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2004 J. Phys.: Condens. Matter 16 1803

(http://iopscience.iop.org/0953-8984/16/10/012)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) 1803–1811 PII: S0953-8984(04)70816-4

# Preparation and enhancement of critical current density in $MgB_2$ wires and tapes

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Received 23 October 2003
Published 27 February 2004
Online at stacks.iop.org/JPhysCM/16/1803 (DOI: 10.1088/0953-8984/16/10/012)

**Abstract**
We have successfully prepared monofilamentary $MgB_2$ wires and tapes with different sheathed metals such as Cu, Ta/Cu and Fe by the powder-in-tube method. The phase composition, superconducting properties and microstructure features are investigated by x-ray diffractometer, the standard four-probe technique, SQUID magnetometer, SEM and TEM. The results indicate that $J_c$ in $MgB_2$/Ta/Cu wires is higher than $10^5$ A cm$^{-2}$ at 5 K in 0.1 T and $10^4$ A cm$^{-2}$ at 20 K in 1 T. By Ti-doping, $J_c$ can be significantly improved. $MgB_2$/Fe wires show very high transport critical current densities of $1.43 \times 10^5$ A cm$^{-2}$ (4.2 K, 4 T), $3.72 \times 10^4$ A cm$^{-2}$ (15 K, 4 T) and $2.34 \times 10^4$ A cm$^{-2}$ (25 K, 3 T). Also the results indicated that small grain size should respond to the large $J_c$ in Ti-doped $MgB_2$ tape and $MgB_2$/Fe wire.

## 1. Introduction

The discovery of superconductivity at 39 K in $MgB_2$ by Nagamatsu *et al* [1] has generated a great deal of excitement in both the fundamental and practical investigations of this material. The transition temperature $T_c$ of $MgB_2$ is much higher than $Nb_3Ge$ (by almost a factor of 2) having the highest $T_c$ in conventional superconductors. The advantage of $MgB_2$ is its applications in the higher temperature (20–30 K) region, where conventional superconductors cannot play any role due to their low $T_c$. Also, the progress in cryogen free cooling techniques in the temperature region 20–30 K promotes the development and application of $MgB_2$. Some investigations, including the observation of the isotope effect, band structure and tunnelling measurements of the superconducting gap, suggest that $MgB_2$ is a conventional phonon-mediated BCS superconductor [2–4]. In contrast to the BCS theory, another model was proposed to explain superconductivity in $MgB_2$ by the pairing of dressed holes [5].

  

