JOURNAL OF MATERIALS SCIENCE 14 (1979) 1901–1906

Growth of Mg_2TiO_4 single crystals by the floating zone method

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Single crystals of the peritectic compound Mg_2TiO_4 up to 8 mm diameter and 80 mm long along the [1 0 0] and [1 1 1] directions, were grown by the travelling solvent float zone (TSFZ) technique using a halogen lamp image furnace. The optimum conditions were as follows: sintering temperature of the charge rod, 1500° C, the growth rate, 2 mm h^{-1} and the composition of the charge rod in molar ratio, $MgO:TiO_2 = 2:1.01$. The chemical composition of the solvent zone was determined by application of the EPMA technique and the peritectic nature of Mg_2TiO_4 was proved. The refractive index of the grown crystal was 2.05.

1. Introduction

Mg_2TiO_4 is a cubic crystal with a crystal structure of the inverse spinel type. Coughanour and Deprosse [1] reported that it melted congruently, while Massazza and Sirchia [2] pointed out its incongruent nature. A detailed study of the system $MgO–TiO_2$ by Woermann *et al.* [3] suggests that the peritectic interpretation is the correct one.

Few papers have reported the gorwth of Mg_2TiO_4 single crystals. Taki [4] showed that the Mg_2TiO_4 single crystals could be grown by the Verneuil method, as did Dittmann and Petzett [5]. Assuming that the conclusion by Woermann *et al.* is correct, considerable difficulties must be encountered in the application of the Verneuil method to the single-crystal growth of Mg_2TiO_4 due to the fact that the chemical composition of Mg_2TiO_4 is covered by the primary crystallization field of MgO and that the molten charge will crystallize MgO before Mg_2TiO_4 during cooling. Taki's report mentions some of these difficulties.

Recently, reported the successful single-crystal growth of the peritectic compounds YFe_2O_4 [6] and $Y_3Fe_5O_{12}$ [7] by what may be called the travelling solvent float zone (TSFZ) method. The TSFZ method is essentially identical to the floating zone method, with the exception that the chemical composition of the grown crystal is appreciably different from that of the melt zone.

Fig. 1 shows the phase diagram of the system $MgO–TiO_2$ after Woermann *et al.* [3]. It is noted that Mg_2TiO_4 can co-exist under equilibrium with the liquid phase corresponding to the portion from A to B of the liquidus curve. An experiment to confirm the peritectic nature of Mg_2TiO_4 was attempted prior to single-crystal growth. For a peritectic material, the melt zone should establish an appreciably different chemical composition from that of the solidified material after passing the zone over a certain length of the charge. Thus the melt zone is eventually brought to a dynamical equilibrium under which the solidified material has the same chemical composition as that of the charge. An analysis of the crystallization sequences in the solidified rod as well as that of the chemical composition of the melt zone thus formed will reveal whether or not the material melts incongruently. A congruently melting material neither gives crystals of different phases in the solidified material nor establishes a melt zone, the composition of which differs significantly from that of the charge. In the present experiment, Mg_2TiO_4 was found to give crystals of MgO in early stages and to form a melt zone with a different chemical composition from that of the charge, and was confirmed to be a peritectic compound.

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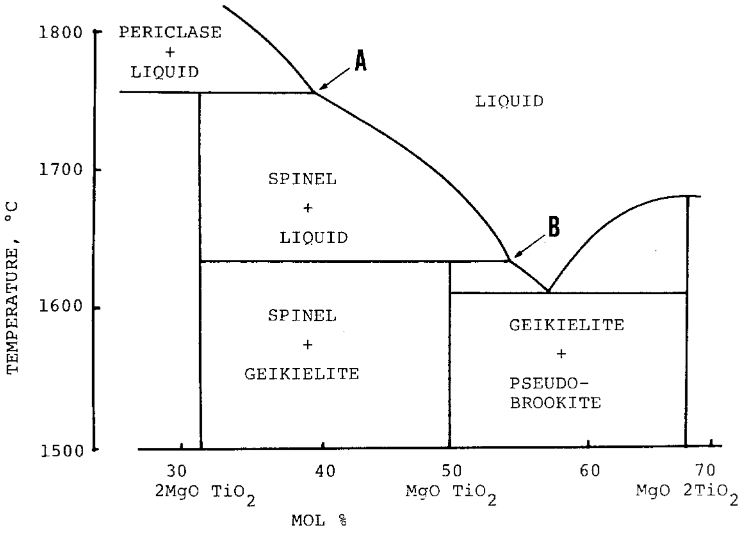

Figure 1 Phase relations in the system MgO–TiO$_2$ (Woermann *et al.* [3]). The portion of the liquidus from A to B represents the liquid composition in equilibrium contact with Mg$_2$TiO$_4$.

