Recent Progress of Iron-Based Superconducting Round Wires

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Abstract. Recent progress of round wires using iron-based superconductors is reviewed. Both transport and magnetic \(J_c\) have been enhanced by several techniques such as purification of polycrystalline powders, high-pressure sintering (HIP), and control of drawing and sintering conditions. The present record of transport \(J_c\) of round wires is realized when the wire with 122-type compounds is processed at 175 MPa with a value at 4.2 K under 100 kOe being 38 kA/cm\(^2\) using (Ba,K)Fe\(_2\)As\(_2\). We also discuss HIP round wires of (Sr,K)Fe\(_2\)As\(_2\) and recently fabricated CaKFe\(_3\)As\(_3\). Details of the optimization of round wires to achieve large \(J_c\) values are described.

1. Introduction

Iron-based superconductors (IBSs) are one of promising candidates for future high-field applications of superconductors because they have high critical temperature, \(T_c\), large upper critical field, \(H_{c2}\), and relatively low anisotropy compared with cuprate superconductors [1,2]. Among IBSs, 122-type compounds of \((AE,K)Fe_2As_2\) \((AE = Ba, Sr)\) have been studied as promising materials for future application, because high critical current density, \(J_c\), is realized in superconducting wires and tapes using \((AE,K)Fe_2As_2\) [3-17]. For fabrication of superconducting wires and tapes, application of pressure is the most effective method to eliminate weak links between superconducting wires. For tapes, uniaxial press is effective for enhancement of \(J_c\) in (Ba,K)Fe\(_2\)As\(_2\) or (Sr,K)Fe\(_2\)As\(_2\) pressed tapes [3-8]. Recently, \(J_c\) in press tape under high magnetic field of 100 kOe achieved 1.5 x 10\(^5\) A/cm\(^2\), which is higher than the practical level of 10\(^3\) A/cm\(^2\) [8]. In the case of round wires, hot isostatic pressing (HIP) technique is used for the fabrication [9-17]. As shown in figure 1, highest \(J_c\) in the HIP wire achieved approximately 2 x 10\(^5\) A/cm\(^2\) under self-field and 3.8 x 10\(^4\) A/cm\(^2\) under 100 kOe, respectively. Although \(J_c\) in the HIP round wires is still lower than that in pressed tapes, they are more promising for high-field applications because its round shape is much more advantageous and convenient than the textured tapes for a wide range of applications.
In this report, recent progress of round wires using 122-type IBSs, mainly (Ba,K)Fe$_2$As$_2$, is reviewed. Both transport and magnetic $J_c$ have been enhanced by several techniques such as purification of polycrystalline powders, HIP process, and control of drawing and sintering conditions. The present record of transport $J_c$ of round wires is realized when the wire is processed at 175 MPa with a value at 4.2 K under 100 kOe being 38 kA/cm$^2$. We have also fabricated HIP round wires of (Sr,K)Fe$_2$As$_2$, and 1144-type IBSs of CaKFe$_4$As$_4$ for the first time. Details of the optimization of round wires to achieve large $J_c$ values and the dependence on raw materials are discussed below.

![Figure 1. Evolution of transport $J_c$ at 4.2 K under several magnetic field of the HIP round wires fabricated by our group and other groups [9,10,12,14,15,17].](image)

2. Experiments
All superconducting wires were fabricated by ex-situ powder-in-tube (PIT) method. Polycrystalline powders of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$, Sr$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ and CaKFe$_4$As$_4$ were prepared by the solid-state reaction. Details of powder preparation are described in previous papers [10-12,15,18]. Fabrication process of wires is schematically shown in figure 2. Ground powder was filled in a silver tube with an outer diameter of 4.5 mm and an inner diameter 3 mm. Here, three different fabrication processes were employed. First, Ag tubes filled with powder were cold drawn into a round shape with a diameter ~1.2 mm using dies with circular holes (“drawn”). Second, they were fabricated using only a groove roller with square grooves (“rolled”). Third, they were swaged using a rotary swaging machine (“swaged”). Obtained three kinds of wires were cut into short pieces. They are put into a 1/8 inch copper tube and redrawn into a square shape with a groove roller down to a diagonal dimension of ~1.2 mm. After the drawing process, both ends of the wire were sealed by using an arc furnace. The sealed wires were sintered using the HIP technique. All wires were heated up to 400-700°C in argon atmosphere, and sintered under different pressures of 0.1-170 MPa and for 0.5-12 h. HIP processes under the highest pressure 170 MPa were performed at National Institutes for Quantum and Radiological Science and Technology (QST), and others were performed at the University of Tokyo. The critical current measurements in high magnetic fields were carried out by using the 15T-SM at High Field Laboratory for Superconducting Materials, IMR, Tohoku University. Current–voltage ($I$–$V$) characteristics up to 140 kOe were measured by the four-probe method with solder for contacts. Bulk magnetization was measured to evaluate $T_c$ and magnetic $J_c$ by a superconducting quantum interference device (SQUID) magnetometer (MPMS-5XL, Quantum Design). Magnetic $J_c$ is evaluated using the extended Bean model. Vickers hardness, $H_v$, was measured on the polished surface of the wire core. For MO imaging, the HIP wire and tape were cut and the transverse cross sections were polished with lapping films. An
iron–garnet indicator film was placed in direct contact with the sample and the whole assembly was attached to the cold finger of a He-flow cryostat (Microstat-HR, Oxford Instruments). MO images were acquired by using a cooled-CCD camera with 12-bit resolution (ORCA-ER, Hamamatsu). The phase identification and the evaluation of texturing of the core of the HIP wire were carried out by powder XRD with Cu-Kα radiation (Smartlab, Rigaku).

