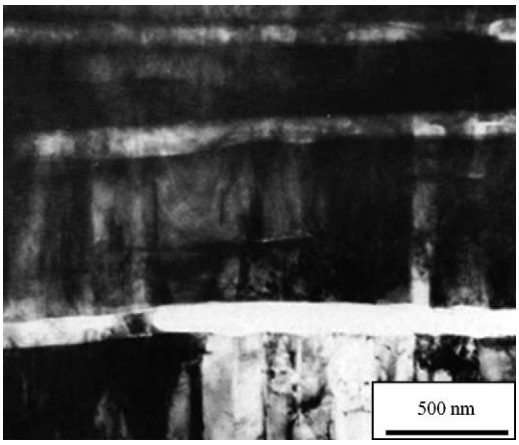

Fig. 13. Electron micrograph of 11 mol% MgO–ZrO_2 aged at 1573 K for 432 ks.

are non-sensitive to a small amount of solute, because any materials, even eutectic components, are dissolved solute.

3.4. Structure similar to that of directionally solidified eutectics

Generally, the eutectic structure has two morphologies, i.e., a fibrous and a lamellar microstructure. These structures are obtained by eutectoid decomposition and phase decomposition during deposition. Fig. 13 shows an electron micrograph of 11 mol% MgO–ZrO_2 aged at 1573 K for 432 ks.[19] This eutectoid consists of MgO rods in the monoclinic ZrO_2 phase elongated along 1 0 0 monoclinic ZrO_2 direction. The orientation relationship indicated that the interface between MgO and ZrO_2 consisted of (1 1 1)m//(1 0 0)z, which was the same as the relationship, which appeared in the directionally solidified eutectic. Because the decomposition temperature is lower than the temperature of the eutectic reaction, the structure formed by the eutectoid is much finer than that of the eutectic.

Fig. 14 shows a bright field image of a plan-view of a Co ferrite film sputter-deposited at a substrate temperature of 670 K.[20] The film consists of two phases, indicating the presence of precipitates of rectangular shape in the Co ferrite matrix. Electron diffractions and an electron micrograph of a cross-sectional view reveal that the precipitates are Co and are elongated in a filament-like fashion in the direction of growth. This result indicates the possibility that the formation by deposition of such structure is equivalent to the directional solidification.

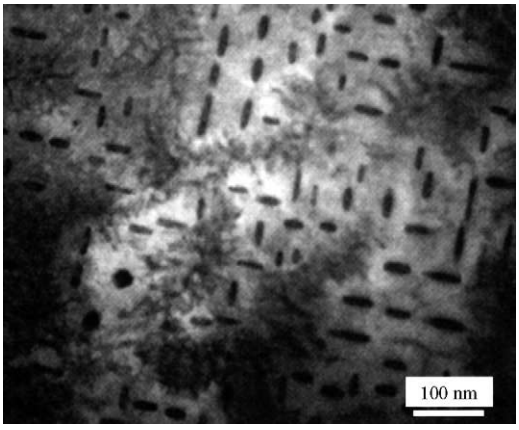

Fig. 14. Bright field image of a plan-view of a Co ferrite film sputter-deposited at a substrate temperature of 670 K.

4. Conclusion

The morphology and orientation relationships between two phases were investigated in directionally solidified oxide eutectic systems using the high-resolution transmission electron microscopic technique. The morphology was determined by the volume fraction of the minor phase, the misfit at the interface, and the growth direction of the eutectics. The interface included misfit dislocations and steps with an atomic height to accommodate the misfit at the interface.

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