On the other hand, it is found that supercurrent flow in $MgB_2$ bulk material is not reduced by grain boundaries [6], which are well known in high-$T_c$ ceramic superconductors. As revealed by the irreversible magnetization experiment [7], the behaviour of the magnetic hysteresis loops of $MgB_2$ is dominated by bulk pinning. Furthermore, measurements of $H_{c2}(T)$, the dynamics critical field and $J_c$, suggest that $MgB_2$ is a typical type-II superconductor, similar to $Nb_3Sn$ except for the extremely high $T_c$ [8, 9]. In addition, it is reported that the grain boundaries may be the main source of vortex pinning in $MgB_2$, as in $Nb_3Sn$ [10]. The recent investigation of $MgB_2$ wire under different heat treatments indicates that $MgB_2$ bulk samples fabricated by the solid-state reaction method contain many small $Mg(B, O)_2$ precipitates within the $MgB_2$ matrix, which are suitable as pinning centres [11]. For the electrical application of superconductors, high critical current density is required. Therefore, much work has been carried out to improve the superconducting characteristics of $MgB_2$ in its various shapes, either bulk, thin film or wire. Just recently, a very high $J_c$ of $1.2 \times 10^7$ A cm$^{-2}$ at 4.2 K in zero-field was obtained in the *in situ* epitaxial $MgB_2$ thin film, suggesting that $MgB_2$ can reach extremely high intrinsic $J_c$ [12]. However, $J_c$ of $MgB_2$ wires and tapes, especially in high fields, is very low. Canfield *et al* fabricated high-density $MgB_2$ wires (160 $\mu$m in diameter) through the exposure of boron filaments to Mg vapour [13]. Also, recent reports on the preparation of $MgB_2$ wires by powder-in-tube (PIT) using either Ag or Cu sheath and $MgB_2$ strands, by filling Nb-lined monel tubes with commercial $MgB_2$ powders, were the first steps to putting $MgB_2$ superconductors into applications [14]. By using Cu as a sheath, transport $J_c$ of 50 000 A cm$^{-2}$ at 15 K in self-field was obtained in $MgB_2$ wires. For the non-sintered $MgB_2$/Ni tape, $J_c$ reached around $10^5$ A cm$^{-2}$ at 4.2 K in self-field [15]. Recently, Wang *et al* [16] reported their results on a Fe-clad $MgB_2$ wire, in which $J_c$ achieved $4.2 \times 10^5$ A cm$^{-2}$ at 4.2 K in self-field. $J_c$ is further improved to $1.7 \times 10^4$ A cm$^{-2}$ in 1 T at 29.5 and 33 K in self-field [17]. Also, transport $J_c$ of 8700 and 55 830 A cm$^{-2}$ at 4.2 K in self-field were measured for Cu and Fe/Cu sheathed $MgB_2$ square wires by using commercial $MgB_2$ powder [18]. To date, two important factors of low density and poor flux pinning are the main obstacles to obtaining $J_c$ in $MgB_2$ samples. In this paper, a series of $MgB_2$ wires and tapes was successfully fabricated by the powder-in-tube method. Phase composition, superconducting properties and microstructure features were investigated.

## 2. Experimental details

Single filamentary $MgB_2$ composite wires and tapes with and without Ti-doping were prepared by the *in situ* powder-in-tube process. Mg (or Ti) powder and amorphous B powder were used as starting materials in an atomic ratio of Mg (or Ti):B = 1(99%):(1%):2. 5% extra Mg was added to compensate the loss of magnesium in high temperature. The mixture of these powders was well ground and filled into an iron, tantalum or copper tube of 6 mm in diameter. The composite tube was swaged and drawn down to a wire of 2.0 mm in diameter with an intermediate annealing (400–450 °C). For tapes, the wires were rolled to the dimension of 3.4 mm × 0.25 mm. Finally, the wires and tapes were sintered at 600–900 °C for 2 h in argon at ambient pressure.

The phase composition was analysed by x-ray diffraction measurements. The microstructure features of these wires and tapes were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The TEM sample was obtained by mechanically grinding the $MgB_2$ samples to a thickness of about 40 $\mu$m and further thinning them using the polishing system. The current–voltage characteristics of the wires were measured at various fields and temperatures by the standard four probe method. The field is perpendicular to the current and the criterion used to determine critical current is 1 $\mu$V cm$^{-1}$.

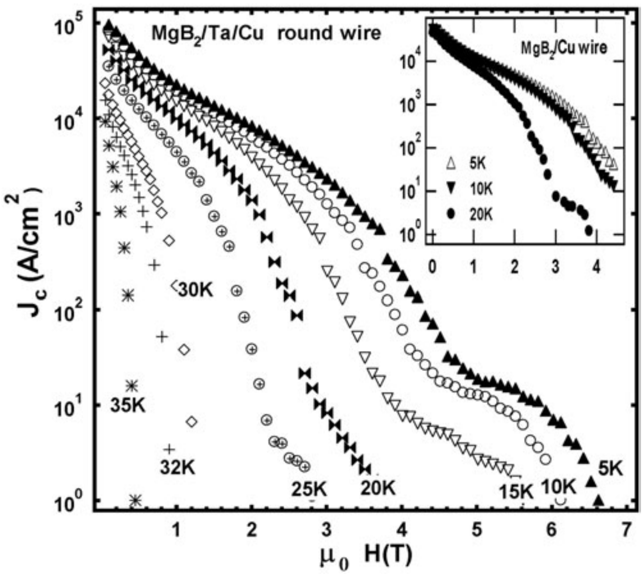


**Figure 1.** Field dependent critical current density of $MgB_2$/Ta/Cu wires at 5, 10, 15, 20, 25, 30, 32 and 35 K. $J_c$ is about $10^5$ A $cm^{-2}$ at 5 K in 0.1 T. Inset: field dependence of magnetic $J_c$ for $MgB_2$/Cu wire.

