FeTe$_{0.6}$Se$_{0.4}$ bulk single crystals with high critical current densities under magnetic fields

Y Tanaka$^1$, Y Mizuguchi$^1$ and O Miura$^1$

$^1$Dept. of Electrical and Electronic Engineering, Tokyo Metropolitan University, Hachioji 192-0397, Japan
e-mail: tanaka-yuuji1@ed.tmu.ac.jp

Abstract. We have fabricated FeTe$_{0.6}$Se$_{0.4}$ large-size bulk single crystals with high critical current densities ($J_c$) under magnetic fields. FeTe$_{0.6}$Se$_{0.4}$ single crystals were prepared by the melting method with two stage heat treatments. The X-ray diffraction (XRD) analysis and the remanent magnetization method showed that the fabricated bulk crystals are intrinsically single crystals from viewpoint of the critical current flow. Temperature dependence of magnetization revealed that low-$T_c$ region exists inside the crystals. The magnetization curves indicated the typical fishtail type, and the magnetic $J_c$ under the magnetic field parallel to the c-axis at 4.2 K achieved 0.36 and 0.2 MA/cm$^2$ at 0 T and 5 T respectively. From the temperature scaling behavior of flux pinning properties we speculated that low-$T_c$ regions near excess Fe moderately distributed inside the crystal are dominant pinning centers in high fields at low temperatures.

1. Introduction

The discovery of iron-based superconductors (IBSs) at 26 K in LaFeAsO (1111 system) doped with fluoride was a surprise since most Fe compounds are magnetic [1]. Soon after the first report, the superconducting transition temperature ($T_c$) was raised to as high as 55 K by replacing La with other rare earths such as Ce [2], Pr [3], Nd [4], Sm [5], or Gd [6]. In addition, other crystal structure types of layered Fe compounds were found to become superconductors; for example, Ba$_{1-x}$K$_x$Fe$_2$As$_2$ (122 system) [7], Li$_{1-x}$FeAs (111 system) [8], and FeSe (11 system) [9]. FeSe has the simplest crystal structure among the IBSs and less toxicity as compared to the FeAs systems, which are advantageous for applications. Partial substitution of Se by Te can effectively enhance $T_c$ to around 14 K [10]. Furthermore, upper critical field ($H_{c2}$) is as high as around 50 T [11]. Due to their high superconductivity performance in high magnetic fields, FeTe$_{1-x}$Se$_x$ wire fabrication has been studied by several researchers [12-14]. We have fabricated FeTe$_{0.6}$Se$_{0.4}$ superconducting tapes by a newly developed chemical-transformation powder-in-tube method [15]. However, the critical current densities ($J_c$) was as low as 3.0 $\times$ 10$^3$ A/cm$^2$ at 4.2 K, which was not enough for practical use. This is due to the formation of non-superconducting phase at the grain surface of crushed crystal resulting in the low electrical connectivity between the grains [16]. Therefore, to improve $J_c$ properties for FeTe$_{1-x}$Se$_x$ system the fabrication of large-size bulk single crystals and studies for the flux pinning mechanisms are needed.

In this paper, we have fabricated FeTe$_{0.6}$Se$_{0.4}$ large-size bulk single crystals with high $J_c$ by the melting method with two stage heat treatments. $J_c$ in magnetic fields and the flux pinning properties were investigated. We also studied the effective pinning centers in the crystals.
2. Experimental

FeTe_{0.6}Se_{0.4} was prepared by the melting method. Iron powder (99.9%), selenium chips (99.999%) and tellurium chips (99.999%) were used as starting materials. The stoichiometric quantities of 2 g were put into small double quartz tubes, evacuated at less than 5 Pa, and sealed. Then it was heated up to 850 °C and kept for 10 h, followed by slow cooling down to 600 °C at a rate of 4 °C / h. After that, the temperature was rapidly cooled down to 400 °C and kept for 200 h for crystal homogenization. Finally it was cooled down to room temperature by shutting down the furnace. The as-grown sample is a columnar shape single crystal with 8 mm in diameter and 10 mm in length. The crystal structure was confirmed by X-ray diffraction (XRD) with Cu Kα radiation ($\lambda = 1.541841 \text{ Å}$).

