Enhancement in transport critical current density of \textit{ex situ} PIT Ag/(Ba, K)Fe$_2$As$_2$ tapes achieved by applying a combined process of flat rolling and uniaxial pressing

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Abstract
We report that the transport critical current density $J_c$ of \textit{ex situ} powder-in-tube (PIT) processed (Ba, K)Fe$_2$As$_2$ (Ba-122) tapes can be significantly enhanced by applying uniaxial cold pressing at the final stage of deformation. The tapes were prepared by packing high quality precursor powder into an Ag tube, cycles of rolling and intermediate annealing, and pressing followed by the final heat treatment for sintering. The $J_c$ values in applied magnetic fields were increased by almost one order of magnitude compared to the tapes processed without pressing, exceeding $10^4$ A cm$^{-2}$ at 4.2 K. We achieved the highest $J_c$ (at 4.2 K and 10 T) of $2.1 \times 10^4$ A cm$^{-2}$ among PIT-processed Fe-based wires and tapes reported so far. The $J_c$–$H$ curves measured at higher temperatures maintain small field dependence up to around 20 K, suggesting that these tapes are promising for applications at higher temperatures as well as at liquid helium temperature. The microstructure investigations reveal that there are two possible causes of the large $J_c$ enhancement by pressing: one is densification and the other is the change of crack structure. Optimization of processing parameters such as the reduction ratio of rolling and pressing is expected to yield further $J_c$ enhancement.

1. Introduction

The discovery of superconductivity at 26 K in LaFeAsO$_{1-x}$F$_x$ [1] in early 2008 aroused enormous interest in iron-based superconductors, and to date many material families such as REOFeAs (1111 type) [2], LiFeAs (111 type) [3], BaFe$_2$As$_2$ (122 type) [4], FeSe (11 type) [5] and pnictides with a perovskite-type blocking layer [6] have been found to show high temperature superconductivity up to 56 K with appropriate doping. Among these, the K-doped BaFe$_2$As$_2$ and SrFe$_2$As$_2$ superconductors are potentially the most useful for magnet applications due to their high $T_c$ value of $\sim$39 K, $H_{c2}$ of over 50 T [7] and relatively small anisotropy [8]. Furthermore, it was reported that the transport $J_c$–$H$ curve maintains a small magnetic field dependence at temperatures up to 20 K [9], indicating that 122 superconducting wires are promising for magnet applications at intermediate temperatures of cryogenic cooling or liquid hydrogen as well as in liquid helium.

In order to evaluate the potential for wire applications, the development of wire processing techniques is essential. For Ba-122 and Sr-122, powder-in-tube (PIT) and coated conductor processes have been developed for wire or tape fabrication. A very high transport critical current density $J_c$
of well over $10^5 \text{ A cm}^{-2}$ at 4 K and 10 T was reported for a coated conductor tape with Co-doped Ba-122 film, which was grown on a textured MgO buffer layer on a metal substrate [10, 11]. On the other hand, the transport $J_c$ of PIT processed wires reported at an early stage of development [12–17] was disappointingly low due to the weak link grain boundaries problem [18]. This might be due to the presence of numerous cracks and voids along grain boundaries and/or misorientation between grains. Recently, there have been several advances in improvement of grain connectivity reported for PIT processed 122 wires. Weiss et al. [19] reported a transport $J_c$ as high as $\sim 8 \times 10^4 \text{ A cm}^{-2}$ 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 by applying cold isostatic pressing (CIP) and hot isostatic pressing (HIP). The results indicate the importance of the quality of the precursor used and densification of the 122 core. On the other hand, Wang et al. [20] and Gao et al. [21] demonstrated that strong texture of the $c$-axis alignment can be achieved by applying a rolling process for Fe-sheathed Sr-122 wires, and this is effective to improve the grain connectivity as well as densification. They reported a $J_c$ value (at 4.2 K and 10 T) of $1.7 \times 10^4 \text{ A cm}^{-2}$ [22], which is the highest $J_c$ among the PIT processed iron-based superconducting wires reported so far. These results are encouraging further advances in the development of the PIT process for Fe-based superconductors.

