Enhanced high-field transport critical current densities observed for ex situ PIT processed Ag/(Ba, K)Fe$_2$As$_2$ thin tapes

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Abstract

We found that the transport $J_c$ of ex situ PIT (powder-in-tube) processed (Ba, K)Fe$_2$As$_2$ (Ba-122) wires with a single Ag sheath can be significantly enhanced by repeating a combined process of rolling and heat treatment. A transport $J_c$ (4.2 K and 10 T) of $4.4 \times 10^3$ A cm$^{-2}$ ($I_c = 15.7$ A) was obtained for a thin tape (0.3 mm thick) produced by this method, which is the highest reported so far for Ag-sheathed Ba-122 and Sr-122 wires processed by the conventional PIT route. The measurement by a hybrid magnet showed that the $J_c$–$H$ curve maintains a very small field dependence up to the strong magnetic field of 28 T, as expected from the previously reported high $H_c^2$ value. The core of the thin tape shows dense grain structure with fewer cracks and voids, which is considered to be responsible for the large enhancement of $J_c$. We believe that this new approach is useful for further development of 122 wires with higher transport $J_c$.

(Some figures may appear in colour only in the online journal)

1. Introduction

The discovery of superconductivity at 26 K in LaFeAsO$_{1-x}$F$_x$ [1] in early 2008 aroused enormous interest in the iron-based superconductors. To date, many families such as REOFeAs(1111-type) [2], LiFeAs(111-type) [3], BaFe$_2$As$_2$(122-type) [4], FeSe(11-type) [5] and the pnictides with perovskite-type blocking layer [6] have been found to show high temperature superconductivity up to 56 K by appropriate doping. In addition to the high transition temperature, $T_c$, the iron-based superconductors were reported to have a very high upper critical field, $H_{c2}$, bringing hope of high-field applications as wires and bulks [7–9].

In order to evaluate the potentiality for wire applications, the development of a wire processing technique is essential. Until now, the powder-in-tube (PIT) process is most widely employed for the fabrication of 1111 [10, 11], 11 [12] and 122-type [13–16] superconducting wires and tapes using various sheath materials such as Fe, Ag, Nb and Ta. However, the transport critical current densities, $J_c$, reported at an early stage were disappointingly low due to the weak link grain boundaries problem [17]. This arises from the presence of numerous cracks and voids along the grain boundaries as well as the misorientation between the grains.

Very recently, there has been some progress in improving the grain connectivity of the PIT processed 122 wires. Weiss et al [18] reported the transport $J_c$ of as high as $\sim 8 \times 10^3$ A cm$^{-2}$ at 4.2 K and 10 T for ex situ PIT processed Cu/Ag/Ba-122 round wires, which was achieved by using a high quality precursor prepared by high energy ball milling and applying cold isotropic press (CIP) and hot isotropic press (HIP). The results indicate the importance of the quality of the precursor and the densification of the 122 core. On the other hand, Wang et al [19] demonstrated that strong...
texture of c-axis alignment can be achieved by applying the rolling process for Fe-sheathed Sr-122 wires and is effective to improve the grain connectivity as well as the densification. The sheath material used was Fe because the heat treatment was carried out at a high temperature for a short time. They reported a $J_c$ value (at 4.2 K and 10 T) of $3.5 \times 10^3$ A cm$^{-2}$ [20] and more recently above $10^4$ A cm$^{-2}$ (at 4.2 K and 10 T) [21] which is the highest $J_c$ among the PIT processed iron-based superconducting wires reported so far. Matsumoto et al [22] carried out the first measurement of transport $J_c$ at temperatures above 4.2 K using a Ag/Ba-122 wire and found that the $J_c$–$H$ curve maintains a small magnetic field dependence at temperatures up to 20 K. Those results indicate that the PIT processed 122 superconducting wires are promising for magnetic field applications at medium temperatures of cryogenic cooling or liquid hydrogen as well as in liquid helium.

