Transport properties and microstructure of mono- and seven-core wires of FeSe$_{1-x}$Te$_x$ superconductor produced by the Fe-diffusion powder-in-tube method

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Abstract
We report the successful fabrication of mono- and seven-core superconducting wires of FeSe$_{1-x}$Te$_x$ using an in situ Fe-diffusion process based on the powder-in-tube (Fe-diffusion PIT) method. The reacted layers in these wires were found to have composite structure with the composition nearly FeSe and FeTe for the inner and outer layers, although a single layer of composition FeSe$_{0.5}$Te$_{0.5}$ was supposed to be formed. The self-field transport $J_c$ values at 4.2 K were found to be 226.2 A cm$^{-2}$ and 100.3 A cm$^{-2}$ respectively for mono- and seven-core wires. The $J_c$s of these wires dropped rapidly at low fields and then showed a gradual decrease with increasing magnetic fields. In addition, the seven-core wire showed higher $J_c$ than the mono-core wire under higher magnetic fields, indicating that the seven-core wire of FeSe$_{1-x}$Te$_x$ superconductor produced using the Fe-diffusion PIT method is advantageous for superconducting wire applications under high magnetic fields.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
The discovery of superconductivity in iron oxypnictides [1] has generated strong interest in understanding the fundamental properties as well as pursuing potential applications. To date, several families of iron-based superconductors have been discovered [2–5] and the transition temperature $T_c$ has been raised above 50 K [1, 6]. Among these iron-based superconductors, FeSe with $T_c \sim 8$ K is a particularly important material for elucidating the mechanism of superconductivity in iron-based superconductor owing to its simple crystal structure composed solely of stacked iron–chalcogenide layers along the $c$-axis [4]. The $T_c$ of FeSe is found to increase up to 15 K on the partial substitution of Te or S for Se [7–10]. The $T_c$ also shows a dramatic increase with applied external pressure reaching values as high as 37 K [11–13]. Earlier studies have shown that the upper critical field ($H_{c2}$) of FeSe$_{0.5}$Te$_{0.5}$ can be as high as $\sim 50$ T [14]. The starting materials for these chalcogenides are less toxic compared to the FeAs-based compounds. These aspects make the iron chalcogenides potential candidates for applications among the new iron-based superconductors.

We have succeeded in observing the transport critical current density $J_c$ of FeSe$_{1-x}$Te$_x$ tape [15] using an in situ Fe-diffusion process based on the powder-in-tube (Fe-diffusion PIT) method. The interesting aspect of this process is that the Fe sheath plays the role of not only the sheath but also the raw materials for synthesizing the superconducting phase. This process is very simple and advantageous for fabricating superconducting wires. In our previous report on
superconducting tapes of FeSe$_{1-x}$Te$_x$ [15], we have adopted an annealing temperature of 400 °C. Such a low temperature was used to prevent evaporation of chalcogen during a treatment. However, in order to enhance $J_c$, much better grain connectivity is required, which calls for higher sintering temperatures. Therefore, we decided to sinter the wires at 700 °C, which is the temperature used for the synthesis of polycrystalline bulk samples of FeSe$_{1-x}$Te$_x$. For high-temperature sintering, the effective diffusion distance of Fe needs to be shortened so that Fe reacts with chalcogen before it evaporates. For this purpose, the wires were thinned down with a wire-drawing die. We also fabricated multi-core wires, where the cross-sectional area of the individual wires are even smaller, leading to better possibilities for reaction without the escape of chalcogen atoms. This paper provides the details of the fabrication and the superconducting properties of mono- and seven-core wires of FeSe$_{1-x}$Te$_x$ superconductor produced using the Fe-diffusion PIT method.

2. Experimental details

We prepared the SeTe precursor with a ratio of 1:1 by solid-state reaction. The precursor obtained was ground and filled into a pure Fe tube with an outer diameter of 6.2 mm, an inner diameter of 3.5 mm and a length of 48 mm. The tube was rolled into a rectangular rod of about 2.5 mm in size using groove rolling. After that, in order to reduce its diameter, it was drawn into a wire of 1.1 mm in diameter using a wire-drawing die. This wire was cut into pieces. Some wire pieces were used as samples of mono-core wires. A seven-core wire was produced by packing seven unsintered pieces of mono-core wire into another Fe tube. The seven-core composite was drawn into a wire with a final diameter of 2.0 mm. The seven-core wire was cut into short pieces. These mono- and seven-core wires were sealed inside a quartz tube evacuated and back-filled with argon gas. These sealed wires were heat treated at 700 °C for 2 h.