The magnetization measurements were performed on a commercial superconducting quantum interference device (SQUID) magnetometer at different temperatures in a magnetic field up to 7 T.

## 3. Results and discussion

The deduced $J_c$ of $MgB_2$/Ta/Cu wire from the hysteresis loops, by using the Bean model, according to relation $J_c = 30\Delta M/d$ (where $d$ is the diameter of the sample), is shown in figure 1. It is interesting to note that $J_c$ at low temperatures (from 5 to 15 K) and low fields are very close, which is quite different from high-$T_c$ ceramic superconductors. A similar feature has been found in the high-pressure sample [19]. At 5 K in 0.1 T, the $J_c$ of our wire has reached a value around $10^5$ A $cm^{-2}$. The $J_c$ also achieves $10^4$ A $cm^{-2}$ at 20 K and 1 T, which is comparable to the high-pressure sample. However, it can be seen from the inset of figure 1 that $J_c$ is much lower in $MgB_2$/Cu wire than that in $MgB_2$/Ta/Cu wire, which should be related to the serious reaction between $MgB_2$ and Cu.

As reported by our previous work, Ta is a good candidate for the buffer layer for preparing $MgB_2$ wires. Figure 2 illustrates the TEM image of the interfaces between $MgB_2$ grains and Ta. There is no reaction between them. By EDAX analysis, some MgO particles are found as marked as 1, 2, 3 and 4 in this sample. Also, the size of these particles is very small, less than 50 nm. However, a serious reaction of Mg and Cu is observed in the $MgB_2$/Cu wires without a Ta buffer layer. A $MgCu_2$ compound is formed within the $MgB_2$ core/Cu-sheath interface, which leads to a big reduction in $J_c$ as shown in the inset of figure 1. A similar result was also reported in [14]. Furthermore, typical TEM images for the $MgB_2$/Cu wires with and without a Ta buffer layer are shown in figure 3. The $MgB_2$/Cu sample has the smaller and more homogenous $MgB_2$ grains, while the superconducting grains are larger in $MgB_2$/Ta/Cu wire. As observed by Gumbel *et al* [10], the grain boundary pinning is very effective in