For practical applications, the process should be simple and easy to scale up to the long length wire production, requiring little sophisticated equipment. Like Bi-based high temperature superconductors, Ag looks the most suitable sheath material for 122 phases such as (Ba, K)Fe$_2$As$_2$ and (Ba, Sr)Fe$_2$As$_2$. This is because Ag does not react with 122 superconductors and is expected to serve as a stabilizing material of the conductor due to its low electrical resistivity. Very recently, Yao et al [23] reported the successful fabrication of multi-filamentary Sr-122 wires with an Fe/Ag double sheath.

In this paper, we demonstrate that a large enhancement of transport $J_c$ can be obtained for the ex situ PIT processed Ag/Ba-122 tape by repeating a combined process of ordal cold rolling and heat treatment. The method is basically the same as the commercial production process of Bi$_2$Sr$_2$Ca$_2$Cu$_2$O$_8$ (Bi-2223) superconducting tapes [24]. We also report the critical current measurement in very high magnetic fields up to 28 T using a hybrid magnet in order to evaluate the high-field performance of the PIT processed Ba-122 superconductor.

2. Experimental details

Starting materials for the preparation of the precursor were BaAs, KAs and Fe$_2$As compounds, which were synthesized by reacting constituent elements. By using these compounds instead of each element, the loss of volatile elements such as K and As can be minimized. The powders of BaAs, KAs and Fe$_2$As were mixed with the nominal composition of (Ba$_{0.8}$K$_{0.4}$)$_2$Fe$_2$As$_2$ and reacted in an alumina crucible sealed in a stainless steel tube in a nitrogen atmosphere [25]. A small amount of excess KAs was added in order to compensate the loss of K and As through the reaction process. The assembly was then heat treated at 800 °C for 20 h to form Ba-122 phase. The obtained (Ba$_{0.8}$K$_{0.4}$)$_2$Fe$_2$As$_2$ precursor has a fairly good quality, as shown in the magnetization versus temperature curve and the powder x-ray diffraction pattern of figure 1. The detail of the preparation will be published elsewhere.

![Figure 1.](image-url) (a) Magnetization versus temperature curve and (b) x-ray diffraction pattern of the (Ba$_{0.8}$K$_{0.4}$)$_2$Fe$_2$As$_2$ precursor.

The precursor was ground into a powder and mixed with Sn powder with a molar ratio of (Ba$_{0.8}$K$_{0.4}$)$_2$Fe$_2$As$_2$Sn$_{0.5}$ using an agate mortar in a glove box filled with a high purity argon gas. The Sn was added in order to improve the grain connectivity, as reported for the Sr-122 system [19]. The powder mixture was packed into a Ag tube (outside diameter: 6 mm, inside diameter: 4 mm), which was subsequently groove rolled and swaged into a wire of 2 mm diameter. A short piece of ~40 mm in length cut from the wire was then subjected to the first heat treatment of 850 °C for 10 h for sintering. After the first heat treatment, the wire was deformed into a tape using a flat rolling machine, initially to a thickness of 0.6 mm, followed by the second heat treatment of 850 °C for 10 h and finally rolled to a thickness of 0.3 mm followed by the third heat treatment of 850 °C for 10 h. Figure 2 shows the optical micrographs of the transverse cross sections observed for a round wire of 2 mm in diameter, and tapes of 0.6 and 0.3 mm in thickness, hereinafter abbreviated as 2 mm$^2$ wire, 0.6 mm$^2$ tape and 0.3 mm$^2$ tape, respectively. The photographs of the tapes show that the composite was deformed uniformly even after the previous heat treatment for sintering.

After each heat treatment, the $I_c$ measurement was carried out in liquid helium (4.2 K) using a 12 T superconducting magnet. The magnetic field was applied perpendicularly to the sample length and, in the case of the tapes, parallel to the tape surface. $I_c$ was determined using the voltage criterion of 1 $\mu$V cm$^{-1}$. Transport critical current density,
Figure 2. Cross sections of the wire of diameter 2 mm and the tapes of thickness 0.6 and 0.3 mm.

