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High-energy ball-milling for the synthesis of Ag–B superconducting materials

J.-H. Ahn[a,*], S. Oh[b]

[a] Department of Materials Engineering, Andong National University, Songchun-dong, Andong, Gyungbuk 760-749, South Korea
[b] Fusion Technology Development Group, National Fusion Research Institute, Gwahakro 113, Yusong-ku, Daejeon 305-333, South Korea

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ABSTRACT

Superconducting Ag–B (1:2) materials were obtained by high-energy ball-milling. The planetary ball-milled powder exhibited a $T_c = 8$ K which is higher than the previously reported value ($T_c = 6.7$ K) in thin films. Superconductivity appeared under a specific milling condition and a subsequent anneal suppressed superconducting transition. Although the existence of AgB_2 was not clearly confirmed, the observed superconductivity might be related to this phase or other unspecified minor phases formed during milling.

1. Introduction

High-energy ball-milling has been employed to fabricate various superconducting materials. For instance, ball-milling has been used in A-15 compounds and MgB_2 to induce atomic disorder and lattice defects, as well as nano-sized dispersoids, which serves as pinning centers of vortices. This results in a significant increase in critical current density (Jc) at high magnetic fields [1–3]. The degradation of crystallinity is correlated with the enhancement of upper critical field (Hc_2) [1,4]. In peritectic systems, such as A-15 compounds or $YBa_2Cu_3O_{7-\delta}$, on the other hand, the technique can facilitate a more complete reaction, resulting in enhanced superconducting properties [5].

High-energy ball-milling can also be used for synthesizing exotic superconducting materials which have limited mutual solubility or need high temperature or pressure for fabrication. This should be the case of AgB_2, which we present in this work. Immediately after the discovery of MgB_2 superconductor with critical temperature (T_c) of 39 K [6], Kwon et al. predicted a possible superconductivity with higher T_c in some noble metal borides such as AgB_2 and AuB_2 [7]. Several works have been performed to verify the superconductivity in AgB_2. However, conventionally prepared AgB_2 did not exhibit superconductivity. For example, bulk samples did not show any superconducting transition by a measurement down to 12 K [8]. This might be due to difficulties in synthesizing bulk samples by conventional methods, such as melting or sintering. The superconductivity in Ag–B system was only reported in thin films, i.e., a T_c of 6.7 K has been reported in thin film AgB_2 [9]. The purpose of the present work is to verify a possible superconductivity of this material in a bulk state. We have employed high-energy ball-milling to synthesize bulk AgB_2 and examined its superconductivity.

2. Experimental procedure

Pure Ag (>99.9%, 5 μm) and partly amorphous B (>99%, 2 μm) powders were used as starting materials. The elemental powders were mixed to give the composition of AgB_2 (B 66.6 at.%). High-energy ball-milling was carried out in a planetary ball mill (Fritsch 6) at a rotation speed of 300 r.p.m. Both milling vial and balls were WC–Co. The diameter of the ball was 6 mm, and the ball-to-powder weight ratio was 150:1. A portion of the ball-milled powders was die-compacted and put into a sealed quartz tube which was previously evacuated to 10^{-4} torr. The sealed tube was heat-treated at 300 °C for 0.5 h.

The phase identification was examined both by a diffractometer (Rigaku D-MAX 2000) and by a micro-beam diffractometer (D/Max Rapid S) using Cu Kα radiation. The Pt-coated microstructures were examined by a field emission scanning electron microscope (JSM-6700F). The elements were examined by an Electron Probe MicroAnalyzer (Shimadzu, EPMA-1600).

For the measurement of superconductivity, the ball-milled powders were die-compacted into rectangular compacts of 2 mm × 2 mm × 4 mm. The superconducting transition temperature (T_c) was measured by a superconducting quantum interfere device (SQUID) magnetometer at the temperature 5–40 K. The T_c was determined as the onset of the diamagnetism.

3. Results and discussions

Fig. 1 shows the changes in the X-ray diffraction patterns of Ag–B (33.3% Ag and 66.6 at.% B) before and after planetary ball-milling. The diffracted crystalline peaks of Ag gradually broadened with decreasing intensity as the milling proceeded, indicating grain

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* Corresponding author. Tel.: +82 54 820 5648; fax: +82 54 820 6126.
E-mail address: jhahn@andong.ac.kr (J.-H. Ahn).