In addition to a high transport $J_c$, the process for forming wires should be simple and easy to scale up to long length wire production, as it doesn’t require sophisticated equipment and processes. Like Bi-based high temperature superconductors, Ag seems to be the most suitable sheath material for the 122 phase, as for (Ba, K)Fe$_2$As$_2$ and (Sr, K)Fe$_2$As$_2$. This is because Ag does not react with 122 superconductors and is expected to serve as a stabilizing material for the conductor due to its low electrical resistivity. We have been studying the PIT process for the fabrication of Ba-122 wires and tapes using an Ag single sheath. In a previous paper [23], we demonstrated that the combined process of flat rolling and subsequent heat treatment is effective in enhancing the transport $J_c$. This process is similar to that developed for the commercial production of Bi-2223 superconducting tapes in the early 1990s [24]. In the course of developing PIT Bi-2223 tapes, several researchers reported that cold pressing is more effective for the enhancement of transport $J_c$ than flat rolling [25, 26]. The advantages of cold pressed tape are a higher density of the Bi-2223 core and crack direction formed longitudinally along the tape, in contrast to the rolled tape, in which cracks appear in the transverse direction. The positive influence of the crack direction of the pressed tape for current flow along the tape was directly evidenced by using magneto-optical imaging [27]. Cold pressing was also applied to the PIT process of MgB$_2$ [28] and K-doped 122 superconductors [29, 30]. Ding et al. [29] achieved the $J_c$ of $2.8 \times 10^4 \text{ A cm}^{-2}$ (4.2 K and self-field) for a Cu-sheathed Ba-122 wire, which is nearly twice as large as that for the unpressed tape, and more recently Yao et al. [30] reported that the $J_c$ of Fe-sheathed Sr-122 wires increases with an increase of pressure, reaching a maximum $J_c$ of $1.68 \times 10^4 \text{ A cm}^{-2}$ (4.2 K and self-field) at 1.4 GPa. In this paper, we demonstrate that uniaxial pressing causes a dramatic improvement of transport $J_c$ for the ex situ PIT processed Ba-122 tapes, when it is properly combined with flat rolling. Cold pressing was applied at the final stage of the ex situ PIT process for thin tapes fabricated by a combination of flat rolling and intermediate annealing.

2. Experimental details

The precursors of (Ba$_{0.6}$K$_{0.4}$)Fe$_2$As$_2$ were prepared from Ba filings (99%), K plates (99.5%), Fe powder (99.9%) and As pieces (99.99%). These elemental materials were mixed to the nominal composition of (Ba$_{0.6}$K$_{0.4}$)Fe$_2$As$_2$ in an Ar atmosphere using a ball-milling machine and placed into a Nb tube of 6 mm outer diameter and 5 mm inner diameter for the heat treatment. The Nb tube was put into a stainless steel tube, both ends of which were pressed and sealed by arc welding in an Ar atmosphere. The heat treatment was carried out at 900 °C for 10 h followed by furnace cooling in a box furnace. The (Ba$_{0.6}$K$_{0.4}$)Fe$_2$As$_2$ precursor obtained has fairly good quality, as shown in the powder x-ray diffraction pattern and magnetization versus temperature curve in figures 1(a) and (b), respectively. The x-ray diffraction (XRD) pattern was taken after pressing the powder on a glass plate. All peaks are identified as those from the Ba-122 structure and no peaks from impurity phases were observed in the pattern. The (00l) peaks from the basal plane show very high relative intensity compared to the random structure, indicating that each grain has a plate-like morphology of a single crystal and was forced to align parallel to the glass plate. The magnetization versus temperature curve measured by a SQUID magnetometer (MPMS) shows a sharp drop with the onset at around 37 K, which is another indication of the high quality of the precursor.

The precursor was then ground into powder using an agate mortar in a glove box filled with high purity Ar gas. The powder was packed into an Ag tube (outside diameter 6 mm, inside diameter 4 mm), which was subsequently grooved rolled into a wire with a rectangular cross-section of $\sim 2 \text{ mm} \times \sim 2 \text{ mm}$ and then heat treated at 850 °C for 2 h. After the first heat treatment, the wires were deformed into a tape form using a flat rolling machine, initially into 0.6–0.7 mm thickness followed by a second heat treatment at 850 °C for 2 h. After the first heat treatment, the wires were deformed into a tape form using a flat rolling machine, initially into 0.6–0.7 mm thickness followed by a second heat treatment at 850 °C for 2 h. After the first heat treatment, the wires were deformed into a tape form using a flat rolling machine, initially into 0.6–0.7 mm thickness followed by a second heat treatment at 850 °C for 2 h. The tape was then cut into 35 mm lengths and uniaxially pressed between two hardened steel dies. The pressure was changed between 0.15 and 0.4 GPa, which brought a thickness reduction ratio of 5–20%. The pressed tape was then subject to a final heat treatment at 850 °C for 10 h in a box furnace for sintering followed by furnace cooling. All heat treatments were carried out after placing the samples into a stainless steel tube, both ends of which were pressed and sealed by arc welding in an Ar atmosphere.
3. Results and discussion

