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Influence of thermal treatment on the phase properties of $HoNi_2B_2C$

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Abstract

The influence of thermal treatment on the superconducting properties of the quaternary compound $HoNi_2B_2C$ and its correlation to the volume of the unit cell is investigated by X-ray diffractometry and ac-susceptibility measurements. Our results reveal that the annealing process carried out on arc-melted intermetallic samples of $HoNi_2B_2C$ strongly influences the interplay between superconductivity and magnetism in this compound. The re-entrant behaviour, observed for polycrystalline $HoNi_2B_2C$ samples annealed at 1100°C for 4 days, can be transformed into pure-superconducting behaviour by subsequent annealing at 800°C for 10 days and vice versa. The results can be explained by mutual substitution of atoms on lattice sites which varies the degree of the long-range crystallographic order. Partially irreversible behaviour can be attributed to the formation of vacancies on lattice sites. © 1997 Elsevier Science S.A.

Keywords: Phase properties; Superconductivity; Re-entrant behaviour; Long-range crystallographic order

1. Introduction

The quaternary intermetallic compounds RNi_2B_2C (R = Tm, Er, Ho and Dy) show interplay between superconductivity and magnetism. While co-existence between superconductivity and anti-ferromagnetic order is observed for the compounds with R = Tm, Er and Dy [1–5], re-entrant behaviour occurs for $HoNi_2B_2C$ [2,6]. After a transition into the superconducting state at around 7–8 K, the $HoNi_2B_2C$ system undergoes a partially re-entrant transition to the normal state at approximately 6 K due to a pairbreaking modulated magnetic structure [7,8]. At 5 K superconductivity is regained and co-exists with commensurate anti-ferromagnetic order at lower temperatures.

A further peculiarity of this compound is the fact that the superconducting behaviour of $HoNi_2B_2C$ is strongly sample dependent. For flux-grown single crystals only an ordinary superconducting transition has been observed in zero magnetic field [10–12] while for polycrystalline samples the described re-entrant behaviour occurs [2,6,9]. This can be understood from the existence of a homogeneity range of $HoNi_2B_2C$, where the physical properties vary as a function of phase composition meaning the chemical composition of the $HoNi_2B_2C$ phase. In a detailed study of this homogeneity range, we were able to show that different low temperature behaviour occurs in dependence on phase composition: re-entrant behaviour, co-existence between superconductivity and magnetism, and non-superconducting, magnetic behaviour [13,14]. These three '$HoNi_2B_2C$ states' are transformed into each other mainly by substitution effects due to changing phase composition. In order to shed more light on the occurrence of the different kinds of low-temperature behaviour, we carried out a study of the influence of the thermal treatment on the

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superconducting behaviour of the phase $HoNi_2B_2C$ for samples with equal phase composition.

2. Experimental

The samples were prepared from the elements in an arc-melting furnace under argon atmosphere. For thermal treatment, the samples were sealed in quartz capsules under 30 kPa Argon and annealed at different temperatures in a muffel furnace. Details of the annealing process will be discussed in the next section. All samples were characterized by X-ray powder diffraction patterns taken on a Seifert XRD 3000 P powder diffractometer equipped with secondary monochromator (CuKα radiation). The lattice parameters were refined with the method of least squares using Si as internal standard. The superconducting behaviour was determined by ac-susceptibility measurements at 18 Hz with an ac-amplitude of 1 Oe.

3. Results and discussion

The reason for carrying out thermal treatment on a sample prepared by arc-melting, is to establish a thermodynamic equilibrium state to get single phase samples at the annealing temperature and to tune the degree of long range crystallographic order (LRO). The degree of LRO is defined by the occupation of atomic positions. In a sample with a high degree of LRO, most atomic positions are occupied according to the chemical structure formula. In contrast, a sample with a low degree of LRO shows rather a statistical distribution of the atoms on the respective sites. An arc-melted sample prior to annealing exhibits a high amount of disorder, so that thermal treatment is necessary to establish an ordered state.

