

Crystal growth of Gd_2PdSi_3 intermetallic compound

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Abstract: Gd_2PdSi_3 single crystals were grown by a vertical floating zone method with radiation heating at a zone traveling rate of 3 mm/h. The compound exhibited congruent melting behavior at a liquidus temperature of about 1700 °C. The slightly Pd-depleted composition of the crystal, with respect to the nominal Gd_2PdSi_3 stoichiometry, led to gradual accumulation of Pd in the traveling zone and to a decreasing operating temperature during the growth process. Thin platelet-like precipitates of a GdSi phase were detected in the stoichiometric feed rod growth crystal matrix which can be reduced by annealing treatment. Feed rod composition shift crystal growth was proved to be a better way of getting high quality of Gd_2PdSi_3 single crystal.

Key words: Gd_2PdSi_3 ; floating zone technique; single crystal growth; rare earth compounds; precipitates

1 Introduction

The class of R_2TSi_3 intermetallic compounds (R =rare earth, T =transition metal) with hexagonal AlB_2 -type crystallographic structure are well studied because of their interesting physical properties and their potential application in semiconductor [1,2]. First, tri-arc Czochralski method was applied to grow this class of compounds Ce_2PdSi_3 [3], then floating zone (FZ) techniques with radio frequency inductive heating were successfully applied for compounds with Ce, Tb, Dy and Ho [4–7]. The floating zone (FZ) method with optical radiation heating was applied to grow this class of compounds due to its containerless melting and high stability of the floating zone. Another benefit of the radiation heating method is the applicability of high pressures of the Ar atmosphere in the growth chamber, which reduces the evaporation losses and enables the growth of the compound containing the volatile element. Measurements on single crystalline R_2PdSi_3 specimens have revealed considerable anisotropy of the magnetic behavior, giant negative magnetoresistance, and even magnetocaloric properties [3,7–11].

Till now, high quality Gd_2PdSi_3 single crystal has not been grown and studied. The aim of the present work is to get high quality single crystal of Gd_2PdSi_3 compound through vertical floating zone technique. Magnetic measurements on polycrystalline samples of Gd_2PdSi_3 are quite interesting and complicating. Therefore, Gd_2PdSi_3 single crystals are highly desirable for discovering the basic properties.

2 Experimental

Stoichiometric feed rods of Gd_2PdSi_3 were prepared in a two-step melting process, which reduced possible evaporation losses at high temperature. First, a binary PdSi_3 alloy was arc melted on a water-cooled copper hearth under a Zr-gettered Ar atmosphere from bulk pieces of 99.95% Pd and of 99.9999% Si (mass fraction). The button of PdSi_3 alloy was co-melted with an appropriate portion of 99.99% Gd in a Hukin-type copper cold-crucible and cast into a 6 mm diameter feed rod with length of 55 to 70 mm. The FZ crystal growth process with radiation heating was performed in a laboratory type apparatus URN-2-ZM (MPEI, Moscow) with a vertical double ellipsoid optical configuration

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and a 5 kW air-cooled xenon lamp positioned at the focal point of the lower mirror [4]. The growth process proceeded in a vacuum chamber under 0.1 MPa flowing Ar atmosphere purified with a Ti-getter furnace leaving oxygen content less than 1×10^{-6} . Axially symmetric counter-rotation of crystal (30 r/min) and feed rod (10 r/min) and growth rates from 3 to 5 mm/h were applied to growing Gd_2PdSi_3 single crystals of about 6 mm in diameter and up to 20 mm in length. The operating temperature of the floating zone and longitudinal temperature profiles were measured in situ with a two-color pyrometer by a stroboscopic method, which enabled a proper control of the growth process [12].

The orientation of single crystals was determined by the X-ray Laue back scattering method. Composition, microstructure and crystal perfection of the samples were investigated by optical microscopy on a polarization microscopy Axiovert 25 equipped with a Carl Zeiss digital camera, and scanning electron microscopy (SEM) Philips XL 30. The composition of crystals was characterized by electron probe microanalysis (EPMA) applying the EDX-mode. The phase constituents of the quenched last zone were determined for revealing principal features of the crystallization process.

