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Solidification study of vertical float zoned $CeCu_2Si_2$

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Abstract

The heavy fermion compound $CeCu_2Si_2$ has been prepared by the vertical float zone technique. A detailed microstructural study has been carried out on both zoned and subsequently annealed samples. The vertical float zoned sample prepared from nominal copper excess alloy shows large columnar grains with good crystallinity. Examination of the as-grown samples reveals the existence of an inter-dendrite Cu-rich phase in all samples; this phase is significantly reduced by subsequent annealing. The results are discussed in conjunction with the phase diagram and the solidification process.

1. Introduction

The ternary compound $CeCu_2Si_2$, which crystallizes in the tetragonal $ThCr_2Si_2$ structure, shows a variety of unusual superconductive and magnetic properties [1]. The observation of these novel phenomena, however, is complicated by their delicate dependence on sample quality [2]. Experiments [3,4] have already revealed some controversial results from various samples prepared with different techniques. Although some efforts have been made to produce good quality crystalline samples of this ternary compound, the extent of success is limited and, in particular, the microstructural development during crystal growth and subsequent annealing is unknown.

Thin plate-like crystal samples of millimetre size have been obtained by the Bridgman technique with either alumina or BN crucibles [5,6]; and the Czochralski method with either BN or W crucibles under high pressure (~10 atm) [7]. However, some of the crystal samples have a deficiency in Cu and show no superconductivity [4]. Other investigations indicated that small copper deficiencies can dramatically affect the superconducting properties of the compound [8,9]. Therefore, it was suggested that only samples prepared from copper excess alloys exhibit superconductivity, although characterization of the samples showed no significant deviation of the composition from stoichiometry [6].

Recent work [10] on horizontal cold boat zoning has achieved $CeCu_2Si_2$ single crystal samples of size up to $2 \times 2 \times 2$ mm^3 from copper excess alloys. Although a very slow zoning rate (~5 mm/h) has been used during the horizontal zoning, the effect of cold boat chilling could dramatically reduce the large temperature gradient across the solid–liquid interface and lead to thermal instability. It is obviously an advantage if the application of vertical free standing float zoning can be adapted to the preparation of this compound.

In this work, experiments on single crystal growth of $CeCu_2Si_2$ compound have been carried out by vertical float zoning; and, in particular, the microstructure of the as-grown samples was characterized by optical and transmission electron microscopy (TEM) in order to assess the factors influencing the quality of the crystals. The effect of heat treatment on the redistribution of secondary phases is discussed.

2. Experimental details

The master alloys used throughout this research were prepared from high purity start materials by arc melting. The vertical float zoning (VFZ) was conducted on 8-mm diameter rods under purified Ar at 1.5 atm. Once the molten zone, which was controlled at about 8 mm wide, was stable, the rod was driven downwards to pass through the RF concentrator at a steady speed [11]. Heat treatment on VFZ samples was performed by sealing the samples in a Ta can and then annealing in a vacuum furnace.

3. Results

Preliminary work on vertical float zoning indicated that it is necessary to use nominal copper excess alloys in order to maintain a slow and stable zoning, which is consistent with previous results [6,10]. Microstructural

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examination of a sample zoned from an alloy with nominal composition of $CeCu_{2.5}Si_2$ at a rate of 38 mm/h shows that the as-grown sample consists of many columnar grains with size up to 2–4 mm across. Each grain contains small parallel dendritic sheets with thin inter-dendrite phase (Fig. 1(a)). Composition analysis on the SEM indicates that the inter-dendrite phase is Cu-rich with less than 5 at.% Si. Discontinuities of the dendritic structure have been observed along the zoning axis although the size of the columnar grains was unchanged. The regions showing the discontinuity of the dendritic structure show no secondary phase but many small cracks, which suggests that the lack of the ductile Cu-rich phase between the dendrites increases the formation of the thermal cracks. This regular discontinuity of dendritic structure has been noticed in some vertical float zoned Terfenol-D compound [12], which was suggested to form by a peritectic reaction [13].

