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Anomalous melting behavior of polycrystalline bismuth quenched at high temperature and high pressure

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ABSTRACT

Under ambient conditions, bismuth (Bi) adopts a rhombohedral A7 structure, yet Bi treated at high temperature and high pressure (HTHP) has been proven to have derivative structural polytypes that coexist with the common A7 structure. This paper studies the melting behavior of HTHP-treated polycrystalline Bi using differential scanning calorimetry (DSC) and *in situ* transmission electron microscopy (TEM) measurements. The Bi samples quenched at a pressure of 2 GPa and a temperature above 2000 °C show an additional endothermic peak before the common melting peak of A7-Bi in the DSC curves. This is probably due to the high-temperature relaxation of the distorted A7 configuration. The samples maintain their initial morphology characteristics during repeated heating cycles, indicating the incomplete melting of distorted Bi polytypes.

1. Introduction

Extensive research has been conducted on the structures and physical properties of the semimetal element bismuth (Bi) due to its special status between metals and nonmetals [1–5]. The common structure of Bi under ambient conditions is the so-called rhombohedral A7 structure, which can be considered a distortion of the simple cubic structure and is stabilized by the Peierls-Jones mechanism [1,6]. The shortest metallic bonds in the Bi structure have some covalency, resulting in a layer-like network, compared with the weak bonding observed between layers. Therefore, the unique bonding environment of Bi results in rich physical behaviors such as solid or liquid transitions at various pressures [7–11], unique melting properties [5,11,12–14], and quantum transport [15–18]. Recent research has studied some special forms of Bi such as Bi nanowires [19], Bi nanotubes [20], Bi clusters [21–23], and polycrystalline Bi bulk with distorted A7 structures [24]. As is well known, the microstructure of matter determines its macrophysical properties. For example, Bi with a common A7 structure is classified as a semimetal with a small band overlap, while Bi nanostructures become semiconductors with a small direct band gap due to the quantum size effect [20]. In this paper, *in situ* differential scanning calorimetry (DSC) and transmission electron microscopy (TEM) measurements are used to study the unique melting behavior of polycrystalline Bi samples quenched upon HTHP treatment. We show that a variety of derivative polytypes with distorted A7 structures exist in these samples. These show an extremely interesting large magnetoresistance effect at ambient pressure [25].

2. Material and methods

Bi granules (Alfa Aesar, 99.999%) were sintered and formed into polycrystalline Bi cylinders using an HTHP method similar to that reported in [24]. For simplicity, the quenched Bi samples after the HTHP treatment are denoted as Bi-*T*-*P*, where *T* and *P* represent the quench temperature and the applied pressure, respectively. A Perkin-Elmer differential scanning calorimeter (DSC 8000) was used to monitor physical or chemical reactions, including phase transitions (such as solid-solid or solid-liquid), crystal-glass transitions, decomposition, and combination. The Bi samples were shaped to form small cuboids with a mass of 30–35 mg. These were placed in an aluminum pan and treated under defined temperature programs of various thermal scan rates and heating cycles under an inert argon atmosphere. The obtained DSC curves were calibrated by eliminating the background effect of the empty aluminum pan, which was exclusively tested. Both the raw granules and the quenched bulk samples were ground in an agate mortar. Then, the fine pieces were loaded into a copper microgrid for selected area electron diffraction (SAED). TEM measurements were carried out on a JEM-2100 with an accelerating voltage of 200 kV. During the measurements, a similar electron beam with

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low intensity was used by narrowing the diaphragm to block 80–90% of the electron beam.

3. Results and discussions

Fig. 1a shows the DSC curves of the HTHP-treated samples and the raw Bi material during the first heating cycle with a heating rate of 10 °C/min. For the raw Bi, a decalescence peak is noted at a temperature T_1 of 275 °C, which is a little higher than the reference melting point of 271.3 °C for the common Bi crystal [7]. This represents a normal melting peak. However, for the samples quenched at a pressure of 2 GPa and temperatures above 2000 °C, a second decalescence peak appears at the temperature T_2, which is lower than the normal melting T_1 for common Bi. At measurement temperatures up to 300 °C, these samples slowly cooled at a rate of 10 °C/min to room temperature. After the first heating cycle, the second heating cycle begins with the same heating rate and test temperatures. The shoulder peak is observed again and becomes more significant for the HTHP-treated samples during the second heating cycle (Fig. 1b). In comparison, the decalescence peak of the raw Bi is still the same as the common melting signal. The appearance of the additional decalescence peak during the heating cycles indicates that a distinct thermodynamic process occurs in the HTHP-quenched Bi. The morphologies of the HTHP-treated Bi samples after the heating cycles show large differences compared to the morphologies of the raw Bi. As shown in Fig. 1b inset, the raw Bi changes its bulk shape from an original irregularity to a neat ball, indicating that it normally melted during the heating cycles. However, the HTHP-treated Bi samples retain their initial rectangular morphology even after 12 heating cycles. The existence of some original pits and scratches indicate that the samples did not melt completely.