3 Results and discussion

3.1 Stoichiometric Gd_2PdSi_3 crystal

Figure 1(a) shows stoichiometric Gd_2PdSi_3 crystal grown from the left to the right hand side by the FZ method. The FZ growth process lasted 9 h under 0.1 MPa flowing Ar atmosphere at an initial operating temperature of about 1830 °C. A traveling speed of 5 mm/h was applied in the first 4 h, and then the traveling speed was reduced to 3 mm/h when the growth

process had stabilized. A cast polycrystalline rod (Fig. 1(b)) was used as a seed. The cross-section of the crystal before the end of growth process, shown in Fig. 1(c), exhibits a large single crystalline region which covers nearly the whole cross-section. Near the surface tiny parasitic grains are visible in the optical image in polarized light. This may be associated with the disturbance of a cylinder symmetric temperature field due to the faceted growth of the crystal. The facets are formed from the seed with circular cross-section when coarse grains penetrate to the rod surface after the start of FZ process. They are still more pronounced in the single crystal [13]. SEM image reveals minor volume fraction of platelets with very small thickness of binary GdSi phase in the crystal (Fig. 1(d)). They are not formed during the crystallization but precipitated on post-solidification cooling from the Gd_2PdSi_3 matrix because of the retrograde solubility of Gd and Si through our experiences. Annealing treatment at 1100 °C for 20 h was applied to the crystal, and the SEM image shows that the volume fraction of GdSi phase is obviously reduced but not eliminated (Fig. 2).

The obvious alignment of the striations in the stoichiometric crystal corroborates that they are not formed during the crystallization but precipitated on post-solidification cooling from the as-grown crystal matrix because of the retrograde solubility of Gd_2PdSi_3 analogous to other members of this class of intermetallics [4,5].

3.2 Composition shift of $\text{Gd}_{33.1}\text{Pd}_{16.9}\text{Si}_{50}$ crystal

In order to get high quality Gd_2PdSi_3 crystal which is nearly free of GdSi precipitate phase, feed rod with a composition of $\text{Gd}_{33.1}\text{Pd}_{16.9}\text{Si}_{50}$ was chosen. In Fig. 3 Gd_2PdSi_3 crystal grown by the FZ method is shown

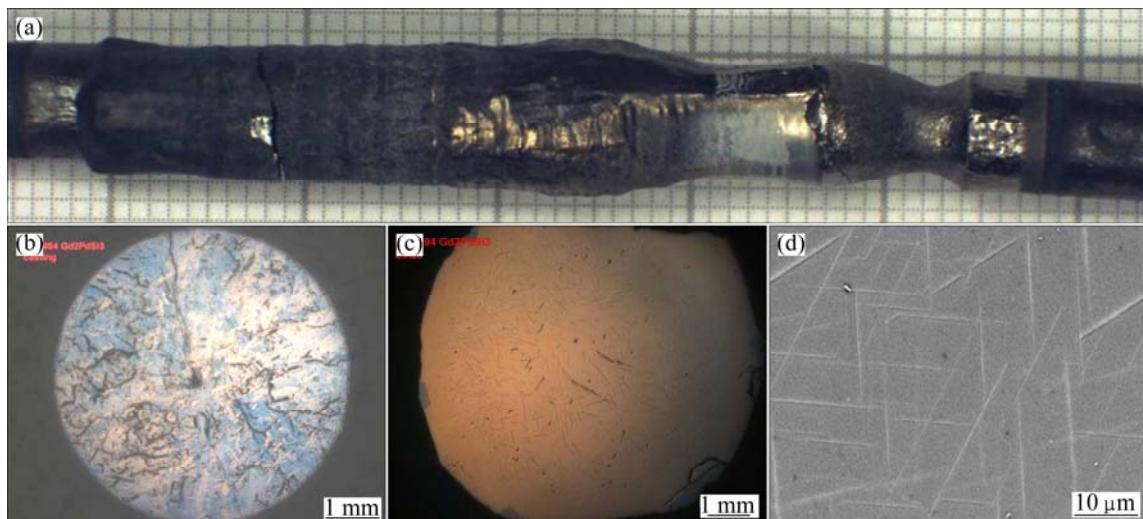


Fig. 1 Image of Gd_2PdSi_3 crystal grown by FZ method from stoichiometric composition (a), cross-sectional optical image of polycrystalline feed rod (b), cross-sectional optical image of crystal near the end of Gd_2PdSi_3 crystal (c) and SEM image of grown Gd_2PdSi_3 crystal with small thickness of well oriented GdSi phase (d)