For proper application of the TSFZ technique, it is necessary to prepare the solvent zone material separately from the charge material and introduce it between the charge and the seed, as found in our earlier study [7]. The composition of the solvent zone material may be chosen from those corresponding to the portion from A to B of the liquidus curve in Fig. 1.

2. Experimental details

2.1. Growth apparatus

The apparatus used was an image furnace with a 1.5 kW halogen lamp as the radiation source. The details of this apparatus can be found elsewhere [8] and only brief descriptions are given here. The apparatus has a mirror of the shape of an ellipsoid. One of the focus positions is occupied by the halogen lamp. The upper charge feeding and the lower seed holding shafts are located so that the other focus position is always occupied by the melt zone, into which the charge is dissolved and from which crystallization takes place on to the seed. Growth is carried out in the chamber isolated by a fused quartz tube for atmosphere control. The apparatus is designed in such a fashion that the external solid–liquid boundary can be observed during the run.

2.2. Preparation of charge rods

Powders of MgO (99.9% pure, Marincrodt Co) and TiO$_2$ (99.9% pure, Kojundo Kagaku Kenkyusho) were mechanically mixed in the molar ratios of 2:1 and 3:2 for preparation of the materials of the Mg$_2$TiO$_4$ charge and the solvent zone, respectively. Each of the mixed batches was placed into a sealed rubber tube and hydrostatically pressed under a pressure of approximately 1000 kg cm^{-2} to give a rod of a desired diameter (5 to 10 mm) and a desired length (20 to 200 mm). In order to grow high quality crystals it was found to be essential to prepare straight, uniform and homogeneous charge rods. The desired amount of the pressed solvent zone material, usually disc shaped, was put to one end of a pressed charge rod and they were again hydrostatically pressed, as in the earlier case, to give a charge rod with the solvent material affixed. The rod was then fired at temperatures above 1500° C in an oxygen atmosphere to sinter to a degree which corresponds to the apparent density of approximately 85% of the theoretical value.

2.3. Crystal growth

The sintered charge rod was suspended from the charge shaft and a seed crystal of a sintered polycrystalline body was fixed to the seed shaft. The atmosphere of pure oxygen was introduced into the growth chamber and the solvent material at the bottom of the charge rod was brought into the maximum temperature zone of the apparatus while heating was carried out, and the two shafts were counter-rotated at 30 rpm. When the solvent material was melted, it was connected to the seed crystal and the TSFZ system was established in the form of a vertical sequence of the charge rod, the molten solvent zone and the seed. The charge and the seed shafts were simultaneously driven downward at a rate in the range 1 to 5 mm h^{-1}

which automatically determined the growth rate. The seeded growth was attempted along the [1 0 0] and [1 1 1] directions. The oriented seed crystals were taken from the single crystals obtained in the runs where polycrystalline bodies were used as the seed.

2.4. Quenching of TSFZ system

The crystal growth procedures described above were followed using a single-crystal seed. The solvent zone material was not affixed to the charge rod in this experiment in order to check whether or not Mg_2TiO_4 was a peritectic compound. After growth of 40 to 50 mm on the top of the seed, the whole power supply to the apparatus was cut off. The rotation of the shafts stopped quickly and the float zone was quenched rapidly.

2.5. Study of polished sections

The grown crystals and the quenched bodies were cut and polished so that either perpendicular or parallel cross-sections to the growth direction could be observed. The polished sections were studied by means of optical microscopy and EPMA. The refractive index measurement was carried out by the duc de Charlnes method using a polished plate.

3. Results and discussion

Large Mg_2TiO_4 single crystals up to 8 mm diameter and 80 mm long were grown on a polycrystalline seed. One of them is shown in Fig. 2. The seeded growth was successfully attempted along the [1 0 0], [1 1 0] and [1 1 1] directions. The facets parallel to [1 1 1] appeared on the surface of the crystals grown along the [1 1 0] direction, while four growth ridges were found on the surface of those grown along the [1 0 0] direction. The grown crystals turned colourless and transparent after annealing for 12 h at 1000° C in an oxygen atmosphere. The annealed and sectioned crystals are shown in Fig. 3.

