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Directional solidification and interface structure of Fe_3O_4–YIG eutectic

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The directional solidification and interface structure of Fe_3O_4–$Y_3Fe_5O_{12}$ (yttrium iron garnet, YIG) eutectic grown in flowing air were investigated. The microstructure of the eutectic consisted of grains of broken and deformed lamellae. The orientation relationship between Fe_3O_4 and YIG is (0 1 1) Fe_3O_4‖(5 1 3) YIG, (1 1 1) Fe_3O_4‖(2 1 1) YIG and (2 1 1) Fe_3O_4‖(3 1 1) YIG. The two phases of the eutectic showed the same orientation relationship mentioned above, even when the growth rates were changed from 5–90 mm h^{-1}. High-resolution TEM revealed that a disorder of the garnet structure of YIG occurs along the interface with a width of two or three atomic layers.

1. Introduction

The directional solidification of eutectics is a method used to produce an anisotropic composite directly from the melt. Attention is focused on mechanical properties of directionally solidified eutectics at high temperatures due to high structural stabilities up to the melting temperature [1–4]. Although the morphology has been investigated in directionally solidified oxide eutectic systems, little information on the orientation relationships and the interface structure has been reported [3]. Because the formation of an interface has taken place during solidification, which allows atoms to diffuse to form the stable interface, it is suitable to investigate the interface structure of dissimilar materials.

The Fe_3O_4–$Y_3Fe_5O_{12}$ (yttrium iron garnet, YIG) eutectic system is an interesting material because Fe_3O_4 and YIG are known to be ordered materials with a large unit cell [5]. Observation at the atomic scale should reveal information on the interface structure of such complex ordered materials. The aim of this study was to investigate the growth morphology, orientation relationship, and interface structure of directionally solidified Fe_3O_4–$Y_3Fe_5O_{12}$ eutectic.

2. Experimental procedure

Starting materials were prepared for solidification by blending weighed powders of Fe_3O_4 (99.99% purity) and Y_2O_3 (99.99% purity), pressing them into a rod with a diameter of 5 mm and a length of 80 mm. This rod was sintered at 1470 K for 3.6 ks. The eutectic composition was determined from the phase diagram of the Fe_2O_3–Y_2O_3 system proposed by Cassedanne, the given eutectic composition of which is 37 mol % Y_2O_3 for Fe_3O_4–$Y_3Fe_5O_{12}$ eutectic [6]. Directional solidification was conducted by the floating zone melting method using a single ellipsoid image furnace at a growth rate of 10–90 mm h^{-1} [7].

Directionally solidified eutectics were cut and polished perpendicular to the growth direction. Thin foils were prepared by sectioning the directionally solidified eutectics. After grinding down to 0.1 μm using a diamond polisher, the section was ion-beam thinned in argon at 5 kV at an angle of 30°. The resulting foil was examined by H-800 and JEOL-1250 transmission electron microscopes.

3. Results and discussion

Fig. 1 shows optical photographs of samples perpendicular to the growth direction of the directionally solidified Fe_3O_4–YIG eutectic. The growth rate was changed from 10–90 mm h^{-1}. The structure of the directional solidification was retained up to a growth rate of 90 mm h^{-1} without any cell structure. The growth morphology of this system is a plate structure, i.e. a structure with broken and deformed lamellae. When the growth rate was above 40 mm h^{-1}, the so-called Chinese script morphology was observed, such morphology being formed by the connection of the plates with each other [3]. Fig. 2 shows an optical micrograph of the sample parallel to the growth direction of the directionally solidified Fe_3O_4–YIG eutectic. Both phases grew in the growth direction, though the interface between them was not flat and straight. Fig. 3 shows an example of another type of growth morphology, one with a round-shaped second phase, observed in this system grown at a rate of 10 mm h^{-1}. The smaller the spacing of the lamellae, the larger was the growth rate. In directionally solidified eutectics, the spacing between the two phases has been plotted

