
Single crystals of Tb$_{0.3}$Dy$_{0.7}$Fe$_2$ grown by Czochralski method with cold crucible

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Abstract

Single crystals of Tb$_{0.3}$Dy$_{0.7}$Fe$_2$ have been obtained by CZ technique with cold crucible. The formation mechanism of defects such as RFe$_3$ strips, Widmanstatten precipitates (WSP), twins and inclusions were investigated in detail. They are generated by different phase relations and conditions of solidification. The geometrical morphology depends on the crystallographic orientation or the position of the interface. The relationship between growth conditions and compositions of starting materials has been discussed based on the normal freezing theory for rare earth-rich growth environment. Various growth rates were selected for growing defect-free single crystals of Tb$_{0.3}$Dy$_{0.7}$Fe$_2$. Optimized conditions are a growth rate of 10–30 mm/h, temperature gradient of 110–140$^\circ$C/cm and starting composition of Tb$_{0.3}$Dy$_{0.7}$Fe$_2$ ($y = 1.78–1.85$).

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1. Introduction

The rare earth iron compound Tb$_{0.3}$Dy$_{0.7}$Fe$_2$, known as Terfenol-D, exhibits very large magnetostrictive strains which points to its potential applications [1]. It has been known that the single crystal of Tb$_{0.3}$Dy$_{0.7}$Fe$_2$ has the best magnetostrictive properties and has the largest magnetostriction strain in the $\langle 111 \rangle$ direction. Therefore, various growth techniques, such as Bridgman method [2], floating-zone method [3], and Czochralski method (CZ) [4–8] have been used to prepare single crystals. In previous reports, single crystals of Tb$_{0.3}$Dy$_{0.7}$Fe$_2$ were obtained by Czochralski technique [9] and floating-zone method [4]. However, various defects, such as WSP, RFe$_3$ (R stands for rare earth) second phase, and twins are still very easy to be generated in the grown crystals, because of the peritectic melting of the material. An incongruent growing
environment, R-rich starting composition has to be used to avoid the peritectic reaction, in which rare earth-rich inclusions might be caused due to unstable growth. Those defects could cause polycrystallization and dramatic decrease of the magnetostriction [10]. We report here on the formation mechanism of defects in Tb₀.₃Dy₀.₇Fe₂ and optimum growth conditions used for its single crystal growth. The achievement of these conditions is based on the detailed observation and investigation of the formation mechanism of the various defects. The experimental results have been discussed taking into account the phase relationship and the stable growth theory based on the normal freezing model.

2. Experimental procedures

Single crystals of Tb₀.₃Dy₀.₇Fe₂ were grown by the MCGS-3 CZ system with magnetic levitation cold crucible [9]. Growth rates of 2–45 mm/h and rotation rates of 20–30 rpm were used, respectively. Starting materials were prepared with the composition of \( y = 1.4–2 \) for Tb₀.₃Dy₀.₇Fe₂. An infrared thermometer measured the in situ temperature gradient at the growing interface. In the present work, temperature gradients were varied in a range of 110–140 \(^\degree\)C/cm. The conventional decanting technique [11] has been modified in order to observe the interface morphology. During the growth period, growing crystals under given conditions were extracted from the melt quickly. In this way, the in situ morphology of the solid–liquid interface would be observed at the end of the grown crystals and then could be clearly observed by scanning electron microscopy (SEM).

The exact orientation of the growing crystal rods was determined by X-ray Laue back-reflection technique. The slices with the important crystallographic directions were cut from the different positions of the growing rods for various examinations. Chemical etching agent of Nital’s (2% nitric acid in ethanol) has been employed for clearly revealing the grown defects, such as WSP, RFe₃ strips, twin lines, and rare earth-rich inclusions. Composition analysis was determined by inductive coupled plasma atomic emission spectroscopy. SEM and optical micrography were used for interfaces and etched slices observation.

3. Results and discussion

Single crystals of Tb₀.₃Dy₀.₇Fe₂ have been obtained with diameters of 6–12 mm and a maximum length of about 80 mm, as shown in Fig 1. The optimized conditions have been experimentally found for single crystal growth, as shown in Table 1. One can see that the optimized growth occurs in a quite narrow range. This is due to the limitation from the complicated phase relations of this system, such as homogeneous range, peritectic reaction and unstable growth as discussed below. By using the optimized growth parameters, the defect-free single crystals of Tb₀.₃Dy₀.₇Fe₂ can be obtained reproducibly. Earlier work [12] has reported that the measured magnetostriction on \( <111> \) oriented single crystal of Tb₀.₃Dy₀.₇Fe₂ were \( \lambda_{111} = 1640 \times 10^{-6} \) in free samples and \( 2375 \times 10^{-6} \) in 24 MPa pre-stressed samples, respectively.