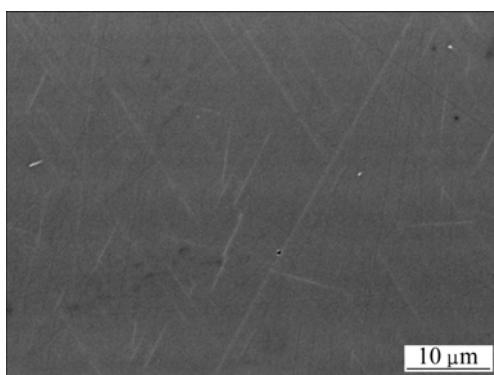


Fig. 2 SEM image of Gd_2PdSi_3 crystal after annealing treatment

along with two cross-sections. The FZ growth process lasted 9.5 h under 0.1 MPa flowing Ar atmosphere at an initial operating temperature of about 1775 °C. A stable growth speed of 3 mm/h was chosen during the process. Figure 3(a) displays the crystal, which was grown from the left to the right side. A polycrystalline rod with several big grains from a previous growth experiment was used as a seed. Because of the high stability of the floating zone during growth with optical radiation heating, the crystal surface is rather smooth. The last quenched zone, Fig. 3(b), illustrates the good grain selection from the coarse-grained microstructure (left) to nearly single crystal (right). The convex interface of the crystal toward the melt in floating zone process usually indicates proper grain selection and stable growth. The section is comprised of dendrites of the Gd_2PdSi_3 principal phase along with a dark matrix of the GdPd_2Si_2 phase [13–15] which is composed of $(21.2\pm0.5)\%$ Gd, $(29.7\pm0.5)\%$ Pd, and $(49.1\pm0.5)\%$ Si (mole fraction) with a tetragonal Al_4Ba type structure and inclusions of tiny Si particles. The absence of primary phase reveals congruent melting behavior of Gd_2PdSi_3 , which is

consistent with other members of R_2PdSi_3 intermetallics. The cross-section of the crystal at the end of growth process, shown in Fig. 3(c), exhibits a large single crystalline region which covers nearly the whole cross-section. SEM image shows that the crystal is of high quality, nearly free of platelet GdSi phase (Fig. 3(d)). It proves that, compared with annealing treatment, the composition shift is a better way to get high quality crystal.

The operating temperature of the floating zone during the growth process of a Gd_2PdSi_3 crystal, which was measured by a two-color pyrometer, is shown in Fig. 4. The length coordinate $z=tv$ along the crystal is related to the processing time t and the zone traveling velocity v ($v=3$ mm/h). At the beginning, the zone temperature is about 1770 °C, but it is gradually diminished after about 6 mm crystallization length. The time averaged signal visualizes more clearly the continuous decline of the zone temperature with proceeding time. The total temperature drop reached almost 100 °C during the growth process. One obvious reason for the change is the drift in melt composition of the traveling zone at fixed zone length. It is proved by EDX that there are three phases in the melt, Gd_2PdSi_3 phase, GdPd_2Si_2 phase and tiny Si phase. That is, the melt composition of the traveling zone is gradually enriched in Pd with progressing growth. The reason for the accumulation of Pd in the melt is the slightly Pd-depleted growing crystal as described below. The continuous composition shift of the floating zone implies a gradual slope down of the operating temperature of the crystallization, which seemingly originates from the decreasing liquidus temperature with rising Pd concentration similar to the Er-Pd-Si phase diagram [16].