Multiple heating cycles at a rate of 10 °C/min at temperatures up to 300 °C were conducted in order to observe the changes in the double decalescence peaks of the Bi-2000-2 sample previously treated at 2 GPa and 2000 °C. As shown in Fig. 2a, in the initial three cycles, the relative peak intensity and positions of T_1 and T_2 shift irregularly. When the heating cycles are executed more than four times, the DSC curves of the sample became similar. The additional peak is located on the left of the main peak, and the difference $\Delta T = T_1 - T_2$ is constant at 3.8 °C for the last nine heating cycles.

To further consider the effect of the heating rate on the decalescence peaks, the different heating rates of 0.5, 2.5, 10, and 40 °C/min have been tested for the same Bi-2000-2 sample after 12 heating cycles (Fig. 2b). With a decrease in the heating rate, the positions of the double peaks shift towards lower temperatures, and the peak at T_2 becomes sharper and more independent at 0.5 °C/min, indicating that a distinct thermal behavior occurs at this temperature.

The TEM measurement during the in situ heating process is helpful to directly observe the melting behavior of Bi. For the common raw Bi under electron beam irradiation, the sample shape

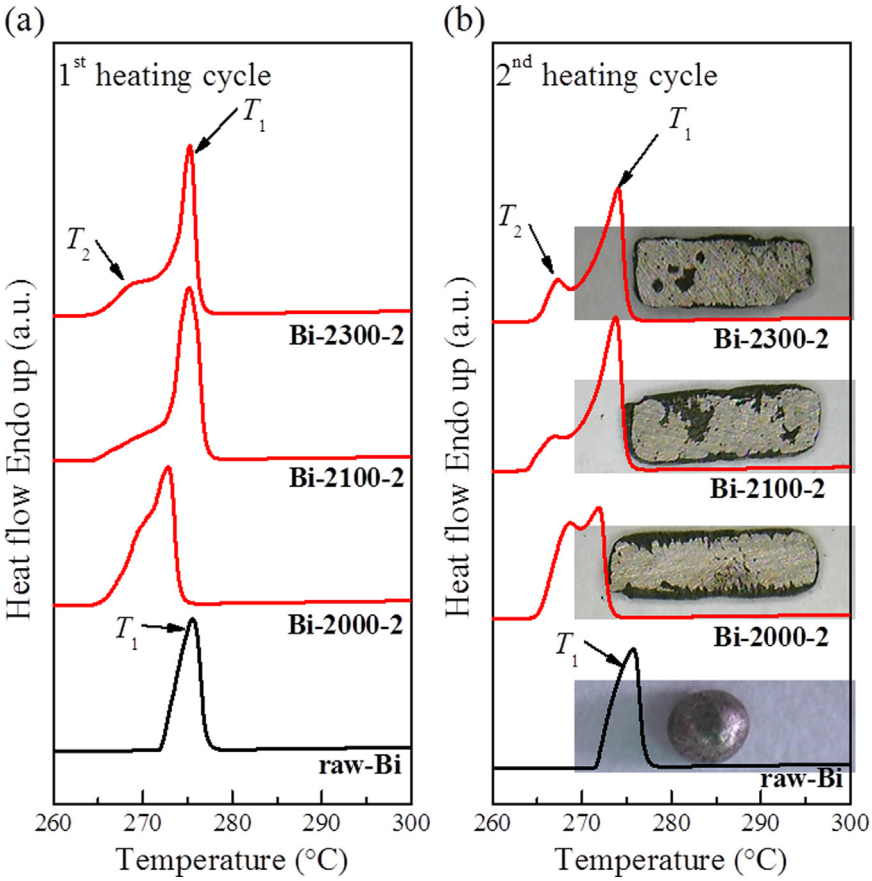

Fig. 1. DSC heating curves measured at 10 °C/min for raw Bi and HTHP treated Bi samples for (a) the first heating cycle up to 300 °C and (b) the second heating cycles up to 300 °C after cool down of the first cycle. Inset: the morphology photos of raw Bi, and HTHP-treated Bi samples.