A photograph of the as-grown single crystal is shown in figure 1. The crystal is easily cleaved perpendicular to the c-axis. The perpendicular direction to the center axis of the as-grown columnar sample is the c-axis direction. Magnetization was measured by a superconducting quantum interference device (SQUID) magnetometer and $T_c$ was determined from the temperature dependence of magnetization when a magnetic field of 10 Oe was applied to the c-axis direction. We confirmed that a large shielding current flows at all over the crystal by the remanent magnetization method [17, 18]. Hence, $J_c$ was estimated from the hysteresis width of magnetization curves by Bean’s critical state model [19].

![Figure 1](image1.png)

**Figure 1.** A photograph of the as-grown single crystal with a cleavage plane.

![Figure 2](image2.png)

**Figure 2.** XRD patterns of the fabricated crystal for (a) powder and (b) a cleavage plane.

3. Result and discussion

Figures 2 show the XRD patterns for (a) powder and (b) a cleavage plane of the fabricated FeTe_{0.6}Se_{0.4} crystal. Figure 2 (a) shows that there are no impurity peaks [10]. Figure 2 (b) shows only the peaks of the (0 0 l) planes. Therefore, we confirmed that it is a highly pure and c-axis oriented crystal.

Figure 3 shows the temperature dependence of magnetization when applying a magnetic field of 10 Oe to the c-axis direction under ZFC and FC conditions. It shows the sharp transition with $T_c$ onset of 14 K. This indicates that the fabricated crystal is a relatively uniform single crystal. On the other hand, the positive magnetization due to excess Fe was observed. The excess Fe concentration at the interlayer sites between Fe$_2$Te$_2$ layers can be turned by initial amount of Fe and annealing conditions [20]. A slight decrease in diamagnetism was also observed between 5 to 8 K in the ZFC conditions. It probably comes from low-$T_c$ regions with a relatively high Fe concentration moderately distributed inside the crystal. They have the potential to act as effective flux pinning centres as well as dislocations in the crystal.
Figure 3. Temperature dependence of magnetization applying 10 Oe to the c-axis direction. (a) of insets shows enlargement near Tc. (b) of insets shows enlargement near 5 to 8 K in ZFC.

Figure 4. Magnetic field dependence of magnetization applying magnetic field to the c-axis direction for each temperature.

Figure 5. Temperature dependence of (a) $J_c$-B properties (b) $F_p$-B properties.

Figure 4 shows the magnetic field dependence of magnetization for each temperature when a magnetic field is applied to the c-axis direction. Fishtail shape magnetization curves appear from 4.2 K to 10 K. The fishtail shape indicates that the pinning force densities ($F_p$) in the magnetic fields is strong. As the temperature increases, the magnetization and the fishtail shape decreases.

$J_c$ was estimated from the Bean model using the magnetization width ($\Delta M$) of $M$-$B$ curves. Temperature dependence of $J_c$-B properties under magnetic fields is shown in figure 5 (a). $J_c$ at 4.2 K achieved 0.359 and 0.195 MA / cm$^2$ at 0 T and 5 T respectively. In addition, it keeps over 0.10 MA / cm$^2$ in higher magnetic fields. Figure 5 (b) shows temperature dependence of $F_p$-B properties. $F_p$ achieved 115 GN / m$^3$ at 4.2 K under 6.5 T. As the rise of temperature, $F_p$ decreased and the peak $F_p$ shifted to the low magnetic field side.
Figure 6 shows the irreversible fields (B_{irr}) for the crystal where the magnetization hysteresis disappears. When the irreversible temperature (T_{irr}) is defined as the temperature where the magnetization hysteresis derived from the pinning current disappears, the fitting was estimated from the formula of \( B_{irr}(T) = B_{irr}(0)[1-(T/T_{irr})^2] \) [21] with \( B_{irr}(0) = 16.6 \text{ T}, T_{irr} = 11.6 \text{ K}. \)