Investigations of the phase diagrams of Tb–Fe [13], Dy–Fe [14] and (Tb, Dy)Fe₂ [15] indicated that (Tb₀.₃Dy₀.₇)Fe₂ solidified with peritectic reaction which is very harmful for single crystal growth. The product of the peritectic reaction is the RFe₃ interlaying in the host as a second phase. On the other hand, in order to avoid the peritectic

Fig. 1. Single crystal rods of Tb₀.₃Dy₀.₇Fe₂ grown by CZ technique with cold crucible. Grid size is 1 mm.
reaction, the starting material is usually a rare earth-rich composition [16], which may cause unstable growth [9]. Peritectic reaction and unstable growth cause different defects in the grown crystal. Therefore, it is important to investigate the formation mechanism of the various defects for growing high quality crystals of (Tb0.3Dy0.7)Fe2.

Our experimental results indicate that the peritectic reaction occurred, and that the second phase is (Tb,Dy)Fe3, when the composition of the melt is iron-rich, stoichiometrical, or even slightly R-rich. The RFe3 phase is formed in two kinds of morphology: thin and needle-like networks, the WSP [15], and the relative large dimension of strip, as shown in Fig. 2. SEM back-scattered electron micrography revealed that these two second phases have the same Fe content. When the starting composition was $y = 1.90$, only needle-like WSP appeared. Fig. 2a shows the WSP in a crystal grown near the [1 1 1] direction. One can see that the WSP of RFe3 shows a regular triangular array, which is apparently consistent with the crystallographic orientation of the host phase of RFe2. It implies that these WSP were not solidified with the host at the same stage of growth, and most likely were precipitated after the host had been solidified. The crystallographic configuration of the WSP reveals an anisotropy for forming the WSP by a diffusion mechanism in the solid state. This conclusion is consistent with the observation in Westwood’s work [15]. They found that the annealing treatment could create WSP in casting polycrystalline samples, thus they concluded that the homogeneous range of RFe2 shifts to the rare earth side below the melting point [15].

RFe3 strips in the grown crystal have been observed accompanying high density of WSP when the starting composition is $y = 1.95$ (Fig. 2b). These strips are different from WSP with a significant increase in the dimension (about 10–20 μm), although they belong to the same phase. One can see that the WSP defect on the background is still related to the orientation of the crystal ([1 1 2]), while the configurations of RFe3 strips are independent of the crystalline orientation. It indicates that they were formed in the solidification stage of the melt, rather than during

<table>
<thead>
<tr>
<th>Starting composition</th>
<th>$x = 0.3$</th>
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<tbody>
<tr>
<td>(Tb0.3Dy0.7)Fe2</td>
<td>$y = 1.78–1.85$</td>
</tr>
<tr>
<td>Crystal composition</td>
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</tr>
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<td></td>
<td>$y = 1.98–2.01$</td>
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<tr>
<td>Growth rate(a)</td>
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<tr>
<td>Rotation rate</td>
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<tr>
<td>Temperature gradient</td>
<td>110–140 °C/cm</td>
</tr>
<tr>
<td>Growth direction</td>
<td>(111), (112), (100), (110)</td>
</tr>
</tbody>
</table>

\(a\) $g$ stands for the solidified portion of the starting material.

Fig. 2. SEM back scattered micrography of WSP (a) and RFe3 strips (b) on the etched [1 1 1] oriented slices.
the annealing as the WSP. Their geometrical shapes may be controlled by the morphology of the interface. The existence of the strip-like RFe$_3$ indicates that a strong peritectic reaction occurred during the solidification of the melt. The coexistence of WSP and the strip-like RFe$_3$ observed in some samples shown in Fig 2b, also proves that they were formed during different stages of growth and by different mechanisms. Therefore, WSP usually allows the subsequent single crystal growth, but RFe$_3$ is really harmful with accompanied subgrain boundaries and polycrystalline grains in the grown crystals. This is the reason why a R-rich starting composition is widely adopted for the crystal growth of Tb$_{0.3}$Dy$_{0.7}$Fe$_2$. In this work, the R-rich composition around $y = 1.80$ is selected in the optimized conditions as shown in Table 1.

However, a rare earth-rich composition may raise another serious problem, namely constitutional supercooling, which affects single crystal growth. Stable growth has a planar growing liquid/solid interface, but unstable growth creates uneven interface morphologies, such as facets or cells, or other corresponding defects. In order to investigate the mechanism of defects formed in an unstable growth state, crystals have also been grown purposely under some unstable growth conditions. Setting an unstable growth condition is mainly by using a low temperature gradient beyond the optimized growth condition used in this work. In this way, two kinds of defects, lamella twins and rare earth-rich inclusions, have been found in such unstable growth processes.