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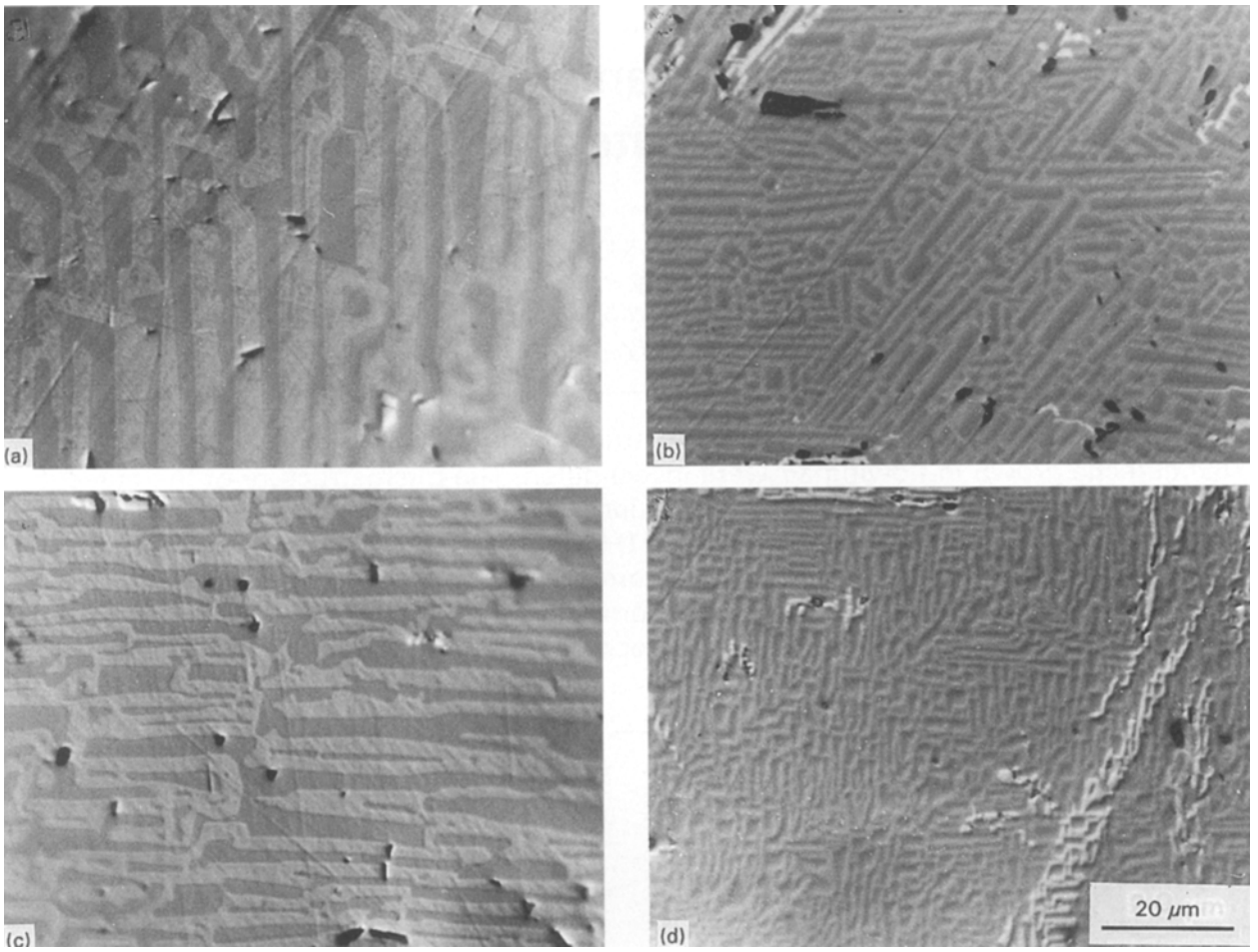

Figure 1 Optical photographs of samples perpendicular to the growth direction of the directionally solidified Fe_3O_4–YIG eutectic. Growth rates: (a) 10 mm h^{-1}, (b) 20 mm h^{-1}, (c) 40 mm h^{-1} and (d) 90 mm h^{-1}.

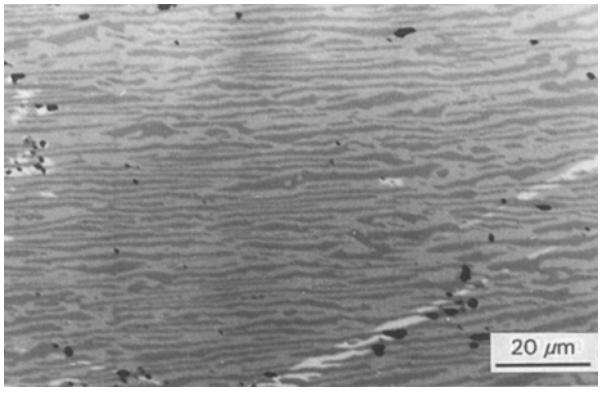

Figure 2 Optical photographs of samples parallel to the growth direction of the directionally solidified Fe_3O_4–YIG eutectic.