The microstructure of these wires was investigated using a scanning electron microscope (SEM) and x-ray diffraction (XRD). The actual composition of the reacted layer was investigated using energy-dispersive x-ray spectrometry (EDX). Transport critical currents ($I_c$) were measured for 4 cm long wires by a standard four-probe resistive method at 4.2 K in magnetic fields. The magnetic fields were applied perpendicularly to the wire axis. The criterion of $I_c$ definition was $1 \mu$V cm$^{-1}$. The $I_c$ was obtained by dividing $I_c$ by the cross-sectional area of the FeSe$_{1-x}$Te$_x$ core excluding the hole, which was measured using an optical microscope.

3. Results and discussion

Figures 1(a) and (b) show optical micrographs of the polished transverse cross-sections of the as-drawn mono- and seven-core wires, respectively. The cross-sections of these wires show uniform deformation of the composite. Figures 2(a) and (b) show the polished transverse cross-sections of mono- and seven-core wires after heat treatment at 700 °C for 2 h.

A reacted layer was observed on the inside wall of the Fe sheath and a hole was formed at the center of each core, where the TeSe precursor was filled in before heat treatment. Theoretically, volume contraction caused by the formation of FeSe$_{0.5}$Te$_{0.5}$ could not happen. Hence, the formation of the hole would be due to the evaporation of Se and Te.

Figure 3 shows the magnetic field dependence of the transport $J_c$ for the mono- and seven-core FeSe$_{1-x}$Te$_x$ wires at 4.2 K. We succeeded in observing the transport $J_c$ for mono- and seven-core FeSe$_{1-x}$Te$_x$ wires. The self-field $J_c$ values for mono- and seven-core wires can be as high as 226.2 A cm$^{-2}$ and 100.3 A cm$^{-2}$ at 4.2 K, respectively. For comparison, the $J_c$–$B$ curve at 4.2 K for the FeSe$_{1-x}$Te$_x$ tape data [15] reported previously is also plotted in figure 3. From this comparison, it is seen that the $J_c$ value of mono-core wire is about 20 times higher than that of the FeSe$_{1-x}$Te$_x$ tape. The $J_c$s of mono- and seven-core wires showed a rapid decrease at low fields and then gradually decreased with increasing magnetic field.
reacted layer

hole

Fe sheath

250 µm

(a) Fe sheath

reacted layer

hole

(b) Fe sheath

reacted layer

500 µm

Figure 2. Optical micrographs of transverse cross-sections for (a) mono-core wire and (b) seven-core wire after heat treatment at 700 °C for 2 h.

Figure 3. Magnetic field dependence of the transport $J_c$ at liquid-helium temperature (4.2 K) for mono- and seven-core wires. $J_c$ was calculated by dividing the $I_c$ by the cross-sectional area of the reacted layer except for the holes. The magnetic field was applied perpendicular to the wire axis. The FeSe$_{1-x}$Te$_x$ tape was heat treated at 400 °C for 2 h [15].

Field. Furthermore, the seven-core wire exhibits higher $J_c$ than the mono-core wire in high magnetic fields, indicating that the seven-core wire prepared by the Fe-diffusion PIT method has clear advantages for technological applications in high magnetic fields. However, the $J_c$ is about three orders of magnitude less than the intra-grain $J_c$ [16]. This implies the presence of weak links between grains. Higher $J_c$ values would be expected from enhancement of the grain connectivity.

The temperature dependence of the resistivity for the mono-core FeSe$_{1-x}$Te$_x$ wires under different applied magnetic fields is shown in figure 4. The resistivity at 0 T began to decrease at 11.6 K and dropped to zero at 9.9 K. It is clear that the $\rho(T)$ curves are shifted to lower temperatures with increasing magnetic field without noticeably broadening. The transition width $\Delta T$ defined by the 90% and 10% points on $\rho(T)$ is less than 2 K. This behavior is similar to that of the low-temperature superconductors with small anisotropy [17, 18]. We have estimated the upper critical field ($\mu_0 H_{c2}$) and the irreversibility field ($\mu_0 H_{irr}$), using 90% and 10% of the normal-state resistivity, respectively. The $\mu_0 H_{c2}$ and $\mu_0 H_{irr}$ are plotted in the inset of figure 4 as functions of temperature. The $\mu_0 H_{irr}$ line is very close to the $\mu_0 H_{c2}$ line. These lines show an upturn curvature near 0 T. Such curves could be ascribed to the effect of excess Fe [19]. Above 2 T, both $\mu_0 H_{c2}(T)$ and $\mu_0 H_{irr}(T)$ lines show a linear curve with slopes of $d\mu_0 H_{c2}/dT = 2.6$ T K$^{-1}$ and $d\mu_0 H_{irr}/dT = 2.5$ K$^{-1}$. Linear extrapolation of the $\mu_0 H_{c2}(T)$ and $\mu_0 H_{irr}(T)$ data suggests $\mu_0 H_{c2}(0) \sim 27$ T and $\mu_0 H_{irr}(0) \sim 22$ T.