The recorded axial temperature profile across the floating zone measured from the feed rod toward the crystal immediately after beginning of its growth is

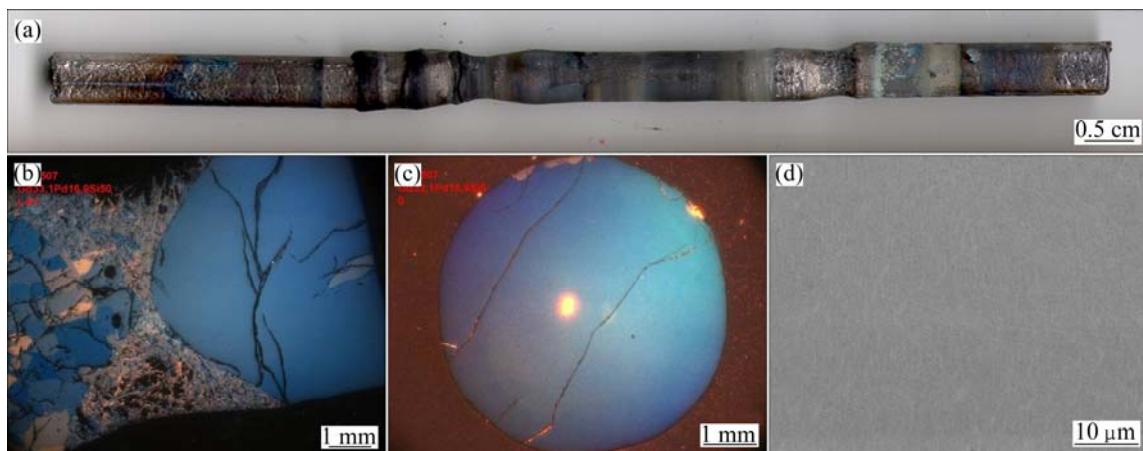


Fig. 3 Image of Gd_2PdSi_3 crystal grown by FZ method from shift composition of $\text{Gd}_{33.1}\text{Pd}_{16.9}\text{Si}_{50}$ (a), optical image in polarized light of longitudinal section of the last quenched zone (b), cross-sectional optical image of crystal near the end of Gd_2PdSi_3 crystal (c) and SEM image of grown Gd_2PdSi_3 crystal (d)

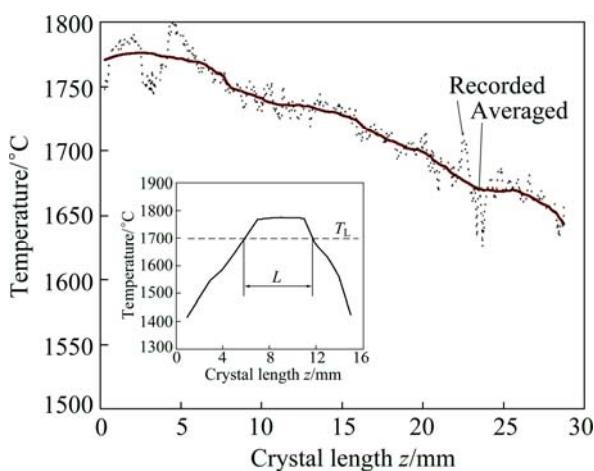


Fig. 4 Operating temperature of floating zone during growth process of Gd_2PdSi_3 crystal (dashed line) and time averaged temperature course (solid line) (Inset: Recorded axial temperature profile across floating zone measured from feed rod (left) to crystal after the start of growth process, where the observed zone length L and the estimated liquidus temperature $T_L \approx 1700$ °C are indicated)

shown in the inset of Fig. 4. The temperature profile in the molten zone is flat, but it transits to steep gradients in the adjacent crystal and feed rod. If we compare the temperature profile with the zone length ($L \approx 6$ mm) evaluated from the video images, we can roughly estimate a liquidus temperature $T_L \approx 1700$ °C of the compound, which is well above the liquidus temperature of other R_2PdSi_3 compounds [5]. This corresponds to a typical overheating of 70 °C of the melt in the floating zone. A more accurate determination of T_L for the Gd_2PdSi_3 compound by differential thermal analysis is hampered by the high reactivity of the melt with crucible materials at elevated temperature. From the recorded temperature profile, the temperature gradient at the growing interface of the crystal $dT/dz = 80$ °C/mm can be calculated approximately. This steep gradient is typical for the vertical FZ technique characterized by a sharply focused radiation profile [13–16]. This is a prerequisite for the suppression of the morphological instability of the crystal/melt interface at moderate growth rates despite the sizeable composition difference between the crystal and the melt in the floating zone.