\( J_c \), was estimated by dividing the \( I_c \) by the cross sectional area of the superconducting core, which was measured by using the image analysis of a laser optical microscope. We also carried out the \( I_c \) measurement in a 28 T hybrid magnet of the Tsukuba Magnet Laboratory (TML) of the National Institute of Materials Science (NIMS). The cross sections of the wire and tapes were observed by an optical microscope (OM) and a scanning electron microscope (SEM). The phase identification was carried out by x-ray diffraction (XRD) analysis.

3. Results and discussion

In the transport \( I_c \) measurement, the voltage versus applied current curves show a rather sharp transition, as can be seen in figure 3(a). Figure 3(b) is the plot of transport \( J_c \) as a function of magnetic field for the 2 mm\(^d\) round wire and the 0.6 and 0.3 mm\(^t\) tapes. The measurement was carried out using a 12 T superconducting magnet.

In order to check the effectiveness of the intermediate rolling and annealing, we prepared a reference sample without the intermediate step, that is, by rolling the 2 mm\(^d\) wire directly to a 0.3 mm\(^t\) tape followed by annealing at 850 \( ^\circ \)C for 10 h. The tape shows the transport \( J_c \) values were less than \( 10^3 \) A cm\(^{-2}\) at 4.2 K and 10 T with poor reproducibility of the result. This is similar to the Bi-2223 tape fabrication, in which too large a reduction ratio before the heat treatment results in an inhomogeneous deformation and poor \( J_c \) and, hence, the tape fabrication is carried out by repeating the intermediate rolling with smaller reduction increased after the rolling and subsequent heat treatment. The enhancement is significant in applied fields, while the \( J_c \) in self-field is not so influenced by the rolling and annealing. The \( J_c \) value at 10 T is increased by about three times (2.1 \( \times \) \( 10^3 \) A cm\(^{-2}\) (\( I_c = 67.5 \) A)) for the 0.6 mm\(^t\) tape and further by about twice (4.4 \( \times \) \( 10^3 \) A cm\(^{-2}\) (\( I_c = 15.7 \) A)) for the 0.3 mm\(^t\) tapes. The \( J_c \) of 4.4 \( \times \) \( 10^3 \) A cm\(^{-2}\) (10 T and 4.2 K) is the highest in the values reported so far for Ag-sheathed wires and tapes processed by the conventional PIT route without high pressure techniques.
rate and annealing [26]. Optimization of various processing parameters for Ag/Ba-122 tape such as the reduction ratio and heat treatment condition is a subject for future research.

$I_c$ measurement using a 28 T hybrid magnet was carried out at 4.2 K for the 0.3 mm$^3$ tape sample used for the measurement of a 12 T superconducting magnet. Figure 4 shows the result together with the data measured with the 12 T superconducting magnet. Typical $J_c$–$H$ curves of the bronze processed (Nb, Ti)$_3$Sn [27] and PIT processed MgB$_2$ [28] superconducting wires are also included for comparison. The data of the hybrid magnet and those of the 12 T superconducting magnet coincide with each other indicating that no degradation occurred during the duration between both measurements (∼1 month). It is noteworthy that the $J_c$–$H$ curve shows an extremely small magnetic field dependence up to the strong magnetic field of 28 T. The $J_c$ at 28 T is 2.9 × 10$^3$ A cm$^{-2}$ ($I_c$ = 10.5 A), which is still two-thirds of that at 10 T. The $J_c$–$H$ curve crosses those of (Nb, Ti)$_3$Sn and MgB$_2$ wires at magnetic fields far below 28 T. This is consistent with the very high $H_{c2}$ of 122 phase as reported in earlier papers [7–9] and shows the good potentiality of 122 wires for high-field generation.