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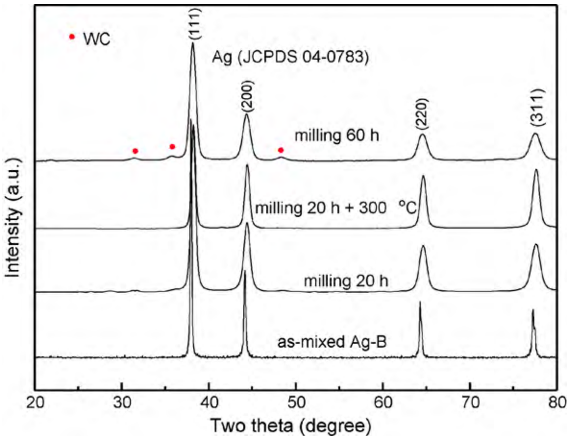

Fig. 1. X-ray diffraction patterns of Ag–B (composition of AgB_2) after planetary ball-milling and a subsequent heat-treatment: (a) elemental powder mixture, (b) ball-milled for 20 h, (c) ball-milled for 20 h, followed by a heat-treatment at 300 °C for 0.5 h in Ar, and (d) ball-milled for 60 h.

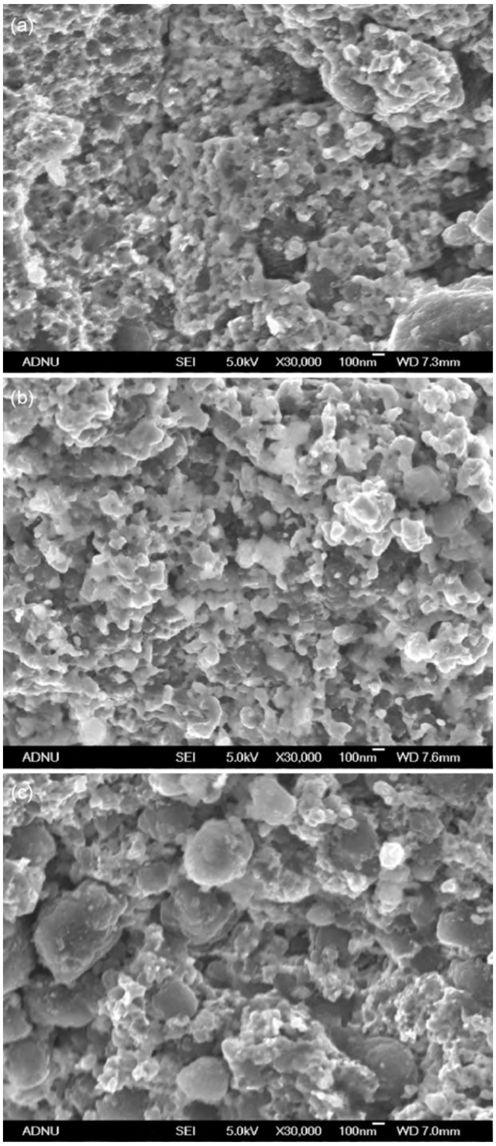

Fig. 2. Field emission SEM morphology of Ag–B (composition of AgB_2) after planetary ball-milling and a subsequent heat-treatment: (a) ball-milled for 20 h, (b) ball-milled for 60 h, and (c) ball-milled for 20 h, followed by a heat-treatment at 300 °C for 0.5 h in Ar (scale bar: 100 nm).