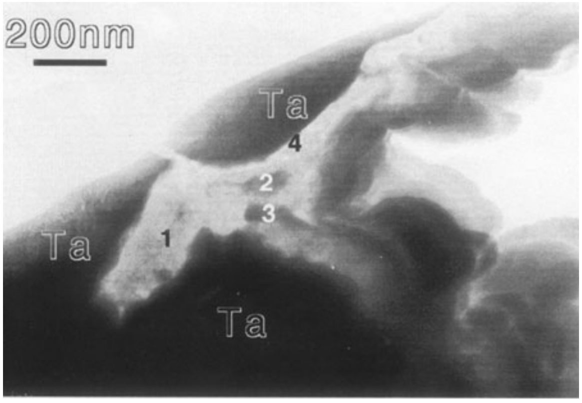


**Figure 2.** TEM image of the interface between $MgB_2$ grains and Ta for $MgB_2$/Ta/Cu.

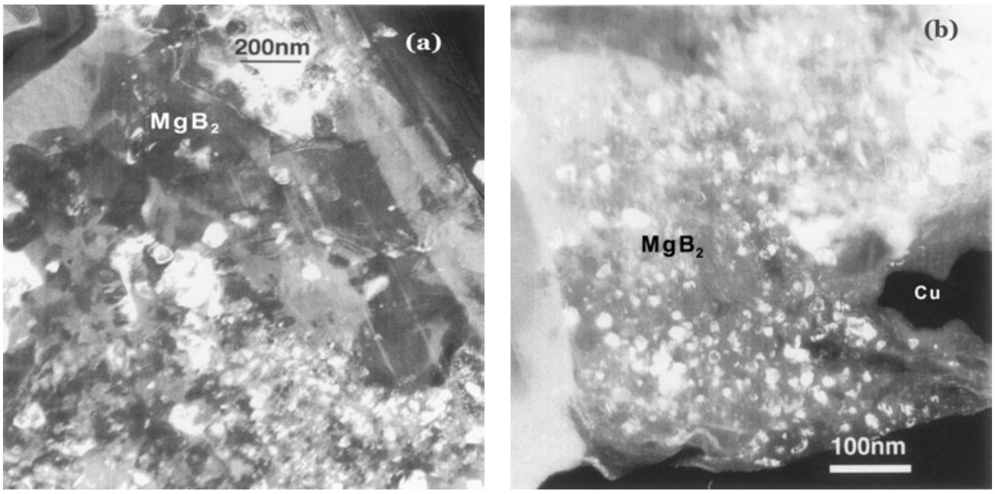


**Figure 3.** Typical TEM images for $MgB_2$/Cu wires with (a) and without (b) Ta.

$MgB_2$ superconductors. The smaller grains should result in the enhancement of flux pinning. However, the serious reaction between Cu sheath and $MgB_2$ and the lower $T_c$ with broader transition lead to a decrease in $J_c$ for $MgB_2$/Cu wires.

Typical x-ray diffraction patterns of pure $MgB_2$ and Ti-doped tapes are illustrated in figure 4. It can be observed that the main phase is $MgB_2$ in the pure $MgB_2$ sample while only few impurity phases of MgO are found in the spectrum. However, some $TiB_2$ phases and fewer MgO can be detected besides the $MgB_2$ phase in the Ti-doped sample. The XRD analysis shows that the lattice parameters are not changed by Ti-doping, suggesting that Ti atoms do not enter the structure of $MgB_2$. The critical temperature (38 K) of the Ti-doped sample is slightly lower than that of pure $MgB_2$ (38.4 K).

Figure 5 shows the magnetic field dependence of $J_c$ for the $MgB_2$/Ta/Cu tapes with and without Ti-doping at different temperatures. The $J_c$ values were deduced from the hysteresis loops by using the Bean model of $J_c = 30\Delta M/d$ (where $d$ is the diameter of the sample). In this figure, the symbols present the experiment data and the lines are the fitting curves of the equation $J_c(B) = J_c(0)\exp(-(B/B_0)^{0.65})$. It can be observed that the $J_c$ value is significantly

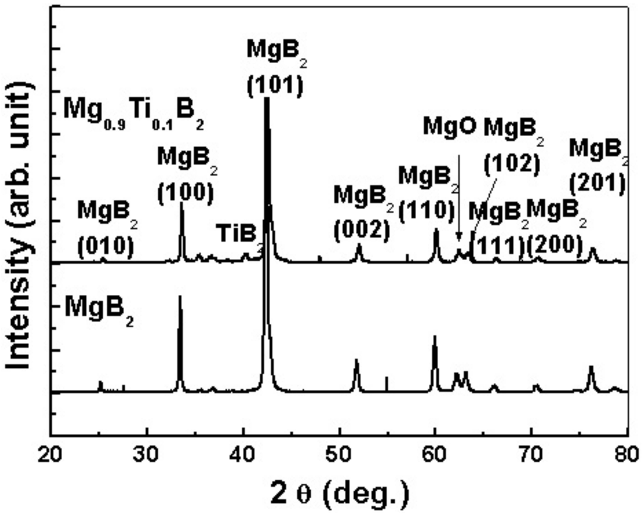


**Figure 4.** X-ray diffraction patterns of $MgB_2$ tape with and without Ti-doping. Few impurity phases of MgO are found in both tapes. $TiB_2$ phases are found in Ti-doped tape.