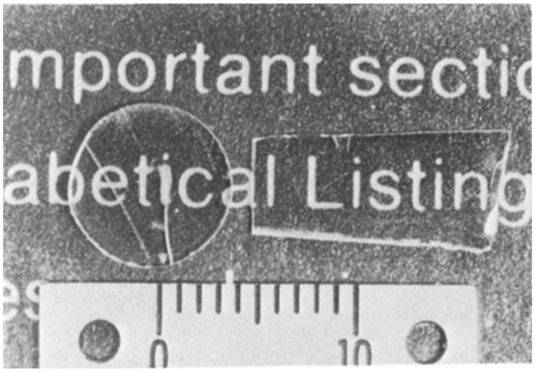

Figure 3 The annealed and sectioned crystals of Mg_2TiO_4 (scale in mm).

The EPMA technique was applied to determine the chemical composition of the melt zone which was brought under dynamic equilibrium with the grown Mg_2TiO_4 crystal. The quenched melt zone was cut along the growth direction of the crystal and a polished cross-section, shown in Fig. 4, was obtained. The quantitative analysis of the composition distribution was carried out on the basis of the calibration curves obtained using $MgTiO_3$ and Mg_2TiO_4 as the standard materials. The results are shown in Fig. 5. When the electron beam diameter was small (3 μm) the fluctuation in each compositional trace is considerable due to the relatively large diameters of the constituent grains in the frozen zone. On the other hand, the traces are smooth with a large beam diameter, as shown in Fig. 5 (b). On an assumption that the traces in the latter represent the averaged contents,

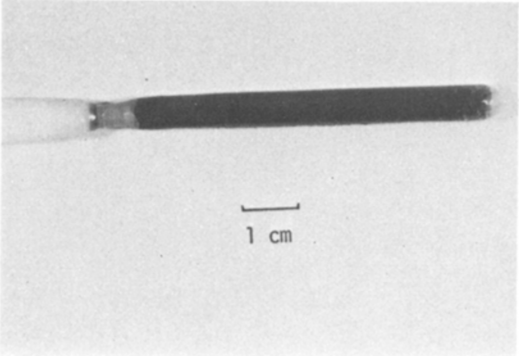

Figure 2 An as-grown boule of Mg_2TiO_4 crystal with a polycrystalline seed.

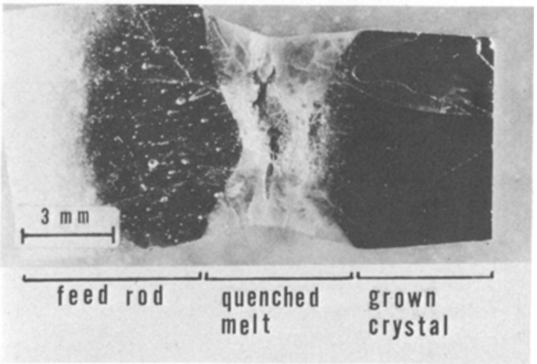

Figure 4 A cross-sectional view of the quenched melt zone and the grown crystal.

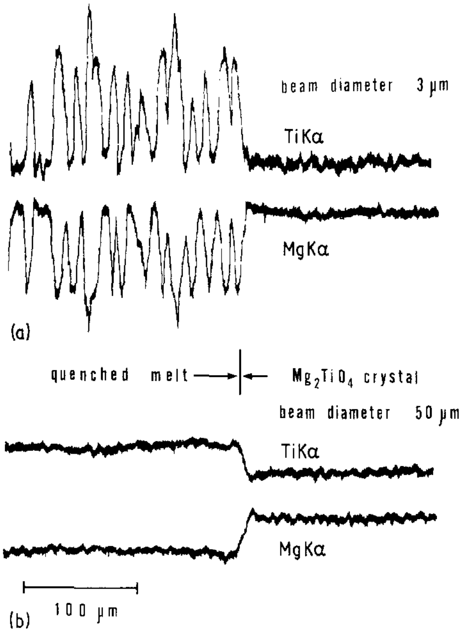

Figure 5 The results of EPMA measurement of the quenched melt zone and the grown crystal. (a) 3 μm beam analysis, (b) 50 μm beam analysis.