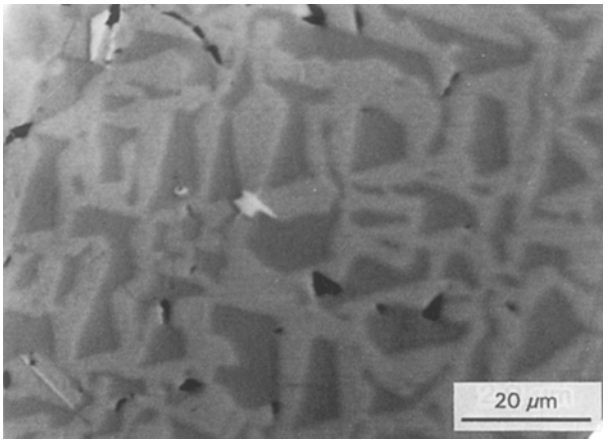

Figure 3 Optical photographs of samples perpendicular to the growth direction of the directionally solidified Fe_3O_4–YIG eutectic, indicating the fibrous morphology. Growth rate 10 mm h^{-1}.

with the inverse of the square root of the growth rate [7], revealing the existence of a linear relation between the two phases, which means that the relation $\lambda^2 R =$ constant, holds in this system as shown in Fig. 4, where λ and R indicate the spacing between the two phases and the growth rate, respectively.

Fig. 5 shows an electron micrograph of a directionally solidified Fe_3O_4–YIG eutectic grown at a rate of 40 mm h^{-1}. The bright-field image indicates a two-phase structure, which consists of a dark and a bright area, and the so-called broken lamellar morphology. The interface was not flat and straight, but wavy. The electron diffraction patterns taken from each area are shown in Fig. 6a and b, indicating indexes of reflections for electron diffraction patterns, and lead to the

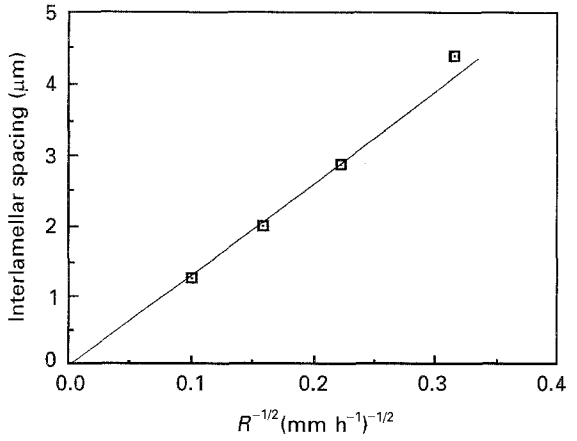

Figure 4 Relation of lamellar spacing to the inverse of the square root of the growth rate of Fe_3O_4–YIG eutectic.

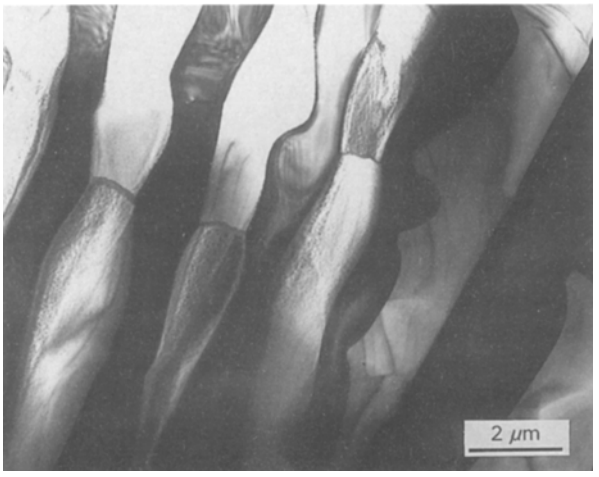

Figure 5 Electron micrograph of a directionally solidified Fe_3O_4–YIG eutectic grown at a rate of 40 mm h^{-1}.

following conclusions. The matrix (dark area) and a second phase (bright area) are cubic Fe_3O_4 (spinel-type crystal structure: $a = 0.839$ nm) and $Y_3Fe_5O_{12}$ (the garnet type-crystal structure: $a = 1.238$ nm) phases, respectively [8].