First, we determined the annealing temperature which is necessary to get single-phase samples in a reasonable period of time. The real part of the ac-susceptibility for different pieces of a sample with nominal composition $HoNi_{1.95}B_{2.05}C$, which were either in an as-cast state or annealed at 650°C, 950°C or 1100°C for 10 days, is shown in Fig. 1. For the as-cast piece of the sample and the pieces annealed at 650°C and 950°C no superconductivity is observed, while re-entrant behaviour occurs for the piece annealed at 1100°C.

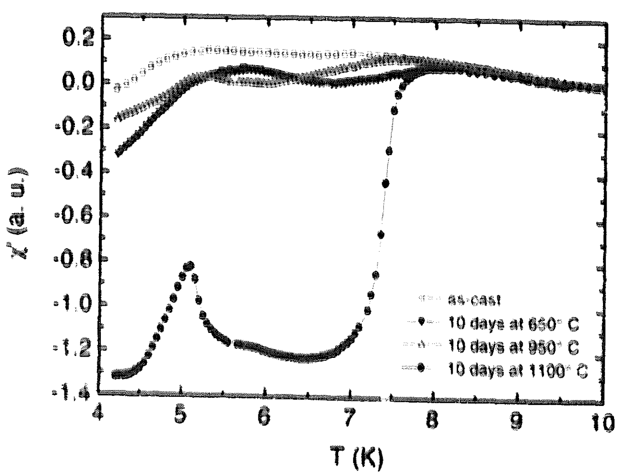

Fig. 1. Dependence of the real part of the ac-susceptibility on the annealing temperature for different pieces of a sample with nominal composition $HoNi_{1.95}B_{2.05}C$.

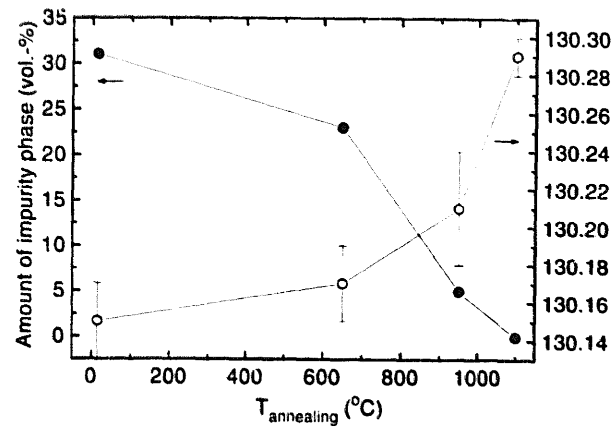

Fig. 2. Annealing temperature dependence of the amount of impurity phase (●) and of the volume V of the unit cell (○) for different pieces of a sample with nominal composition $HoNi_{1.95}B_{2.05}C$.

The amount of impurity phase (HoB_2C_2) present in the as-cast piece of the sample likely due to a thermodynamic non-equilibrium is approximately 30 vol% as estimated from integrated X-ray intensities. The volume fraction of the impurity phase decreases with growing annealing temperature, as can be seen in Fig. 2. The piece of the sample which shows superconductivity after annealing is essentially single-phase, indicating the presence of a thermodynamic equilibrium state. The volume of the unit cell, which is also shown in Fig. 2, increases in a non-linear fashion as a function of the annealing temperature.

Although the phase fraction of $HoNi_2B_2C$ is larger than 70 vol% in all investigated samples, which were annealed at temperatures lower than 1100°C, no superconductivity is observed. For all these non-superconducting pieces of the sample, the volume V of the unit cell is smaller than 130.21 Å³. This is in very good agreement with our previous measurements on $HoNi_2B_2C$ samples with varying phase composition, all annealed at 1100°C where the low-temperature behaviour could be correlated to the volume of the unit cell [13]. Non-superconducting behaviour was observed for $V < 130.2$ Å³, pure-superconducting behaviour for $V > 130.3$ Å³, and re-entrant behaviour for 130.2 Å³ $< V <$ 130.3 Å³. In the following, only results on single phase samples are considered.