The dendritic structure is the dominant feature in all vertical float zoned samples despite the composition variation. Microstructural studies on samples zoned from alloys with nominal composition close to stoichiometry or slightly Cu-deficient alloys indicate that there is still some inter-dendrite Cu-rich phase present co-existing with many granular phases. Compositional analysis by SEM/EDX confirms that the granular phase is Ce_2CuSi_3.

Further experiments with a zoning rate of 18 mm/h show that even samples prepared from nominal composition of $CeCu_{2.6}Si_2$ contain numerous granular Cu-deficient phases due to the prolonged evaporation of copper (the vapour pressure of copper at the solidification temperature (~1545 °C) is about 0.5 mbar). However, when the copper content increased to a nominal composition of $CeCu_{2.8}Si_2$, the as-zoned sample shows a few large columnar grains of about 2.5 mm across with very little internal dendritic structure (Fig. 1(c)). Single crystals of the size of $2 \times 2 \times 5$ mm^3 have been achieved from this slowly zoned sample.

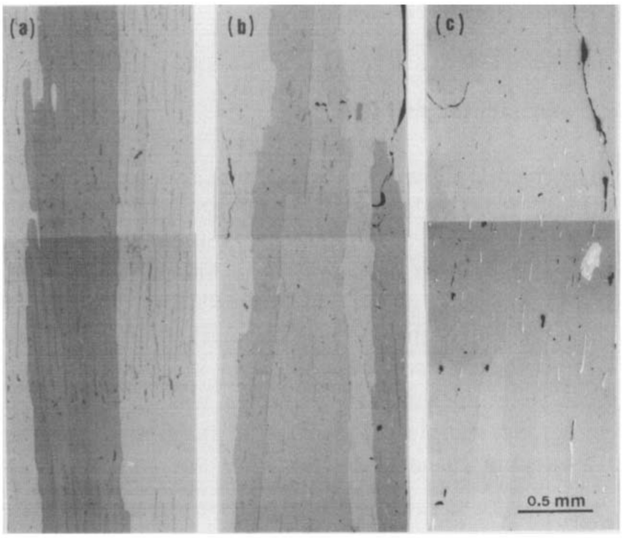

Fig. 1. Optical micrographs of the longitudinal section of (a) $CeCu_{2.5}Si_2$ zoned at 38 mm/h showing the internal parallel dendritic structure and inter-dendrite Cu-rich phase, (b) VFZ $CeCu_{2.5}Si_2$ annealed at 900 °C for 20 days showing the reduction of the interdendrite Cu-rich phase; (c) $CeCu_{2.8}Si_2$ zoned at 18 mm/h showing the large columnar grains with less inter-dendrite Cu-rich phase.

Heat treatment on vertical float zoned $CeCu_{2.5}Si_2$ at 900 °C for 6 days shows that the inter-dendrite phase began to break up, although annealing at 800 °C for 3 days had little effect on them. After 20 days of annealing at 900 °C, the amount of Cu-rich phases is reduced significantly (Fig. 1(b)). However, annealing at 950 °C for 20 days led to the nucleation of new grains, which degraded the crystallinity of the zoned sample.

This observation suggests that suitable heat treatment at elevated temperature results in the dissolution of the inter-dendrite Cu-rich phase and improves the crystallinity of the as-grown samples. Since the annealing was carried out in a sealed Ta can, the loss of copper element is very limited. The total loss of copper element from the bulk sample was further hindered by the slow solid state diffusion through the matrix, although immediate copper evaporation on the sample surface might occur. The Cu-rich phase is, therefore, believed to diffuse into the matrix.