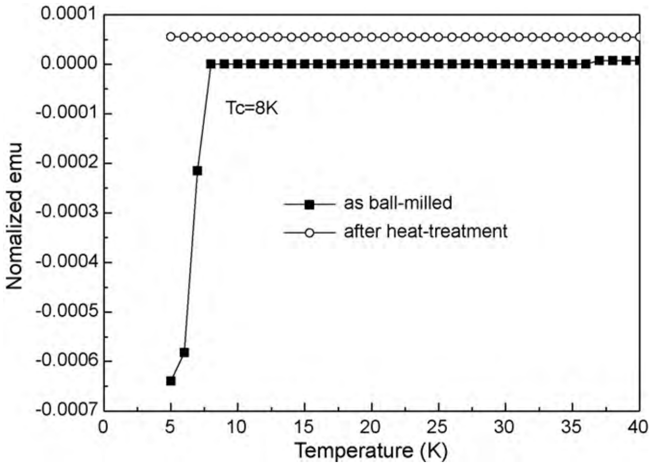

Fig. 3. Magnetic susceptibility curves for Ag–B (composition of AgB_2) after planetary ball-milling for 20 h and after subsequent heat-treatment at 300 °C for 0.5 h in Ar.

refinement by high-energy ball-milling. A trace of WC phase, which stems from the milling media, was detected by XRD after 60 h of prolonged milling time. However, an evidence for the formation of new phases such as AgB_2 was not noticed by XRD. For the powder mixture, which was ball-milled for 20 h, no apparent difference was noticed between before and after the heat-treatment at 300 °C for 0.5 h in Ar.

Field emission SEM morphologies of the ball-milled Ag–B after ball-milling and the subsequent heat-treatment at 300 °C are shown in Fig. 2. The powders, which were ball-milled for 20 and 60 h, have submicron particle size (Fig. 2a and b). Partial grain growth occurred after the heat-treatment at 300 °C for 0.5 h and some grains grew to the size of several micrometers.

In spite of no apparent evidence of the formation of AgB_2 phase by XRD, the result of superconductivity measurement was quite surprising. Superconductivity measured by magnetic susceptibility showed that the powder, which was ball-milled for 20 h, has a sharp onset superconducting transition temperature ($T_c = 8 \pm 0.5$ K) (Fig. 3). On the other hand, the same powder, but subsequently annealed at 300 °C, did not exhibit superconductivity. As well, no transition temperature was observed on the powder ball-milled for the prolonged milling time of 60 h, probably due to the exces-

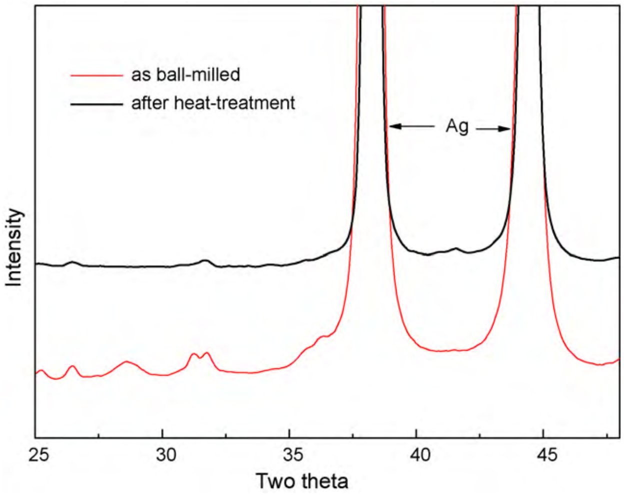

Fig. 4. Micro-beam XRD diffraction patterns of Ag–B (composition of AgB_2) after planetary ball-milling for 20 h and after subsequent heat-treatment at 300 °C for 0.5 h in Ar.

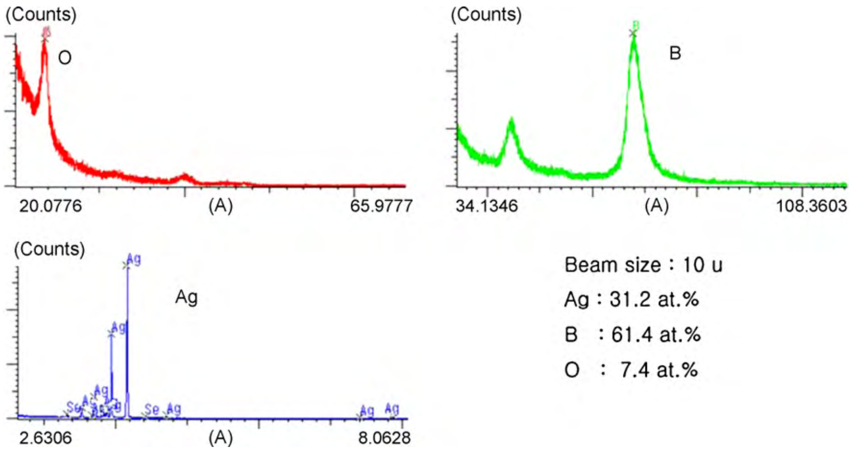

Fig. 5. EPMA result of Ag–B (composition of AgB_2) after planetary ball-milling for 20 h (beam size: 10 μm; *Y*-axis: arbitrary unit).

sive contamination of WC from milling media. Only the powder ball-milled for 20 h showed superconducting transition.