![Figure 6](image_url)

**Figure 6.** The fitting result of \( B_{irr} \) by \( B_{irr}(T) = B_{irr}(0)[1-(T/T_{irr})^2] \).

Figure 7 shows normalized \( F_p/B_{irr} \) properties using estimated \( B_{irr} \) for the FeTe\(_{0.6}\)Se\(_{0.4}\) bulk crystal. In high temperatures above 8.5 K the temperature scaling behaviour of the flux pinning properties was clearly observed with the fitting parameters \( p = 1.7, q = 4.6 \) and \( b_{max} = 0.27 \) using the scaling formula of \( F_p/F_{p_{max}} = Cb^p(1-b)^q \) where \( b = B/B_{irr} \). Here \( p \) and \( q \) are just fitting parameters which are not based on a specific pinning model. This is nearly consistent with previous studies for FeTe\(_{0.6}\)Se\(_{0.4}\) and FeTe\(_{0.7}\)Se\(_{0.3}\) by different fabrication methods reported by Yadav C S et al. [22] and Bonura M et al. [23] respectively. On the other hand, in low temperatures under 8 K the temperature scaling behavior was not observed. The peak \( F_p/F_{p_{max}} \) shifted to high field side with decreasing temperature and reached 0.45 at 4.2 K. This suggests that the different pinning mechanisms are working between low and high temperatures. The likely candidates for pinning centres are both low-T\(_c\) regions and dislocations. In several papers, the coherence length for Fe(Te,Se) has been reported [20, 24]. Since
the precise determination of coherence length of Fe(Te,Se) is difficult, the estimated value could vary depending on the method of analysis. However, we previously evaluated the coherence length of FeTe$_{0.6}$Se$_{0.4}$ as around several nm to tens nm by the effective mass model [20]. Those values may correspond to that for low-$T_c$ regions, which would be expected to work as effective pinning centers. The elementary pinning force $f_p$ for very thin low-$T_c$ superconducting pins in which the spatial variation of the order parameter of superconducting matrix is very small can be expressed by the sum of potential energy interaction and kinetic energy interaction,

$$
\phi_p = 0.479\pi \frac{d_c}{\mu_0} (B_{cp}^2 - B_{c}^2) + 0.296\pi \frac{d_p}{\mu_0} (B_{cp}^2 \xi_p^2 - B_{c}^2 \xi_c^2).$$

Where $\mu_0$ is the permeability in vacuum, $d_c$ is the pin size, $\xi , \xi_p$ and $B_c , B_{cp}$ are the coherence lengths and thermodynamic critical fields of superconducting matrix and superconducting pins, respectively [25, 26]. At low temperatures under $T_c$ for low-$T_c$ regions the kinetic energy interaction is dominant pinning energy, and generates repulsive pinning force. This behavior was first observed on the temperature dependence of $F_p$ for NbTi multifilamentary wires with different kinds of artificial superconducting pins [27-29]. From the observed temperature scaling behavior for FeTe$_{0.6}$Se$_{0.4}$ with low-$T_c$ regions it is speculated that the low-$T_c$ regions act as temperature-induced repulsive pinning centres at low temperatures. On the other hand, at high temperatures the normal conductive pins changed from low-$T_c$ regions and dislocations are considered to work as attractive normal pins, and hence the temperature scaling is expected. Further investigation is needed to identify actual pinning centres.

4. Conclusion
We have successfully fabricated FeTe$_{0.6}$Se$_{0.4}$ large-size bulk single crystals by the melting method with two stage heat treatments. Temperature dependence of magnetization revealed that low-$T_c$ region exists inside the crystals. $J_c$ under magnetic fields parallel to the c-axis at 4.2 K achieved 0.36 and 0.2 MA/cm$^2$ at 0 T and 5 T respectively. From the temperature scaling behavior of flux pinning properties we speculated that low-$T_c$ regions near excess Fe moderately distributed in the crystals are dominant pinning centers in high fields at low temperatures.