**Figure 2.** The fabrication process of PIT-HIP round wires.

3. Results and discussion

**Figure 3.** (a) Magnetization as a function of temperature at 5 Oe for (Ba,K)Fe₂As₂ powders. (b) (116) peaks in x-ray diffraction patterns of (Ba,K)Fe₂As₂ powders. (c) Magnetization as a function of temperature at 10 Oe for (Ba,K)Fe₂As₂ HIP wires #1, #2, and #3 are correspond to the data of ref. [10], ref. [12], and ref. [15], respectively.

Figure 3(a) shows temperature dependence of magnetization of (Ba,K)Fe₂As₂ powders. Powders of #1, #2, and #3 correspond to the data of ref. [10], ref. [12], and ref. [15], respectively. The quality of powder #2 were improved compared to that of powder #1 by changing the synthesis conditions, such as nominal compositions, using elements or precursors as raw materials, heating temperature and time, and so on [10, 12]. Synthesis processes were further improved by adopting the ball milling process to mix raw materials and sintering by packing raw materials in Nb tube, and powder #3 was obtained [15]. As a result, magnetization of the newest powder of #3 shows sharper drop at \( T_c \). Improvements of synthesis processes are also confirmed from x-ray diffraction measurements. No impurity peaks are identified in #3. As shown in figure 3(b), it is obvious that the newest powder #3 shows narrow peak
profile and clear separation of $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks is observed. This narrow diffraction peak also guarantees homogeneity of grains in the wire core. Clear difference of $T_c$ in HIP wires using these polycrystalline powders are shown in figure 3(c). It should be noted that wire fabrication conditions such as sintering pressure and temperature of the HIP wires #2 and #3 are almost the same. Nevertheless, $T_c$ and $J_c$ in the HIP wire #3 are larger than those in the wire #2. These results clearly indicate that purification of polycrystalline powders is effective for enhancement of $J_c$.

In the process of detailed evaluation of the properties of the wire, such as $T_c$ and $J_c$ at each step of the wire fabrication, we unexpectedly found degradation of polycrystalline powders in the wire core, including its superconducting properties, during the drawing process [12]. This is clearly seen in figure 4(a) as a decrease of shielding volume fraction and slight suppression of $T_c$ before sintering as the diameter of the wire becomes smaller. We have also found that degradation of superconducting properties of the core of the HIP wire by the drawing process can be recovered by the following heat treatment. As shown in figure 4(b) the reduced $T_c$ by the repeated drawing processes is partly recovered through the HIP treatment. As the sintering temperature increases, the $T_c$ of the sintered wire increases. The highest $T_c$ of the HIP wire is ~35 K, which is close to $T_c = 38$ K of the as-grown powder. It suggests that sintering at higher temperatures is very effective for the recovery of $T_c$ and shielding volume fraction. It should be noted that the sintering temperature is limited by the melting temperature of Ag/Cu alloy of ~770 °C, in the case of present HIP method using Ag and Cu sheaths. The sintering-temperature dependence of magnetic $J_c$ is similar to that of $T_c$ as shown in figure 4(c). The dashed line indicates the melting point of Ag/Cu alloy of ~770 °C. Similar to the case of $T_c$, $J_c$ in the HIP wire sintered at 713 °C has the highest self-field $J_c$. These results clearly indicate that a higher sintering temperature is favorable for increasing $J_c$. Sintering-temperature dependence of both $T_c$ and $J_c$ implies that damaged polycrystalline powders in the core of the HIP wire during the drawing process are recovered by high-temperature sintering.