Further microstructural characterization has been carried out on a transmission electron microscope interfaced with an X-ray energy dispersive analysis (EDX) system. The thin inter-dendrite phases were revealed as plate-like phases with many fine internal precipitates and dislocations (Fig. 2(a)). EDX analysis with a focused electron beam of 20 nm confirmed that the inter-dendrite phase is Cu with about 3.8 ± 0.5 at.% Si and an undetectable amount of Ce, which is consistent with the SEM result. The total amount of silicon is within the solid solubility range in copper [14] and, therefore, believed to exist in solution. Since the internal precipitates (like GP type zones) are very small in size and embedded within Cu-rich phase, no diffraction or composition information has been obtained from an individual precipitate. The Cu-rich phase contains many internal dislocations as well as interfacial dislocations; this suggests that the relatively soft Cu-rich phase has been subjected to deformation during sample preparation and, thereby, releasing the thermal strains.

TEM analysis of the sample annealed at 900 °C for 20 days shows that the interdendrite phase is almost pure copper with about 1.5 at.% silicon in solution. In other words, the silicon present in the inter-dendrite phase has diffused into the matrix during high tem-

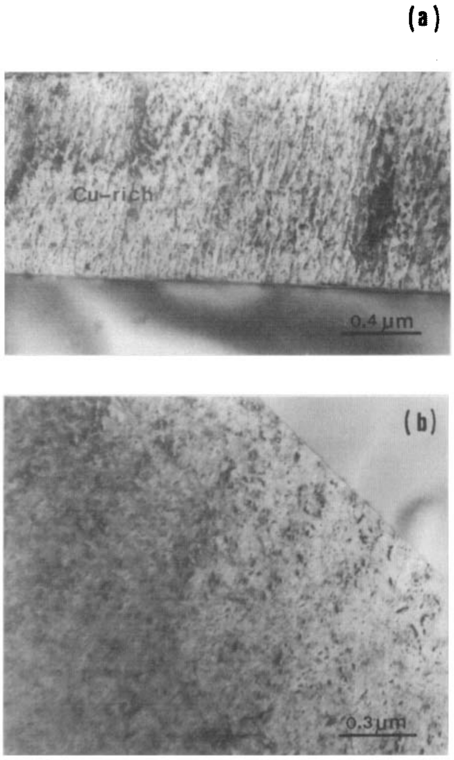

Fig. 2. Bright field TEM micrographs from $CeCu_{2.5}Si_2$ (a) as-zoned showing a plate-like inter-dendrite Cu-rich phase with small internal precipitates and dislocations, (b) after annealing at 900 °C for 20 days showing stable internal precipitates.

perature annealing. However, the small internal precipitates were hardly coarsened (Fig. 2(b)). By carefully focusing a small electron probe on an individual particle at very thin regions, a small Ce peak in the spectrum was just observable; this suggests that the internal precipitates are likely to be Ce-rich phases. The first compound in the Ce–Cu system is $CeCu_6$ [14], but we have insufficient evidence to establish the precise composition of the precipitates. Since Ce has extremely low solid solubility in copper, annealing at high temperature only resulted in slight coarsening of these precipitates. A few low angle grain boundaries, which are believed to be developed during annealing, have been observed with misorientation less than one degree.

4. Discussion and conclusions

Previous studies [8,9] on the phase diagram of Ce–Cu–Si indicate that $CeCu_2Si_2$ forms by a peritectic reaction at 1545 °C and the phase field is elongated in the Cu/Si direction although the exact phase diagram is not clear yet. Among many phases, Ce_2CuSi_3 was suggested to be the most stable compound in alloys prepared from the compositions close to $CeCu_2Si_2$ [8]. In this work, a large granular Ce_2CuSi_3 phase was only observed in samples prepared from Cu-deficient alloys or alloys with slightly nominal copper excess. However, the inter-dendrite Cu-rich phase commonly observed in samples prepared with various nominal composition has never been reported. No evidence of the $CeSi_2$ phase has been observed.