References
[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 Journal of the American Chemical Society 130 3296–97.
[2] Chen G F, Li Z, Wu D, Li G, Hu W Z, Dong J, Zheng P, Luo J L, and Wang N L 2008 Physical review letters 100 247002.
[3] Ren Z A, Yang J, Lu W, Yi W, Che G, Dong X, Sun L, and Zhao Z 2008 Materials Research Innovations 12 56-57.
[4] Ren Z A, Yang J, Lu W, Yi W, Shen X L, Li Z C, Che G C, Dong X L, Sun L L, Zhou F, and Zhao Z X 2008 Europhysics Letters 82 57002.
[5] Z. Ren, W. Lu, J. Yang, W. Yi, X. Shen, Z. Li, G. Che, X. Dong, L. Sun, F. Zhou, and Z. Zhao 2008 Chinese Physics Letters 25 2215.
[6] Cheng P, Fang L, Yang H, Zhu X, Mu G, Luo H, Wang Z, and Wen H 2008 Science in China Series G: Physics, Mechanics and Astronomy 51 719-22.
[7] Rotter M, Tegel M, and Johrendt D 2008 Physical Review Letters 101 107006.
[8] Wang X C, Kiu Q Q, Lv Y X, Gao W B, Yang L X, Yu R C, Li F Y and Jin C Q 2008 Solid State Communications 148 538-40.
[9] Hsu F C, et al. 2008 Proceedings of the National Academy of Sciences 105 14262-64.
[10] Sales B C, Sefat A S, McGuire M A, Jin R Y, Mandrus D and Mozharivskiy Y 2009 Physical Review B 79 094521.
[11] Kida T, Matsunaga T, Hagiwara M, Mizuguchi Y, Takano Y and Kindo K 2009 Journal of the
[12] Ozaki T, Deguchi K, Mizuguchi Y, Kumakura H and Takano Y 2011 IEEE Transactions on Applied Superconductivity 21 2858-61.
[13] Ozaki T, Deguchi K, Mizuguchi Y, Kawasaki Y, Tanaka T, Yamaguchi T, Kumakura H and Takano Y 2012 Journal of Applied Physics 111 112620.
[14] Izawa H, Mizuguchi Y, Ozaki T, Takano Y, and Miura O 2011 Japanese Journal of Applied Physics 51 010101.
[15] Izawa H, Mizuguchi Y, Miura O 2014 Physica C: Superconductivity 504 77-80.
[16] Izawa H, Tanaka Y, Mizuguchi Y, Miura O 2016 Japanese Journal of Applied Physics 55 053101.
[17] Yamamoto A, et al. 2008 Superconductor Science and Technology 21 095008.
[18] Otabe E S, et al. 2012 Progress in Superconductivity and Cryogenics 14 1-7.
[19] Bean C P 1964 Reviews of Modern Physics 36 31.
[20] Hamada K, Izawa H, Mizuguchi Y and Miura O 2013 Physics Procedia 45 81-84.
[21] Matsushita T 2007 Flux Pinning in Superconductors (Berlin: Springer Berlin Heidelberg) p4.
[22] Yadav C S and Paulose P L 2011 Solid State Communications 151 216-18.
[23] Bonura M, Giannini E, Viennois R and Senatore C 2012 Physical Review B 85 134532.
[24] Klein T, et al. 2010 Physical Review B 82 184506.
[25] Matsushita T 1996 Proceedings of the 8th International Workshop on Critical Currents in Superconductors World Scientific 63-68.
[26] Matsushita T 2000 Superconductor Science and Technology 13 730.
[27] Zhu Y, Miura O and Ito D 2002 IEEE transactions on applied superconductivity 12 1117-20.
[28] Zhu Y, Miura O, Okubo T, Ito D and Endo S 2000 IEEE transactions on applied superconductivity 10 1046-49.
[29] Zhu Y, Miura O, Hayakawa K and Ito D 2001 IEEE transactions on applied superconductivity 11 3808-11.