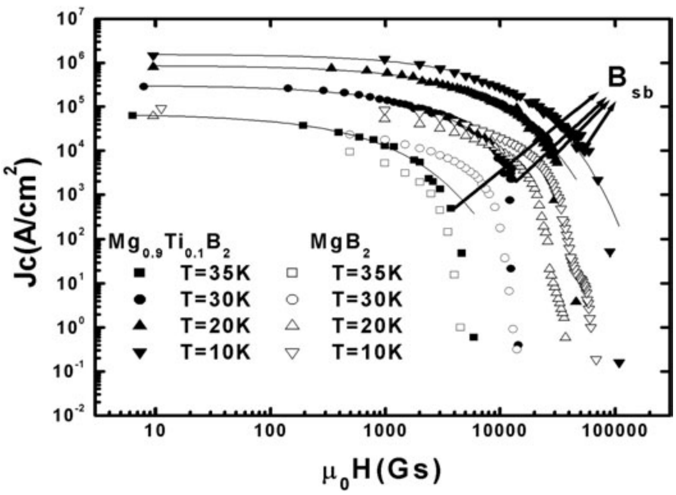


**Figure 5.** Field dependence of magnetic $J_c$ for $MgB_2$/Ta/Cu tape with and without Ti-doping at different temperatures. Fitting curves of the equation $J_c(B) = J_c(0)\exp(-(B/B_0)^{0.65})$ are also shown.

improved by Ti-doping in the $MgB_2$ tape. At 10 K and self-field, the $J_c$ of the Ti-doped tape reaches a high value above $1.5 \times 10^6$ A cm$^{-2}$. As the magnetic field is increased to 1 T, $J_c$ is as high as $2.7 \times 10^5$ A cm$^{-2}$. However, $J_c$ is only around $1.9 \times 10^4$ A cm$^{-2}$ at 10 K in 1 T for pure $MgB_2$ tape. In addition, a plateau region of $J_c$ can be observed from figure 5 at low magnetic fields. At this stage, $J_c$ has a weak dependence on the field. But when the magnetic filed is increased above a crossover field $B_{sb}$, $J_c$ begins to decrease quickly. Also, the crossover field decreases with increasing temperature. The crossover field of Ti-doping $MgB_2$ tapes is relatively high compared to pure $MgB_2$, which indicates that the $Mg_{0.9}Ti_{0.1}B_2$ sample has a very strong flux pinning ability.