In order to discuss the observed microstructure in different compositions, the peritectic reaction of $CeCu_2Si_2$ may be simply represented by a pseudo-binary phase diagram with a Cu-rich end and Si-rich side (see Fig. 3). With copper excess alloys, the solidification is expected to occur by direct nucleation of the $CeCu_2Si_2$ phase with copper content close to stoichiometry. As the solidification proceeds, the composition of the melt shifts towards the copper-rich end and finally the melt solidifies as layers of Cu-rich phase between the dendrites. If the initial composition of the alloys is copper deficient or close to the stoichiometry, the solidification starts with the formation of Ce_2CuSi_3; and as the temperature drops just below the peritectic temperature, the remaining melt will react with the copper deficient phase to form $CeCu_2Si_2$. Since the peritectic reaction can never be completed due to the cooling rate, as the temperature drops further below the peritectic temperature, the remaining melt will solidify in the same way as those with nominal copper excess.

During a vertical float zone process, the solidification proceeds in a small proportion of the sample and creates a relatively large temperature gradient. However, the diffusion of the solute in the front of the solidification interface is limited. The observation of regions with no dendritic structure in the solidified microstructure suggests that the solidification interface might proceed in a rather planar mode, possibly due to the local solute segregation and large temperature gradient. However, the build-up of copper-rich solute in front of the

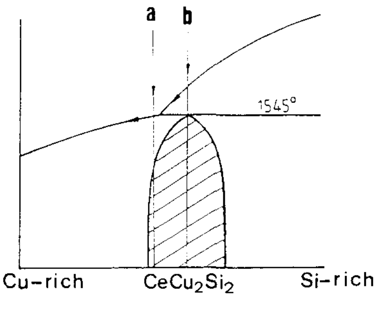

Fig. 3. A schematic illustration of a simplified Ce–Cu–Si phase diagram around $CeCu_2Si_2$ compound with a Cu-rich end and a Si-rich end. (a) $CeCu_2Si_2$ nucleates directly from the melt, as solidification proceeds, the composition of the remaining melt shifts to the copper-rich end; (b) the solidification starts with the formation of Cu-deficient phases, *i.e.* Ce_2CuSi_3, as the temperature cools down to the peritectic reaction, the composition of the melt shifts towards the Cu-rich end and finally solidifies in the same way as (a).

solid–liquid interface quickly disrupts the planar interface which is replaced by cellular solidification and consequent parallel dendritic sheets [15]. The dissolution of copper into the matrix during annealing indicates that the phase field of $CeCu_2Si_2$ may be wider at the annealing temperature than that at the peritectic temperature (see Fig. 3). However, the inter-dendrite Cu-rich phase may never dissolve completely into the matrix, in particular, in samples achieved by a near equilibrium solidification.

The formation of a granular Ce_2CuSi_3 phase in the zoned samples with composition close to stoichiometry suggested that the nucleation of the $CeCu_2Si_2$ phase occurs only in copper excess melt. The large granular phases (Ce_2CuSi_3) are always surrounded by a clear $CeCu_2Si_2$ matrix with composition very close to stoichiometry. However, the regions containing inter-dendrite phases show slight variations of the copper content. In as-grown $CeCu_{2.5}Si_2$, EDX analysis of the matrix on TEM gives an average copper content of 44 at.% which is beyond the elongated phase field of $CeCu_2Si_2$ given by Ishikawa *et al.* [8]. Nevertheless, the cerium content of the matrix remains almost constant. By annealing under a controlled atmosphere for a prolonged period just below the peritectic temperature, the peritectic reaction could further proceed by reducing the Ce_2CuSi_3 phase [10].

In summary, copper-deficient phases can be eliminated by increasing the nominal copper excess in order to promote the nucleation of the $CeCu_2Si_2$ phase. However, copper-rich inter-dendrite phases are commonly observed due to the strong segregation of copper during solidification. The microstructure of the crystal sample obtainable is determined by the formation of the dendritic structure. Annealing at high temperature leads to the partial dissolution of the inter-dendrite Cu-rich phase. Although the growth rate of a free standing vertical float zoning is restricted by the stability of the crystal growth apparatus, further improvement in the crystallinity may be achieved by employing slower growth rates under a controllable ambient pressure followed by a suitable annealing treatment.

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