The critical current, $I_c$, measurement was carried out in liquid helium (4.2 K) using a 12 T superconducting magnet. The magnetic field was applied perpendicular to the tape length and parallel to the tape surface. We found that the pressed samples have a very high $I_c$, even in strong magnetic fields above 10 T. Figure 2(a) shows an example of voltage versus applied current curves measured for the pressed tape of 0.4 mm thickness. The inset is the cross-section of the tape. The measurement at fields lower than 10 T were not carried out for this sample, because the current flow over 130 A causes thermal runaway at the transition, resulting in sample damage. $I_c$ was determined using the voltage criterion of 1 $\mu$V cm$^{-1}$. The transport critical current density, $J_c$, was estimated by dividing the $I_c$ by the cross-sectional area of the superconducting core, which was measured using image analysis in a laser optical microscope.

Figure 2(b) shows the plots of the transport $J_c$ of three pressed tapes with different final thicknesses of 0.35, 0.40 and 0.47 mm. For comparison, the $J_c$–$H$ curves of a groove rolled wire ($\sim$2 mm $\times$ $\sim$2 mm) and a flat rolled tape (0.4 mm thickness) processed without cold pressing are also shown. All wire and tapes were subjected to the final heat treatment of 850°C for 10 h. The figure clearly indicates that the $J_c$ increases with progression of the process from groove rolling to pressing. The $J_c$ of the grooved rolled wire is as low as $\sim$10$^3$ A cm$^{-2}$ in applied magnetic fields. This is consistent with previous papers [9, 17, 31, 32], in which similar low $J_c$ values were reported for Ba-122 and Sr-122 round wires processed by the conventional PIT route. However, $J_c$ increased upon application of the cycles of flat rolling and subsequent heat treatment, as we reported in a previous paper [23]. The most remarkable result obtained in this investigation is further large enhancement by the application of uniaxial pressing. All three pressed tapes show $J_c$ over 10$^4$ A cm$^{-2}$ at 10 T, indicating that a high $J_c$ is obtained with good reproducibility. The $J_c$ of 2.1 $\times$ 10$^4$ A cm$^{-2}$ at 10 T observed for the 0.4 mm thick tape is the highest among the PIT processed Fe-based superconducting wires reported so far. It is expected, from extrapolation of the $J_c$–$H$ curves, that the $J_c$ of these three pressed tapes exceeds 10$^5$ A cm$^{-2}$ in self-field. We also carried out $I_c$ measurements at high temperatures above 4.2 K using the temperature variable cryostat in a 15 T superconducting magnet. The results are shown in figure 3. It can be noted that the tape
Figure 3. Plots of transport $J_c$ of the pressed tape heat treated at 850°C for 10 h as a function of magnetic field, $H$, measured at high temperatures above 4.2 K. The $J_c$–$H$ curve at 20 K for the PIT processed MgB$_2$ wire is shown for comparison [33].

maintains a small field dependence up to around 20 K, keeping a high $J_c$ value over $10^3$ A cm$^{-2}$ at 10 T. This curve shows a crossover with that of the PIT processed MgB$_2$ wire [33] at around 6 T. The result indicates that the tapes are promising for magnet applications at medium temperatures of cryogenic cooling or liquid hydrogen as well as in liquid helium.

In order to study the mechanism of $J_c$ enhancement, we investigated the microstructure change during the process. Figures 4(a)–(c) show the grain structures of the grooved rolled wire, and the flat rolled and pressed tapes, respectively. All of the wire and tapes were finally heat treated at 850°C for 10 h. The observation was made by a scanning electron microscope (SEM) on the fractured surface of the Ba-122 core. The microstructure of the groove rolled wire shows non-uniformity in the grain size distributed widely from $\sim$1 to $\sim$10 µm. However, the tapes show more uniform grain structure whose average size is a few micrometers. We consider that the cycles of deformation and subsequent heat treatment break up larger grains into smaller grains, resulting in the observed uniform grain structure of the Ba-122 core. It is interesting that the grains have an almost equiaxed morphology, although the starting powder was composed of single crystals. This is consistent with the XRD patterns of figures 5(a) and (b) taken from the core surface of the flat rolled and pressed tapes, respectively, after the Ag sheath was peeled off. It is noticed that the relative intensity of the (00$l$) peaks of the tapes is not so high as observed in figure 1(a) and more like random orientation. This is different from the PIT processed Bi-2223 tape, in which the cycles of flat rolling and heat treatment produce strong $c$-axis alignment due to the larger anisotropic morphology of the Bi-2223 crystal [24]. The result is also in contrast to the Fe-sheathed PIT Sr-122 tape [20–22], in which a strong texture was observed, similar to the Bi-2223 tape. It is considered that the difference is caused by the different sheath material and different processing parameters such as reduction ratio. In any case, from almost the same grain morphology and XRD pattern between the rolled and pressed tapes, the texture can be ruled out as a possible origin of the large enhancement of transport $J_c$, at least within the experimental conditions of the present work.