The orientation relationship between cubic Fe_3O_4 and YIG was determined from the electron diffraction pattern shown in Fig. 6c, consisting of patterns of both phases shown in Fig. 6a and b.

Beam direction (0 1 1) Fe_3O_4‖(5 1 3) YIG.
Interface plane (1 1 1) Fe_3O_4‖(1 2 1) YIG.

Because the direction of the beam was almost parallel to the growth direction of the directionally solidified eutectic, the growth direction of the eutectic was [0 1 1] Fe_3O_4 and [5 1 3] YIG. The interface plane, where the morphology can be considered as the lamellar interface, was formed by (1 1 1) Fe_3O_4‖(1 2 1) YIG. Interestingly, reflections of the second layer in the electron diffraction pattern shown in Fig. 6c, were completely coincident with each other and quite similar to the pattern of fcc material with (1 1 1) twins. This means that the lattice spacings perpendicular to [1 1 1] Fe_3O_4‖[1 2 1] YIG, seen from the directions of [0 1 1] Fe_3O_4 and [5 1 3] YIG, are the same.

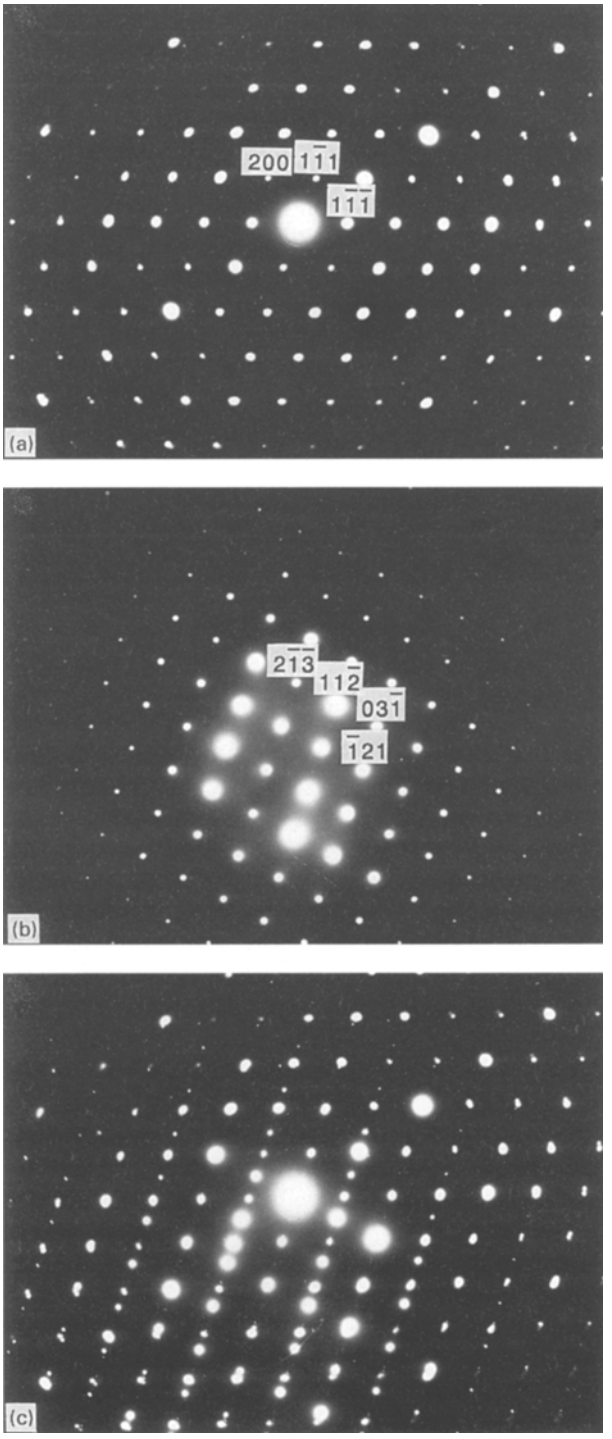

Figure 6 Electron diffraction patterns of a directionally solidified Fe_3O_4–YIG eutectic from (a) a matrix, (b) a second phase, and (c) an interface in Fig. 5.