Superconductivity in Ag–B (1:2) was reported by Tomita et al. with $T_c = 6.7$ K in thin films which were prepared by a pulsed laser deposition method [9]. The reported T_c value is much lower than the theoretically calculated one ($T_c = 59$ K) [7]. Islam et al. theoretically proposed that this discrepancy is due to spin fluctuations in the noble metal borides [10]. The presently observed T_c of 8 K, for the ball-milled powder compact, is also lower than the theoretically calculated value, but higher than that reported by Tomita et al. in thin films. These authors attributed the superconductivity in this Ag–B system to the formation of the AgB_2 phase. An XRD peak at ∼28° was supposed to be a characteristic of the AgB_2. However, there is a bitter controversy about the existence the AgB_2. There are no known phase diagrams for the Ag–B system, and Ag and B are generally known to be mutually insoluble in both solid and liquid states. On the other hand, it has been claimed that the compound AgB_2 was synthesized at an unspecified temperature and identified as having a hexagonal structure (AlB_2 structure) [11]. Following examinations reported, the alloy (66.6 at.% B), which was annealed for 2 months at 900 °C, did not reveal the existence of AgB_2. Recently, Pelleg et al. [12] examined the Ag–B (1:2) thin film prepared by magnetron co-sputtering on Si substrate, which showed no superconductive transition. They also observed the XRD peak at ∼28°, but possibly attributed this to boric acid. In spite of that, they did not totally exclude the existence of metallic bonding such as the formation of AgB_2 compound from their XPS examination results.

To see the possible origins of the observed superconductivity in the ball-milled powder, we carefully examined the phases by a micro-beam XRD (Fig. 4). Compared to the heat-treated powder which showed no superconductivity, the ball-milled powder showed some extra peaks between 25 and 35 °C. The above-mentioned peak at ∼28° is also visible from the ball-milled power compact, but completely disappeared after the heat-treatment. There is a possibility that this peak stems from H_3BO_3. The other minor peaks were persisted, but apparently weakened after the heat-treatment. It seems thus that the appearance of superconductivity in this Ag–B system is related to these peaks. It is not clear, for the present, that the disappearance of these peaks is due to the dilution of a phase(s) which was formed during ball-milling by diffusion, or other causes such as an eventual compositional inhomogeneity. Qualitative examination of composition by EPMA was performed on the surface region of the ball-milled powder (Fig. 5). It is difficult by EPMA to determine the exact composition of the formed phases due to the smallest beam size limit of 10 μm, whereas the supposed phases might have submicron grain size as seen in Fig. 2. The result indicated that the ball-milled powder contains a non-negligible content of oxygen. A similar fact was also reported in the AgB_2 thin film specimens [12]. The oxygen may stem from the surface of starting powders, B powders in particular, in spite of milling in an inert atmosphere. There is also a possibility that the observed minor peaks might be those of the complex compounds of oxide.

4. Conclusions

The present work demonstrated that high-energy ball-milling can be used as an effective method to produce Ag–B (1:2) superconducting materials which cannot be fabricated by conventional melting or sintering technique. So far, superconductivity in this system has been reported only in thin film specimens. The observed T_c of the ball-milled Ag–B (1:2) was higher than that of the thin films ($T_c = 8$ K). It seems that superconductivity in this Ag–B system is related to a small amount of AgB_2 or other unidentified minor phases which formed during high-energy ball-milling. More detailed examination on the phase identification, as well as optimum milling parameters, are needed to clarify the origin of the observed superconductivity and to achieve possibly high critical temperature, as predicted by a theoretical prediction.

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