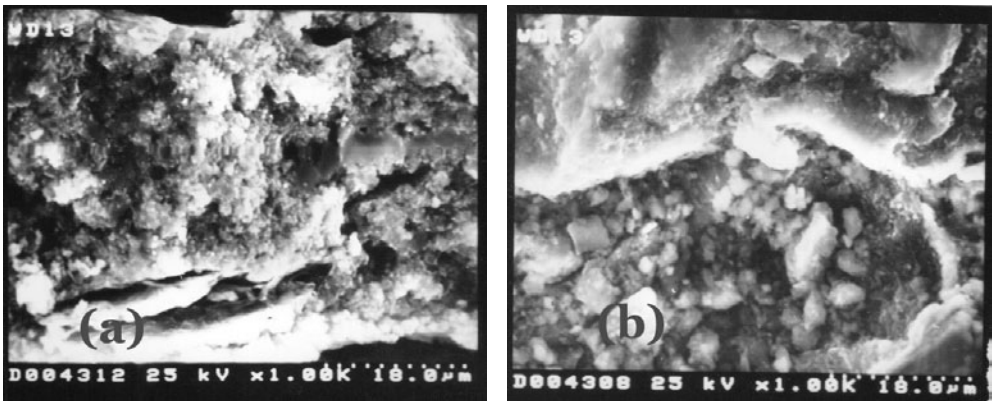


**Figure 6.** Typical SEM photography for the $MgB_2$ tape with (a) and without (b) Ti-doping.

A typical SEM photograph of the cross section in pure $MgB_2$ and $Mg_{0.9}Ti_{0.1}B_2$ tapes are given in figure 6. More voids formed by the evaporation of Mg can be observed in the pure $MgB_2$. However, the $Mg_{0.9}Ti_{0.1}B_2$ sample has a much higher density with few voids. In fact, with Ti-doping, the temperature for forming the $MgB_2$ phase is higher than pure $MgB_2$. Also, the connections between grains are much improved and the fine grains of $MgB_2$ are found in the Ti-doped tape. A very thin layer of $TiB_2$ forms around the $MgB_2$ particles and MgO nanoparticles are observed in Ti-doped $MgB_2$ samples [20]. Therefore, it can be concluded that the $TiB_2$ phases in the tapes may prevent the growth of grain size of $MgB_2$ and lead to the very fine $MgB_2$ particles. Meanwhile, the fine grain size creates many grain boundaries, which may act as the important pinning centres in $MgB_2$ material and enhances the critical current density of $MgB_2$.

Figure 7 shows the $J_c$ values as a function of field at 4.2 K for the $MgB_2$/Fe wires prepared at various temperatures. It is noticed that $J_c$ is very high especially in high fields and $J_c$ exhibits different behaviours in field for these samples. The sample fabricated at 850 °C has the maximum $J_c$ at fields below 4 T, while $J_c$ of the sample prepared at 750 °C is the highest among them in the fields above 4 T. For the sample at 750 °C, $J_c$ is as high as $4.4 \times 10^4$ and 6560 A $cm^{-2}$ even at 6 and 10 T, which is the best data reported for PIT wires and tapes. At 1 T, all the samples have large $J_c$ values above $2.0 \times 10^5$ A $cm^{-2}$ with the highest $J_c$ around $3.2 \times 10^5$ A $cm^{-2}$. Also, in the field range of 4–7 T, the $J_c$ values for all samples are higher than $1.6 \times 10^4$ A $cm^{-2}$. The high $J_c$ in our samples may be due to good grain connectivity and strong flux pinning force. By computer fitting, it is found that $J_c$ decreases exponentially with the field as shown in the inset of figure 7. In addition, the field dependence of transport $J_c$ values at 15 and 25 K is given in figure 8. The $MgB_2$/Fe wire shows the high irreversibility field and excellent performance in high field and high temperature. At 15 K, the sample has a $J_c$ value of $3.72 \times 10^4$ A $cm^{-2}$ in 4 T. Also, it should be noted that $J_c$ reaches $2.34 \times 10^4$ A $cm^{-2}$ even at 25 K in 3 T for the sample. These $J_c$ data are much higher than the best results on undoped $MgB_2$ wires and tapes and even on the bulk samples [21].

It is well known that critical current density is controlled by the flux pinning characteristics of superconductors. A lot of crystal defects with suitable dimensions are the candidates for the flux pinning centres. To date, the grain boundary, fine second-phase particles, nano-MgO particles and dislocations are proposed to be effective pinning centres in $MgB_2$. In order to explore the mechanism of high $J_c$ in high fields for $MgB_2$/Fe wires, the microstructure features of the samples were examined by SEM and TEM. As mentioned above, the $MgB_2$/Fe