Figure 6 Typical occurrence of foreign phase precipitates and voids in a grown crystal (negative phase contrast).

it was found that the molar ratio MgO : TiO_2 in the melt zone was 55:45. This result, along with the fact that MgO crystals were precipitated in the early stages of growth, clearly indicated the peritectic nature of Mg_2TiO_4.

The formation of steady TSFZ system for the successful single-crystal growth depended upon following three essential conditions: the degree of sintering of the charge rod, the growth rate, and the chemical composition of the charge rod. In a successful TSFZ crystal gorwth, a steady solid–liquid interface is essential for avoiding the precipitation of foreign phases on to the growing crystal. When the charge rod is in contact with the molten solvent zone under dynamic equilibrium, the liquid phase penetrates into the charge rod to the point where the temperature corresponds to the invariant situation represented by point A in Fig. 1. As a consequence, that part of the charge rod adjacent to the melt zone swells considerably and tends to lose shape, thus causing an uneven solid–liquid interface. Fig. 4 shows a typical cross-sectional view of the quenched melt zone and its vicinity.

A small amount of liquid phase is observed along the grain boundaries in the adjacent part of the charge rod to the melt zone. The degree of sintering is quite good in this case, for only a small degree of swelling is seen. It is also noted in Fig. 4 that few voids are present in the charge rod. The presence of voids is probably another factor influencing the stability of the solid–liquid interface, for they appear to enter the melt zone and move in a complicated manner before collapsing through bursts. Thus the charge rods must be carefully sintered. In the present experiment, the charge rods were sintered under the conditions stated earlier and proved themselves to be satisfactory for keeping the interface steady.

The experiments indicated that the maximum growth rate of Mg_2TiO_4 single crystals of high quality was $2\,mm\,h^{-1}$. A higher growth rate made the crystals opaque due to foreign phase precipitation and incorporated voids as typically shown in Fig. 6.

It was found that charge rods having the stoichiometric composition were not suitable for growing inclusion-free crystals. In the case of a stoichiometric charge rod, the solid–liquid interface was quite unstable and the resulting crystals were opaque. In order to determine the optimum composition, charges with molar ratios MgO : TiO_2 of 2 : 1.01 and 2 : 1.02 were also tried. In the case of 2 : 1.02, the length of the melt zone

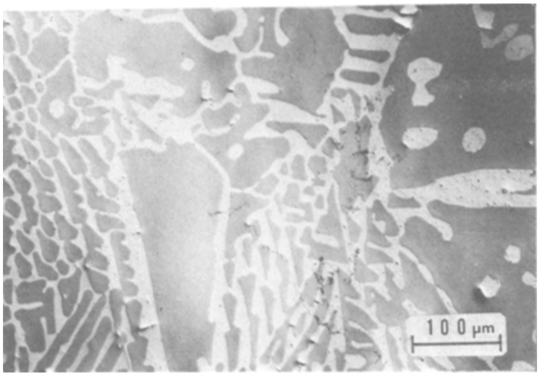

Figure 7 A magnified view of the precipitated $MgTiO_3$ phase (white, reflection-type differential interference contrast).

gradually developed during the run and finally the precipitation of $MgTiO_3$ started. The typical appearance of the $MgTiO_3$ precipitates is shown in Fig. 7. The $MgTiO_3$ phase was identified by EPMA. In the case of 2 : 1.01, on the other hand, the solid–liquid interface was found to be stable and inclusion-free crystals were obtained. This composition was therefore concluded to be optimum for Mg_2TiO_4 crystal growth.

The situation stated above may be interpreted as arising due to the following mechanism. It may be postulated with reasonable certainty that there is a continuous solid solution series between Mg_2TiO_4 and $MgTi_2O_4$, the latter consisting of trivalent titanium. At elevated temperaratures, part of Ti^{4+} in Mg_2TiO_4 may be reduced to Ti^{3+}. The typical sign of this reaction is the dark colour of the as-grown crystals. As a consequence, the composition of the grown crystals may be slightly shifted toward $MgTi_2O_4$, causing the situation of excess MgO which precipitates as a separate phase. The opacity of the crystals obtained from the stoichiometric charge rods may, therefore, be understood as the result of MgO precipitation.