The chemical composition of both phases in the Fe_3O_4–YIG eutectic was analysed by employing a transmission electron microscope equipped with an energy dispersive X-ray spectroscope. The Fe_3O_4 phase consisted almost entirely of Fe_3O_4, though less than 3 mol % Y_2O_3 was detected in the Fe_3O_4 matrix. On the other hand, the atomic ratio of yttrium and iron in the second phase was coincident with the ratio of 3:5 within experimental error.

When the growth rate was 10 mm h^{-1}, a round-shaped fibre was also observed as shown in Fig. 7a.

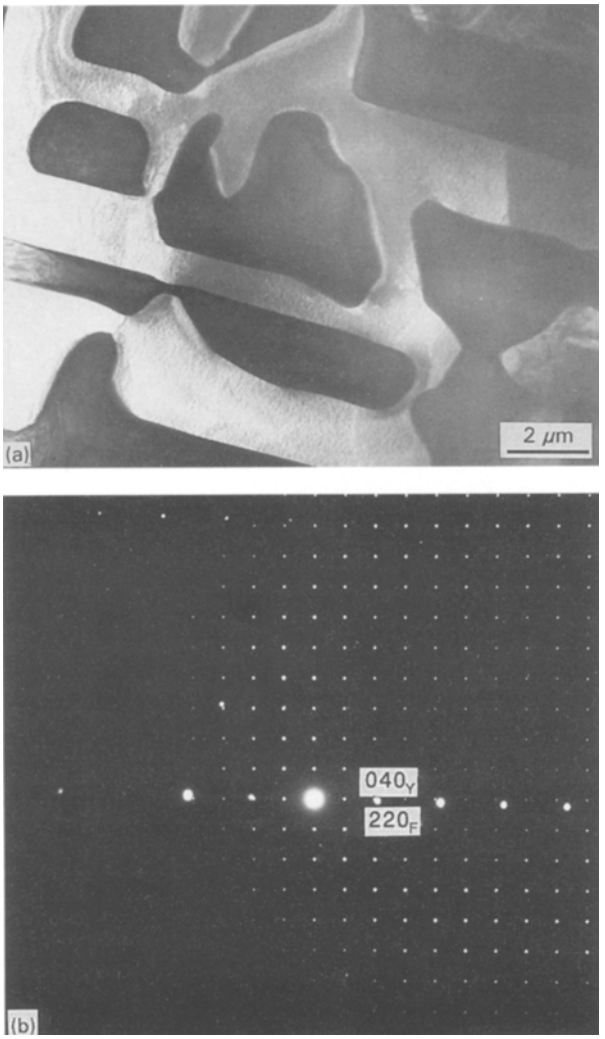

Figure 7 (a) Electron micrograph and (b) electron diffraction pattern of fibrous morphology in a directionally solidified Fe_3O_4–YIG eutectic grown at a rate of 10 mm h^{-1}.

The electron diffraction pattern taken from the growth direction showed that the growth direction and the interface of the fibre and the matrix were [1 0 0] YIG‖[1 1 3] Fe_3O_4 and (0 1 0) YIG‖(1 1 0) Fe_3O_4, respectively, though the growth direction of [1 1 3] Fe_3O_4 was not exactly in this direction, as can be seen from the electron diffraction in Fig. 7b. This orientation relationship observed in the fibrous morphology is the same relationship observed in the lamellar morphology mentioned above. The change of growth morphology may have been caused by the growth direction selected during growth.

The high-resolution lattice image of the interface between YIG and Fe_3O_4 is shown in Fig. 8, in which the growth direction was [0 1 1] Fe_3O_4‖[5 1 3] YIG. The interface was formed by (1 1 1) Fe_3O_4‖(1 1 2) YIG microscopically. Facets can be seen at the interface, the plane of which was determined to be (3 1 1) Fe_3O_4 ‖(1 2 1) YIG based on the electron diffraction pattern shown in Fig. 6c; therefore, the wavy interface consisted of low-indexed interfaces in this orientation. The continuity of lattice planes across the interface was extremely good. Although the atomic arrangement in a unit cell of a garnet is very complicated, especially for oxygen atoms, it is very difficult to determine the