Since any heat treatment for 10 days at temperatures below 1100°C is not sufficient to establish a thermodynamic equilibrium state in the sample, the following, modified annealing procedure was carried out. In the first step, a single-phase $HoNi_2B_2C$ sample, showing re-entrant behaviour at low temperatures, was produced by arc-melting and annealing at 1100°C for 10 days (see ac-susceptibility data in Fig. 3). After determining its superconducting properties the same sample was annealed again at 800°C and the superconducting properties were re-determined. This process was repeated at temperatures of 950°C and 1100°C. As can be seen in Fig. 3, re-entrant behaviour has vanished after post-annealing at 800°C and the sample is purely superconducting, while the transition temperature T_c is shifted about 1 K to higher temperatures. With further thermal treatment at 950°C, T_c decreases again, but the sample remains superconducting. A fourth annealing process at 1100°C causes a re-entrant maximum to form again at approximately 5 K. The re-entrant maximum after post-annealing the sample at 1100°C for 20 days has only about 50% of the starting value, showing that the described procedure is not totally reversible. T_c is higher than the initial value. The investigated sample was single-phase at all steps of the annealing procedure and only a very small change of the volume of the unit cell of 0.02 Å^3 is observed. This is indicative of the effects of LRO, which have been shown by Flükiger and Jorda to be of crucial importance in A15 compounds [15]. Unfortunately, the occupation of the B and C sites is difficult to establish from X-ray patterns. The observation that the re-entrant maximum increases with decreasing transition temperature confirms that the interplay between superconductivity and magnetism in the RNi_2B_2C series and especially in $HoNi_2B_2C$ is strongly influenced by the value of the ratio of the magnetic to the superconducting transition temperature T_N/T_c, which was determined by the investigation of Co-doped borocarbide compounds [16].

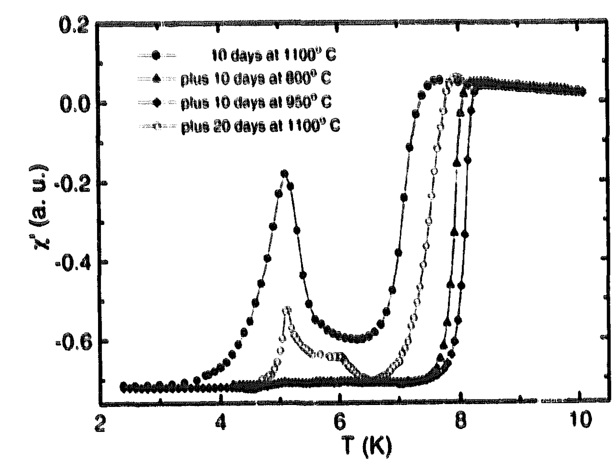

Fig. 3. Low temperature behaviour of the real part of the ac-susceptibility for a sample with nominal composition $HoNi_2B_2C_{1.1}$ after several annealing steps at different temperatures.

In summary, we have demonstrated that it is possible to transform re-entrant behaviour into pure-superconducting behaviour and vice versa by variation of the thermal treatment. This can be explained under the assumption that the shape of the boundary of the homogeneity range of $HoNi_2B_2C$ is temperature dependent. Therefore, it might be possible that the variation of the annealing temperature causes a mutual substitution of atoms on lattice sites (e.g. boron and carbon) and consequently a change of the LRO without changing the phase composition. The decrease of T_c with increasing annealing temperature indicates increased disorder on lattice sites and a lower degree of LRO. The partially irreversible behaviour might be interpreted with an evaporation of small amounts of atoms, due to the long duration of the thermal treatment of 50 days altogether and the associated occurrence of lattice defects.

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