Observations under the transmission-type differential interference contrast microscope revealed the occurrence of a number of small inclusions in the crystals grown along the [1 0 0] direction from the stoichiometric charge. These inclusions were square when viewed along the growth direction and fan-shaped when viewed perpendicular to it. Apparently each inclusion is in the shape of a small pyramid with a square base. The individual pyramids were always found open toward the growth direction. They are shown in Fig. 8. The fact that the shape and orientation of these inclusions are regular suggests that they may be negative crystal cavities, for which the formation mechanism was described by Roedder [9].

The occurrence of the inclusions may be discussed in relation to the precipitation of MgO which was pointed out earlier. Roedder's description seems to suggest the possibility that the pyramidal inclusions were introduced in the following manner. Small crystals of MgO were formed in the melt zone due to the excess MgO content. They rested on the surface of the growing crystal. Further Growth was hindered in the vicinity of these crystals by the retarded diffusion of the solute, forming a re-entrant at each resting point. Under such a situation, the walls of the re-entrants are made of host crystal faces according to Roedder. The re-entrants were covered by uniform growth in the later stages. An effort was made to analyse the chemical composition of the pyramidal inclusions by EPMA, but it was unsuccessful due to their small sizes.

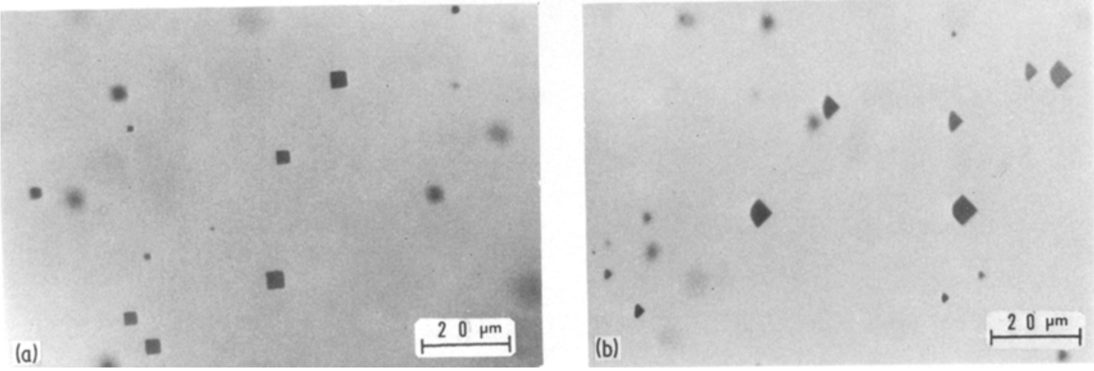

Figure 8 The inclusions observed in a crystal grown from the stoichiometric charge (growth axis [1 0 0], transmission-type differential interference contrast). (a) Squares as viewed in the section perpendicular to the growth direction. (b) Pyramids as viewed in the section parallel to the growth direction.

The refractive index of the grown crystals from the charge of optimum composition was measured to be 2.05 using a plate 1.5 mm thick. The value obtained is in good agreement with that reported by Taki [4].

References

1. L. W. COUGHANOUR and V. A. DEPROSSE, *J. Res. Nat. Bur. Stand.* **51** (1953) 87.
2. F. MASSAZZA and E. SIRCHIA, *Chim. Ind. (Milan)* **40** (1958) 378.
3. E. WOERMANN, B. BREZNY and A. MUAN, *Amer. J. Sci.* **267A** (1969) 467.
4. S. TAKI, *Kogyo Kagaku Zasshi* **59** (1956) 20.
5. R. DITTMANN and D. PETZELT, *J. Crystal Growth* **23** (1974) 77.
6. I. SHINDO, N. KIMIZUKA and S. KIMURA, *Mat. Res. Bull.* **11** (1976) 637.
7. S. KIMURA and I. SHINDO, *J. Crystal Growth* **41** (1977) 192.
8. T. AKASHI, K. MATSUMI, T. OKADA and T. MIZUTANI, *IEEE Trans.* **MAG-5** (1969) 285.
9. E. ROEDDER‘ "Geochemistry of Hydrothermal Ore Deposits" (Holt, Rinehart and Winston, New York, 1967) p. 515.

Received 6 September and accepted 16 November 1978.