3.3 Characteristics of Gd_2PdSi_3 crystal

The X-ray Laue back scattering images proved the hexagonal AlB_2 -type structure of the Gd_2PdSi_3 crystal. They do not show twinning or stress distortions of the bulk crystal and confirm its high perfection (Fig. 5). The crystallographic orientation of the rod axis is basically along $\langle 100 \rangle$ direction within the basal plane of the hexagonal unit cell. The composition of the crystal

matrix determined by EPMA was $(34.0 \pm 0.5)\%$ Gd, $(16.0 \pm 0.5)\%$ Pd, and $(50.0 \pm 0.5)\%$ Si. It turned out that the crystal is slightly Pd-depleted compared to the nominal stoichiometry, which is similar to other R_2PdSi_3 compounds. However, the element segregation within the crystal is inferior. Figure 6 shows the oriented Gd_2PdSi_3 single crystal with a flat (110) plane and inclined (010) plane. The following magnetic properties measured on the single crystal will be reported later.

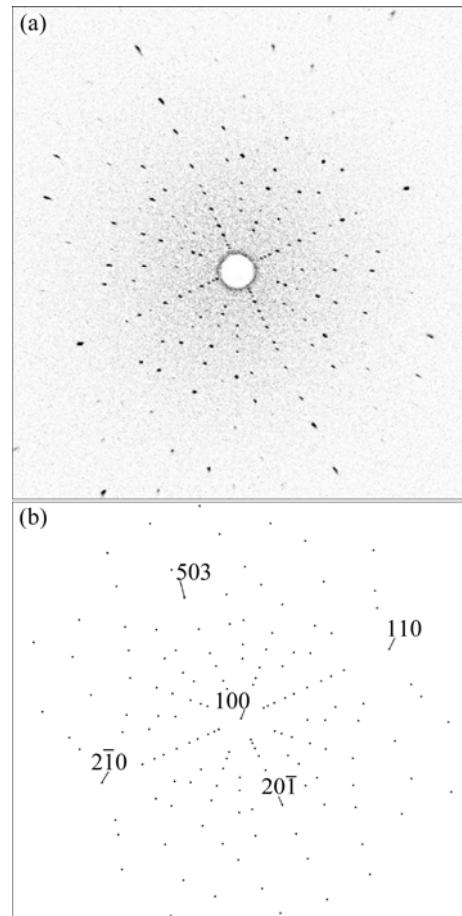


Fig. 5 X-ray Laue back scattering diffraction pattern of Gd_2PdSi_3 single crystal with main reflections (a), simulation of pattern showing that rod axis is basically along $\langle 100 \rangle$ orientation of hexagonal unit cell (b)



Fig. 6 Oriented Gd_2PdSi_3 single crystal

4 Conclusions

1) Gd_2PdSi_3 single crystals were grown by a vertical FZ method with radiation heating. The compound exhibited congruent melting behavior at a high liquidus temperature of about 1700 °C. This enabled crystal growth at a moderate zone traveling rate of 3 mm/h.

2) The actual crystal composition was slightly depleted in Pd. Therefore, the gradual accumulation of Pd in the traveling zone led to a decrease of the operating temperature during the growth process. The crystal matrix contained platelet-like precipitates of GdSi phase, which arose from the retrograde solubility of the Gd_2PdSi_3 matrix phase.

3) Feed rod composition shift crystal growth was proved to be a better way of getting high quality Gd_2PdSi_3 single crystal. The X-ray Laue back scattering images proved its hexagonal AlB_2 -type structure and high perfection.

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三元稀土硅化物 Gd_2PdSi_3 单晶生长

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摘要: 采用光悬浮区熔法以 3 mm/h 的生长速度制备 Gd_2PdSi_3 单晶。该化合物表现为同成分熔融, 其熔点在 1700 °C 左右。与 Gd_2PdSi_3 化学计量成分相比, 制备的晶体中 Pd 含量略低, 导致了熔区内 Pd 的富集以及实验过程中熔区温度的降低。采用标准成分给料棒制备的单晶内含有少量定向的 GdSi 沉淀, 可以通过退火热处理减少其含量但并不能完全消除。采用给料棒成分微调的方法制备出不含 GdSi 沉淀的高质量 Gd_2PdSi_3 单晶。

关键词: Gd_2PdSi_3 ; 悬浮区熔; 单晶生长; 稀土化合物; 沉淀