We also performed the Vickers microhardness ($H_v$) measurement for the groove rolled wire, flat rolled and pressed tapes in order to investigate the influence of density on the transport $J_c$. All of the wire and tapes were finally heat treated at 850°C for 10 h. The measurement was made on polished transverse cross-sections of each sample with 0.05 kg load and 10 s duration in a row at the center of the cross-section; the results are shown in figure 6. For the rolled tape, two different cross-sections were measured, because the hardness varies more widely in the rolled tape depending on the position. We suppose that this is caused by invisible small imperfections of the surface flatness and roundness of our flat rolling machine,
which might have a larger influence for thinner tapes. The figure shows that there is an apparent difference in the average hardness, increasing with the progress of the deformation process. The average $H_v$ numbers of the grooved rolled wire and the flat rolled and pressed tapes are 87.1, 94.0 and 117, respectively. From these results, it is possible that the density is one of the causes of the $J_c$ enhancement as reported for Ag/Bi-2223 tapes by Parrell $et$ $al$ [34], in which there is a strong linear correlation between the transport $J_c$ and $H_v$, which can be well correlated to the density of the Bi-2223 core.

In the case of Ag/Bi-2223 tapes, many researchers reported that the different direction of residual cracks is another important reason for the higher $J_c$ of the pressed tape in addition to the densification [25–27]. In this investigation, we also observed an apparent difference in crack structures between the rolled and pressed tapes as shown in figure 7. The observation was carried out on the tape plane of the as-rolled or as-pressed tapes without subsequent heat treatment. SEM photographs were taken of the core surface after the Ag sheath was peeled off and optical micrographs were taken inside the core after polishing. As shown in figures 7(a) and (b), all cracks observed in the as-rolled tape run transverse to the tape length, while they run parallel to the tape length in the as-pressed tape as shown in figures 7(c) and (d). We consider that the observed difference in crack direction provides another key to elucidate the mechanism of the positive influence of applying the pressing. It is speculated that the stress situation induced by the pressing acts so as to reduce the cracks produced by the previous rolling process, which run transverse to the tape length and reduce the effective cross-sectional area for current flow along the tape length.

The optimum reduction rate for each cold deformation would be determined by the balance between improvement in density and initiation of microcracks which cannot be healed by subsequent heat treatment. We are currently carrying out more systematic investigations to clarify the contributions of densification and crack structure independently and to optimize the various processing parameters such as the number of cycles, reduction rate, heat treatment conditions and so on. The pressing itself is discontinuous and difficult to apply for long length wire production. However, there have been successful attempts at production of long Ag/Bi-2223 wires by periodic pressing [35] and eccentric rolling [36], which might be also applied for the production of long length Ba-122 wires with high transport $J_c$.

4. Conclusions

A high transport $J_c$ exceeding $10^4$ A cm$^{-2}$ at 4.2 K and 10 T was obtained with good reproducibility for Ag-sheathed ex situ PIT Ba-122 tapes by applying uniaxial pressing at the final stage of the deformation. We achieved the highest transport $J_c$ (at 4.2 K and 10 T) of $2.1 \times 10^4$ A cm$^{-2}$ among the PIT-processed Fe-based superconducting wires reported so far. The $J_c$–$H$ curves maintain small field dependence in strong magnetic fields up to 12 T, and this small field dependence is maintained up to the high temperature of 20 K. These results suggest that the Ag/Ba-122 tapes are promising for magnet applications at medium temperatures.
of cryogenic cooling or liquid hydrogen as well as in liquid helium. Microstructure investigations reveal that there are two possible reasons for the large enhancement of transport $J_c$. One is denser structure in the pressed tape, which can be correlated to the better grain connectivity, and the other is the change of crack structure. It is speculated that the application of pressing is effective in reducing the cracks formed by the previous rolling deformation, which run transverse to the tape axis. Further investigation is needed to clarify the contributions of densification and crack structure to enhancing the transport $J_c$. We believe that the results obtained in this study provide useful information for improving the PIT process of Fe-based superconductors so as to have higher density and fewer cracks running transverse to the tape length.

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