In order to identify the different phases formed by heat treatment, XRD analysis was performed for the reacted layer. Figure 5 shows the XRD pattern of the reacted layers obtained from the mono-core FeSe$_{1-x}$Te$_x$ wire. For comparison, calculated data for FeSe and FeTe are also shown in figure 5. It was found that the main peaks could be identified as the FeSe and FeTe ones, and the minor peak was identified as that of the hexagonal phase, indicated with asterisk, although SeTe powders were mixed in an Se:Te = 1:1 atomic ratio to form the mixed composition FeSe$_{0.5}$Te$_{0.5}$. Table I shows the lattice constants $a$ and $c$ of FeTe and FeSe formed in FeSe$_{1-x}$Te$_x$ wire calculated from the XRD pattern. The calculated lattice parameter of FeTe formed in the FeSe$_{1-x}$Te$_x$ wire was somewhat smaller compared to that of the bulk [9, 20]. In contrast, the calculated lattice parameter of FeSe formed in the FeSe$_{1-x}$Te$_x$ wire was somewhat higher compared to that of the bulk [9, 21]. The shrinkage of the lattice parameter of FeTe might be due to the partial substitution of Se for the Te site. On the other hand, the enlargement of the lattice
Figure 4. Temperature dependence of the resistivity for mono-core wires under magnetic fields up to 7 T. The inset shows the temperature dependence of $\mu_0 H_{c2}$ and $\mu_0 H_{irr}$ determined from 90\% and 10\% points on the resistive transition curve.

Table 1. Lattice parameters of FeTe and FeSe formed in FeSe$_{1-x}$Te$_x$ mono-core wire.

|           | a-axis length (Å) | c-axis length (Å) |
|-----------|-------------------|-------------------|
| FeTe      | 3.8163(1)         | 6.2308(6)         |
| FeSe      | 3.7800(7)         | 5.5162(27)        |

parameter of FeSe is likely to arise from the partial substitution of Te at the Se site. In fact, the resistivity of the mono-core FeSe$_{0.5}$Te$_{0.5}$ wire dropped to zero at $T^\text{zero} = 9.9$ K, indicating the partial substitution of Te for the Se site in FeSe, because $T^\text{zero}$ observed for FeSe is only $\sim 8$ K [4, 21].

Figure 6 displays an SEM image and the elemental mapping images for the polished longitudinal cross-section of the mono-core FeSe$_{1-x}$Te$_x$ wire. The Fe distribution is homogeneous in the reacted layer, which indicates that the Fe sheath supplied Fe reasonably well to the reacted layer. It is found that the reacted layer had a composite structure of two main layers: the first layer, where Se is found to be distributed more densely near the Fe sheath, and the second layer, where Te is distributed more densely close to the center of the Fe sheath. A weak concentration of Te was also observed at the interface between the Fe sheath and the reacted layer. Table 2 summarizes the measured composition at points A–E in figure 6. EDX analysis of each spot showed that the reacted layer is composed of a slightly Se-substituted FeTe layer and a slightly Te-substituted FeSe layer. This is consistent with the results from XRD and elemental mapping images. The composition at the interface between the Fe sheath and the superconducting core shows much less Fe and Te than FeSe$_{0.5}$Te$_{0.5}$. Given the XRD pattern result, this might indicate that hexagonal FeSe$_{1-x}$Te$_x$ is formed at the interface.

Table 2. Compositions detected by SEM–EDX for the points indicated in figure 6.

|   | Se  | Te  | Fe  |
|---|-----|-----|-----|
| A | 1.32| 42.61| 56.07|
| B | 1.66| 42.51| 55.83|
| C | 48.79| 1.41| 49.80|
| D | 40.40| 17.47| 42.13|
| E | 0    | 0    | 100  |

(at.%)

The slightly Se-substituted FeTe layer in the FeSe$_{1-x}$Te$_x$ wire might be almost a non-superconductor. We believe that the transport $J_c$ could be improved by increasing the FeSe layer, which might be accomplished by changing the atomic ratio of Te to Se packed into the Fe sheath. Currently work is in progress to check this hypothesis.