Fig. 3a shows that the interface was found when intentionally unstable growth was set by decreasing the temperature gradient from 120°C/cm to 90°C/cm along the [1 1 2] direction. The morphology was structured with cells having roof-like facets and equilateral triangular steps were found on the facet surfaces. It is known that the orientation of the facet is a non-preferential growth direction [17], so there are only the [1 1 1] facets in this cubic system. This is a typical twined growth for the cubic structure compounds in the unstable state [17]. The corresponding defect on the etched slice is lamella twins, as shown in Fig. 3b. If the unstable growth conditions become more serious, the cellular shaped interface changes to a form shown in Fig. 4a formed in the [1 1 2] oriented growth. Due to the serious unstable environment, the valleys shown in Fig. 3a became deeper gaps and the [1 1 1] facets are out of order, and the solidification turned into more irregular cellular growth process. The anisotropy of the growth rate shaped the cells as sheets. The typical defects in this case are also lamella twins, but sandwiching with rare earth-rich inclusions, as shown in Fig. 4b, which was observed in the Tb$_{0.3}$Dy$_{0.7}$Fe$_2$ crystals grown by the Bridgman method [2]. The thick dark strips are inclusions...
filled in the gaps between the RFe$_2$ main phase sheets. The thin and straight lines are twins. In addition, a multi-twined structure and discontinued twin lines were caused by the irregular interface. The different widths of the twin lines between Figs. 3b and 4b stemmed from the different chemical etching conditions.

The unstable growth shown in Figs. 3 and 4 is due to the frozen driving force beyond the interface bigger than that at the interface. If the excess rare earth is treated as “impurity” and its average concentration in the melt during the growth is noted as $C_m$, based on the normal freezing theory and the corresponding assumptions, a criterion for stable growth is [18]

$$G/f \geq -(m/D)(C_m - C_s)\exp[f/\delta D], \quad (1)$$

where $G$, $f$, $\delta$, $m$, and $D$ are the temperature gradient, growth rate, thickness of the boundary layer, slope of the liquidus and the diffusion coefficient of the impurity in the melt, respectively. $C_s$ stands for the concentration of the impurity in the solid phase. Eq. (1) indicates that an unstable growth can be avoided by using a relatively high temperature gradient and a relatively low growth rate. In this work, the optimized growth conditions have been experimentally obtained by using temperature gradients of $G = 110$–$140^\circ$C/cm and various growth rates $f = 10$–$30$ mm/h. Fig. 5 shows the results using the various growth rates, starting compositions, and a constant temperature gradient of $120^\circ$C. One can see that the rare earth-rich compositions of $y = 1.90$ have to be employed to avoid the strip-like RFe$_3$ phase. For $G = 110$–$140^\circ$C/cm and $f = 10$–$30$ mm/h, the optimized starting composition should be Tb$_{0.3}$Dy$_{0.7}$Fe$_y$ ($y = 1.78$–$1.85$). Under those conditions, the peritectic reaction can be avoided by using rare earth-rich growth environment and the unstable growth can also be suppressed by selecting appropriate temperature gradients and growth rates. Fig. 6 shows the chemical etched [1 1 1] cross surface observed by optical microscopy. The
sample was cut from the single crystal grown under the conditions of growth rate 30 mm/h, \(G = 125^\circ\text{C/cm}\), and starting composition of \((\text{Tb}_{0.3}\text{Dy}_{0.7})\text{Fe}_{1.95}\) selected from the condition relation shown in Fig. 5. One can see that none of the defects of RFe\(_3\) or twins can be observed by the heavy chemical etching, which shows a good growth environment.

4. Conclusions

Single crystals of \(\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_2\) have been obtained by using the optimum growth conditions. Although WSP and strip-like iron-rich second phase belong to the same compound of RFe\(_3\), they were generated at different stages of growth. The WSP originated from the precipitation in solid state of the host, while the strip-like RFe\(_3\) was produced by the peritectic reaction. When the growth proceeds in a non-stoichiometric environment, using rare earth-rich composition in the starting materials, the unstable growth state might be caused by a relatively low temperature gradient and/or a relatively high growth rate. Two kinds of defects, lamella twins and inclusions, are produced during growth. Their geometrical morphologies strongly depend on the crystallographic orientation of the grown crystal. The condition for stable growth based on the normal freezing theory suggests a gradual lowering. The optimized growth parameters have been confirmed experimentally in this way.

Acknowledgements

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References