![Figure 4](image_url)

*Figure 4.* (a) Normalized magnetization as a function of temperature of (Ba,K)Fe$_2$As$_2$ powders which were extracted Ag sheathed wires of various rolling steps. Reduction of wire diameter after rolling is shown in the figure. (b) Normalized magnetization as a function of temperature of (Ba,K)Fe$_2$As$_2$ HIP wires which were sintered in argon atmosphere under 9 MPa pressure for 12 h at various temperatures. (c) Sintering temperature dependence of $J_c$ and $T_c$ (midpoint) in HIP wires estimated from the magnetization measurements [12].

Next, we focus on the effects of sintering pressure on physical properties in the HIP wire. To improve weak links between grains, higher density is advantageous. Sintering at higher pressure should be effective for that. Superconducting properties in the HIP wires sintered at 700°C under several pressures were evaluated from magnetization measurements as shown in figures 5(a) and (b). In HIP wire sintered under the highest pressure of 175 MPa, highest $T_c$ and $J_c$ are realized. These results are summarized in figures 5(c) and (d). Clearly, $T_c$ and $J_c$ are correlated to the sintering pressure. Furthermore $Hv$ also shows positive correlation with the sintering pressure shown in figure 5(c). This suggests the improvement of weak-links in grains and promotion of the reaction of raw materials by
densification. It is clearly confirmed systematically in IBS round wire that high core density plays a key role in achieving the practical level of $J_c$, as discussed in IBS pressed tape [3].

**Figure 5.** (a) Normalized magnetization as a function of temperature of (Ba,K)Fe$_2$As$_2$ “swaged” HIP wires which were sintered at in argon atmosphere under several pressures at 700°C. (b) Magnetic $J_c$ as a function of magnetic field of these wires. Sintering pressure dependence of (c) magnetic $J_c$ at 4.2 K under self-filed, (b) $T_c$, and (c) Vickers hardness ($H_V$) in these wires.

Recently, we found that wire-drawing process strongly affect their $J_c$. Magnetic field dependence of transport $J_c$ in “drawn”, “swaged”, and “rolled” HIP wires are shown in figure 6(a). Their raw material of polycrystalline powders and HIP sintering conditions are the same. Nevertheless, $J_c$ at high field of 100 kOe in “drawn”, “swaged”, and “rolled” HIP wires are 38 kA/cm$^2$ [17], 32 kA/cm$^2$, 20 kA/cm$^2$ [15], respectively. Let us discuss the reason why we obtained significantly different values. First possible reason is the difference of degree of degradation of superconducting core caused in the course of different wire fabrication processes. Figure 6(b) shows the temperature dependence of magnetization in these HIP wires. The $T_c$ of the “drawn” and “swaged” HIP wires are approximately 1 K higher compared with that in “rolled” HIP wire. Higher $T_c$ suggests more homogeneous carrier distribution. Considering the fact that the same powder was used for them, wire fabrication with more homogeneous force using dies is effective to suppress the degradation of the core during the drawing process and help recovery in the sintering process as described in figure 4 [12]. Second and most possible reason is the difference of degree of texturing of the superconducting core caused by different wire fabrication processes. Texturing in the core of the HIP wire was analysed using x-ray diffraction. HIP wires were cut and polished to prepare two kinds of surfaces, which are perpendicular (transverse) and parallel (longitudinal) to the current direction, as shown in figures 7(a) and (b), respectively. XRD intensities for (002) and (103) peaks for two kinds of surfaces are shown and compared in figures 7(a) and (b). It should be noted that the intensity in the left part of figure 7(a) is multiplied approximately by 2.2 to normalize the incident x-ray intensity for the comparison with the right part of figure 7(a). Obviously, the ratio of peak intensity of (002) and that of (003), $r$, shows clear difference.
Smaller \( r \) is observed when the x-ray is reflected by the surface perpendicular to the current as shown in figure 7. In the case of pressed tapes, where grains are well-textured along the c-axis, the value of \( r \) becomes much larger than the unity [3]. Reduction of the intensity of the (002) peak shown in figure 7(a) implies that the fraction of grains with their c-axis perpendicular to the current is reduced. 122-type materials are layered compounds and they usually show plate-like shapes. It is suggested that these grains in the core are textured during the drawing and groove-rolling processes, although the degree of texturing is much weaker compared with tapes. During fabrication processes, plate-like grains could be concentrically textured, as shown by the yellow broken lines in inset of figure 7(c). To determine the degree of texturing, we made a series of XRD measurements as the wire core is successively thinned down. The prepared surface is parametrized by \( \alpha \), as described in inset of figure 7(c). It is expected that the intensity of the (002) peaks is enhanced near the surface, while it is suppressed near the center. We repeated the polishing of the HIP wire, and the XRD measurements, alternately. Estimated \( r \) values are plotted as a function of \( \alpha \) in figure 7(c). The general trend of \( r \) as a function of \( \alpha \) is similar to the expected one. This result also suggests that grains in the core are textured during the wire-fabrication process. Furthermore, compared with the “drawn” HIP wire, the value of \( r \) in the “rolled” HIP wire is smaller. This implies that the degree of texturing is enhanced by the drawing process using dies compared with the groove-rolling process. The weaker texturing in the groove-rolled wire may be due to the less symmetric shape of the core.