4. Conclusion

We fabricated mono- and seven-core wires of FeSe$_{1-x}$Te$_x$ by the Fe-diffusion PIT method. The self-field transport $J_c$ values of 226.2 A cm$^{-2}$ and 100.3 A cm$^{-2}$ at 4.2 K were obtained for mono- and seven-core wires, respectively. The seven-core wire exhibits a higher $J_c$ than the mono-core wire in high magnetic fields, indicating that the seven-core FeSe$_{1-x}$Te$_x$ wire could be promising for magnetic applications. The FeSe$_{1-x}$Te$_x$ wire showed practically no broadening of the resistive transition under magnetic fields. This behavior is similar to that of low-temperature superconductors with small anisotropy. The reacted layer was found to be composed of a slightly Se-substituted FeTe layer and a slightly Te-substituted FeSe.
layer, although Te powder and Se powder were mixed in a Te:Se = 1:1 atomic ratio to form the nominal composition FeSe$_{0.5}$Te$_{0.5}$. These results indicate that the optimization of the atomic ratio of Te to Se packed into the Fe sheath and introduction of pinning centers will help in realizing higher $J_c$ and $T_c$ values.

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References

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 J. Am. Chem. Soc. 130 3296
[2] Rotter M, Tegel M and Johrendt D 2008 Phys. Rev. Lett. 101 107006
[3] Wang X C, Liu Q Q, Lv Y X, Gao W B, Yang L X, Yu R C, Li F Y and Jin C Q 2008 Solid State Commun. 148 538
[4] Hsu F C et al 2008 Proc. Natl Acad. Sci. USA 105 14262
[5] Ogino H, Sato S, Kishio K, Shimoyama J, Tohei T and Ikuhara Y 2010 Appl. Phys. Lett. 97 072506
[6] Ren Z A et al 2008 Chin. Phys. Lett. 25 2215
[7] Fang M H, Pham H M, Qian B, Liu T J, Vehstedt E K, Liu Y, Spini L and Mao Z Q 2008 Phys. Rev. B 78 224503
[8] Yeh K W et al 2008 Europhys. Lett. 84 37002
[9] Mizuguchi Y, Tomioka F, Tsuda S, Yamaguchi T and Takano Y 2009 J. Phys. Soc. Japan 78 074712
[10] Mizuguchi Y, Tomioka F, Tsuda S, Yamaguchi T and Takano Y 2009 Appl. Phys. Lett. 94 012503
[11] Mizuguchi Y, Tomioka F, Tsuda S, Yamaguchi T and Takano Y 2008 Appl. Phys. Lett. 93 152505
[12] Medvedev S et al 2009 Nature Mater. 8 630
[13] Masaki S, Kotevagawa H, Hara Y, Tou H, Murakata K, Mizuguchi Y and Takano Y 2009 J. Phys. Soc. Japan 78 063704
[14] Khim S, Kim J W, Choi E S, Bang Y, Nohora M, Takagi H and Kim K H 2010 Phys. Rev. B 81 184511
[15] Mizuguchi Y, Deguchi K, Tsuda S, Yamaguchi T, Takeya H, Kumakura H and Takano Y 2009 Appl. Phys. Express 2 083004
[16] Taen T, Tsachiya Y, Nakajima Y and Tamegai T 2009 Phys. Rev. B 80 092502
[17] Godeke A, Fischer M C, Squitieri A A, Lee P J and Larbalestier D C 2005 J. Appl. Phys. 97 093909
[18] Kumakura H, Kitaguchi H, Matsumoto A, Yamada H, Hirakawa M and Tachikawa K 2005 Supercond. Sci. Technol. 18 147
[19] Ge J, Gao S, Shen S, Yuan S, Kang B and Zhang J 2010 Solid State Commun. 150 1641
[20] Sales B C, Sefat A S, McGuire M A, Jin R Y, Mandrus D and Mozharivskyy Y 2009 Phys. Rev. B 79 094521
[21] McQueen T M et al 2009 Phys. Rev. B 79 014522

Figure 6. Scanning electron microscopy (SEM) image and Fe, Se and Te concentration mappings measured by EDX (energy-dispersive x-ray spectroscopy) on the polished longitudinal cross-section for the mono-core wire.