In order to investigate the mechanism of $J_c$ enhancement, we carried out microstructure observations. Figure 5 shows the comparison of the high magnification optical micrograph between the 2 mm$^3$ wire and the 0.3 mm$^3$ tape. Both structures are composed of a matrix of 122 grains and the dispersed particles which appear white in the figures. However, we can see some differences when looking at the detail. One is that the cracks along the grain boundary, which are observed frequently in the 2 mm$^3$ wire, as indicated by arrows in figure 5(a), are rarely observed in the 0.3 mm$^3$ tape. The other is the grain structure of the 122 phase. The grains of the 2 mm$^3$ wire are equi-axed and the average grain size is ∼5.6 µm. On the other hand, the 0.3 mm$^3$ tape shows more uniform structure with slightly larger grain size. Furthermore, the average grain size shows a slight difference when measured in the directions parallel and perpendicular to the rolling plane, which are 7.5 µm and 5.8 µm, respectively. This indicates that the grains are slightly elongated by the rolling process, although it is not so significant as observed in the Fe-sheathed Sr-122 tapes [20] and the Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ tapes [26].

The anisotropic nature of the tape was also observed by x-ray diffraction. Figures 7(a) and (b) show the XRD patterns of the 0.3 and 0.6 mm$^3$ tapes taken on the core
Figure 6. Micrograph of SEM and mappings of constituent elements detected by an SEM–EDAX on the polished cross section of the 0.3 mm² tape.

surface which was exposed when the sheath was mechanically separated. The XRD pattern of the starting powder mixture of (Ba, K)Fe$_2$As$_2$ + Sn is also shown in figure 7(c) for comparison. Relative intensities of all basal planes (00l) of the tapes are stronger than those of randomly oriented powder mixture. This suggests that the compressive stress of rolling deformation forces the basal plane of the 122 grain to align parallel to the rolling plane. However, the texture obtained in this study is rather weak compared to that achieved in the Bi-2223 superconducting tape, for which the repetition of the rolling and annealing is essential in order to have strong texturing and high performance of critical current properties [26]. The peaks of Sn in the starting powder mixture are not observed in the tapes and, instead, Ag-based alloy peaks appear and become stronger by repeating the heat treatment. This is in accordance with the precipitation of Ag–Sn alloy in the tapes observed by OM and SEM–EDAX.

From these microstructure investigations, we consider that the reduction of cracks and voids is the origin of the large $J_c$ enhancement rather than texturing. This is similar to the case of PIT processed MgB$_2$ wires. A large enhancement of $J_c$ can be attained by the rolling although the texture development is not so significant [29]. Kulich et al [30] reported that an intermediate rolling between the reaction and final heat treatments has a positive effect on the densification and transport $J_c$. We expect that further improvement of $J_c$ could be obtained by achieving a higher degree of texturing as already demonstrated by the work for Fe-sheathed Sr-122 tapes [19, 20]. Since Ag and Fe sheaths have different crystal structures, which have an influence on the various mechanical behaviors such as hardness and work hardening, optimization
of their processing parameters to have stronger texture must be carried out independently of each other. We believe that our results give some progress in the development of PIT processed Ag-sheathed 122 tapes with improved high-field characteristics.

4. Conclusions

We have demonstrated that the transport $J_c$ of Ag single sheathed (Ba, K)Fe$_2$As$_2$ tapes can be significantly enhanced by repeating the combined process of rolling and heat treatment. The transport $J_c$ (4.2 K and 10 T) of $4.4 \times 10^3$ A cm$^{-2}$ ($I_c = 15.7$ A) was obtained for a thin tape of thickness 0.3 mm, which is the highest value reported so far for Ag-sheathed 122 wires and tapes processed by the conventional PIT route. We also found that the $J_c$–$H$ curve shows a very small field dependence up to the strong magnetic field of 28 T as expected from the previously reported high $H_{c2}$ value. The result of microstructure observation shows that the core of the tape has many fewer cracks and voids, which is considered to be responsible for the enhanced $J_c$. We expect that much higher transport $J_c$ could be obtained by achieving a high degree of $c$-axis texturing. We believe that the process presented in this paper is simple using a Ag single sheath and is, therefore, promising for the production of long 122 wires with high transport $J_c$.

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Figure 7. X-ray diffraction patterns for (a) the 0.3 mm$^2$ and (b) 0.6 mm$^2$ tapes. The measurement was done on the surface of the core exposed after the sheath was mechanically separated. The pattern of a starting powder mixture of (Ba, K)Fe$_2$As$_2$ + Sn is also shown in (c) for comparison.
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