Finally, we discuss several IBSs for raw materials of PIT wires. Both the transport and magnetic \( J_c \) for the (Ba,K)Fe\(_2\)As\(_2\), (Sr,K)Fe\(_2\)As\(_2\), and CaKFe\(_4\)As\(_4\) HIP wires from our previous studies are shown in figure 8(a) [11,17,18]. (Ba,K)Fe\(_2\)As\(_2\) HIP wire has the highest transport \( J_c \) among all IBS round wires, at present. From the optical images of the transverse cross sections of the HIP wires in figures 8(b)-(d), copper, silver, and superconducting core regions are clearly identified and no voids are observed. Figures 8(e)-(g) show MO images of the transverse cross section of the core of the HIP wires correspond to figures 8 (b)-(d) in the remanent state at 5 K, respectively. The smooth variation of the trapped magnetic field in the HIP wires at 5 K indicates the presence of a uniform bulk current flowing in the wires core across grains. However, \( J_c \) at magnetic field of 10 kOe in (Sr,K)Fe\(_2\)As\(_2\) and CaKFe\(_4\)As\(_4\) HIP wires are significantly lower than that in (Ba,K)Fe\(_2\)As\(_2\) HIP wire. For (Sr,K)Fe\(_2\)As\(_2\) and CaKFe\(_4\)As\(_4\) HIP wires, the condition of polycrystalline-powder synthesis and wire fabrication processes are still not improved and impurities in the core of the wire still remain [18]. They still remain as candidate of raw materials for high \( J_c \) HIP wire. Actually, the tape of (Sr,K)Fe\(_2\)As\(_2\) reaches significantly high \( J_c \) [4,5]. The value of \( J_c \) in single crystal CaKFe\(_4\)As\(_4\) is comparable to that in single
crystal of (Ba,K)Fe$_2$As$_2$ [19], and further enhancement of $J_c$ in both wires and tapes using CaKFe$_4$As$_4$ is expected [18,20]. Further improvements of wire fabrication process are demanded for them.

![Figure 7](image)

**Figure 7.** (a) (b) Powder XRD data of (002) and (103) peaks for two different cross sections of the HIP wires. Insets show the schematics of each cross section. Intensity in the left part of figure (a) is multiplied by 2.2 to normalize the incident x-ray intensity for the comparison with the right part of figure (b). Inset of (c) shows the schematic of the polished core of wire. $d$ is the diameter of the core and $\alpha$ is the parameter that characterizes the exposed surface of the core. Yellow dotted lines indicate the possible texturing of grains in the core. (c) $\alpha$ dependence of the ratio of intensities of powder XRD peaks of (002) and (103), $r$, of the HIP wire [17].

![Figure 8](image)

**Figure 8.** Transport $J_c$ as function of magnetic field in the HIP wires using (Ba,K)Fe$_2$As$_2$ [17], (Sr,K)Fe$_2$As$_2$ [11] and CaKFe$_4$As$_4$ [18]. Optical micrograph of the HIP wires of (b) (Ba,K)Fe$_2$As$_2$, (c) (Sr,K)Fe$_2$As$_2$, and (d) CaKFe$_4$As$_4$. Corresponding MO images of the HIP wires in the remanent state at 5 K of (e) (Ba,K)Fe$_2$As$_2$, (f) (Sr,K)Fe$_2$As$_2$, and (g) CaKFe$_4$As$_4$.

4. Summary
Recent progress of IBS round wires is reviewed. Transport $J_c$ has been enhanced by successive introductions of several techniques such as purification of polycrystalline powders, high-pressure
sintering, control of drawing and sintering condition, the improvement of links in grains and promotion of the reaction of raw materials by densification, and enhancing the texturing inside the wire core by introduction of dies or rotary swager in the drawing process. The present records of transport \( J_c \) of round wires are realized for that processed at 175 MPa with values at 4.2 K under self-field and 100 kOe being \( 2.0 \times 10^5 \ A/cm^2 \) and \( 3.8 \times 10^4 \ A/cm^2 \), respectively, using (Ba,K)Fe\(_2\)As\(_2\), (Sr,K)Fe\(_2\)As\(_2\) and CaKFe\(_2\)As\(_4\) are also possible candidates of raw materials for high-\( J_c \) round wires. We expect that further enhancement of \( J_c \) in these HIP wires can be realized by further purification of raw materials, enhancing the degree of texturing and further densification of the core using higher pressure.

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