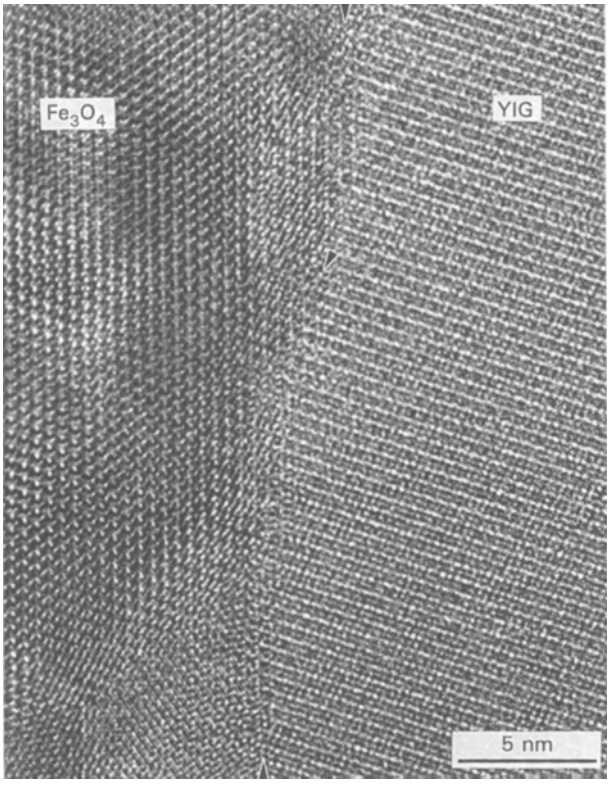

Figure 8 High-resolution lattice image of the interface between Fe_3O_4 and YIG. The beam direction was [0 1 1] Fe_3O_4‖[1 3 5] YIG.

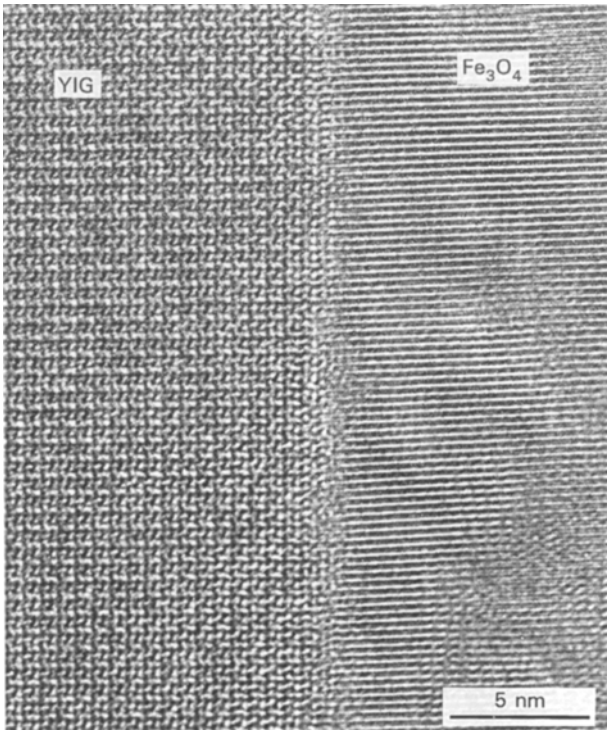

Figure 9 High-resolution lattice image of the interface between Fe_3O_4 and YIG with an orientation relationship of (0 1 0) Fe_3O_4 ‖ (1 1 0) YIG.

interface structure at the atomic level. Nevertheless, the lattice fringes seem to extend to the interface without any distortion of either phase. It should be noted that a domain structure bounded by the anti-phase boundary was observed in the Fe_3O_4 phase. Fig. 9 shows a high-resolution electron micrograph of

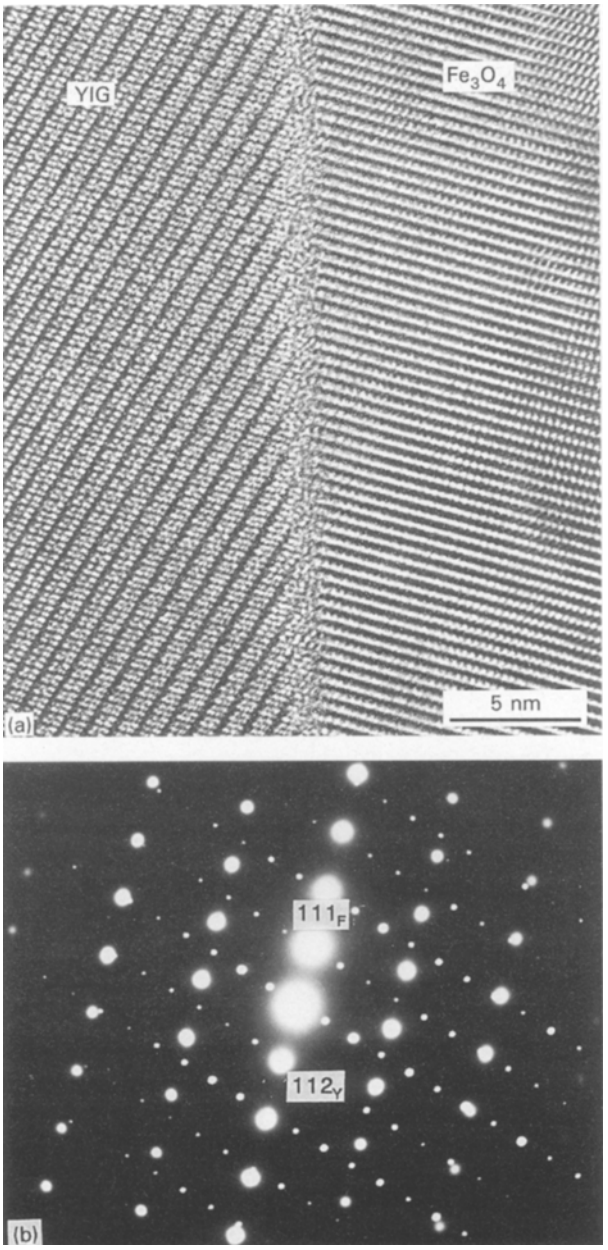

Figure 10 High-resolution lattice image and electron diffraction pattern of Fe_3O_4–YIG eutectic. The beam direction was [1 1 2] Fe_3O_4‖[1 1 3] YIG.

the sample with an orientation relationship of (0 1 0) YIG‖(1 1 0) Fe_3O_4. The interface plane was straight and parallel to (1 0 0) YIG, and the fringes of 1 1 0 Fe_3O_4 were fitted to the fringes of 0 1 0 YIG with a misfit of 4.3%; however, the other low-indexed planes of the Fe_3O_4 phase were not found to be perpendicular to the beam direction. Fig. 10 shows a high-resolution electron micrograph and the electron diffraction pattern of the directionally solidified eutectic. The beam direction, i.e. the growth direction, is (1 1 2) Fe_3O_4‖(1 1 3) YIG, and (1 1 1) Fe_3O_4 is parallel to (1 1 2) YIG. 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 orientation relationship seems to be geometrically determined as planes across the interface matched with small misfit. The interface plane was straight but declined from the low-index plane, and the low-index plane was not continued at the interface. The lattice fringe image of both phases was clear and well-defined from grain to interface in the case of (1 1 1) Fe_3O_4‖(1 1 2) YIG interface, as shown in Fig. 8. On the other hand, as shown in Fig. 10, the lattice fringe image showing the ordered structure of YIG became diffuse near the interface within two to three atomic layers when the 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. As a stable interface was usually obtained by directional solidification due to sufficient mobility of atoms, this is the first observation at the interface of directionally solidified oxide eutectics [9].

4. Conclusions

The directional solidification and the interface structure of Fe_3O_4–$Y_3Fe_5O_{12}$ eutectic were investigated by the floating zone melting method and following results were obtained.

1. The microstructure of the eutectic consisted of grains of broken and deformed lamellae, the so-called Chinese script morphology. The two phases of the eutectic were confirmed to be Fe_3O_4 with the spinel-type crystal structure, and $Y_3Fe_5O_{12}$ with the garnet-type crystal structure.
2. The lamellar spacing, λ, is related to the growth rate, R, by the relation $\lambda^2 R$ = constant.
3. The orientation relationship between Fe_3O_4 and YIG is (0 1 1) Fe_3O_4‖(5 1 3) YIG, (1 1 1) Fe_3O_4‖(1 2 1) YIG, and (2 1 1) Fe_3O_4‖(3 1 1) YIG. The two phases of the eutectic showed the same orientation relationship throughout the present experiment.
4. High-resolution TEM revealed that the order of the garnet-type crystal structure of YIG became disordered along the interface with a width of two or three atomic layers.

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