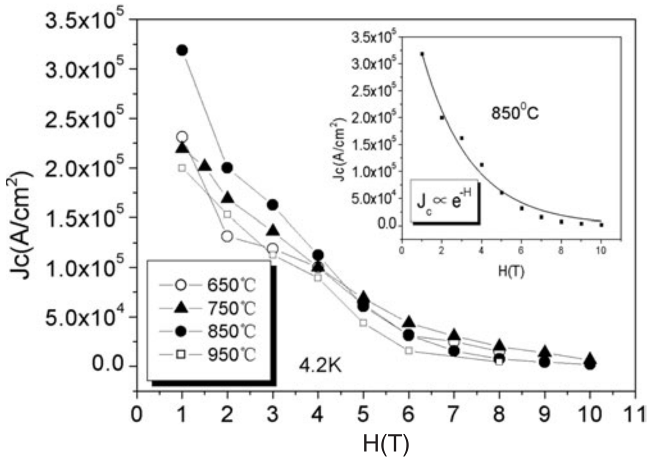


**Figure 7.** Field dependence of transport $J_c$ at 4.2 K for $MgB_2$/Fe wires prepared at different temperatures.

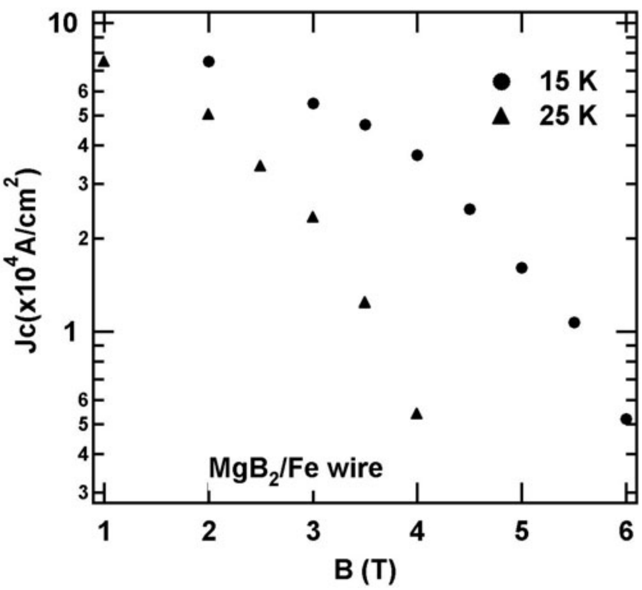


**Figure 8.** Transport $J_c$ as a function of field at 15 and 25 K for $MgB_2$/Fe wires prepared at 750 °C. Note that $J_c$ is very high around $2.34 \times 10^4$ A cm$^{-2}$ at 25 K in 3 T.

wire shows excellent flux pinning, especially in high fields, which should be related to the modification of the microstructure. Figure 9 shows a TEM image of the $MgB_2$/Fe wires treated at 750 °C. Note that the grain size in the sample is small, around 200–500 nm, which is beneficial for the enhancement of grain boundary pinning. In addition, neither voids or MgO are found at $MgB_2$ grain boundaries. However, it is interesting to note that some precipitates with size less than 60 nm can be seen in the $MgB_2$ matrix. These precipitates appear darker than the $MgB_2$ matrix. By using x-ray energy dispersive spectroscopy, these particles are identified to be iron. As reported by other authors, the precipitates can be the candidates for the flux pinning centres [22]. Furthermore, the electron diffraction pattern for $MgB_2$/Fe is shown in

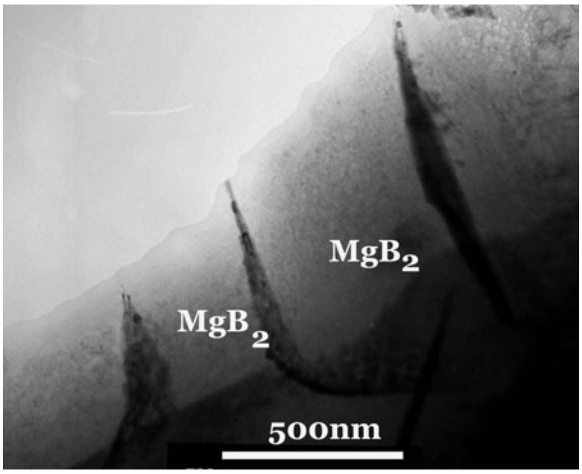


**Figure 9.** Typical TEM image of $MgB_2$/Fe wires, showing small grains and fine precipitates.

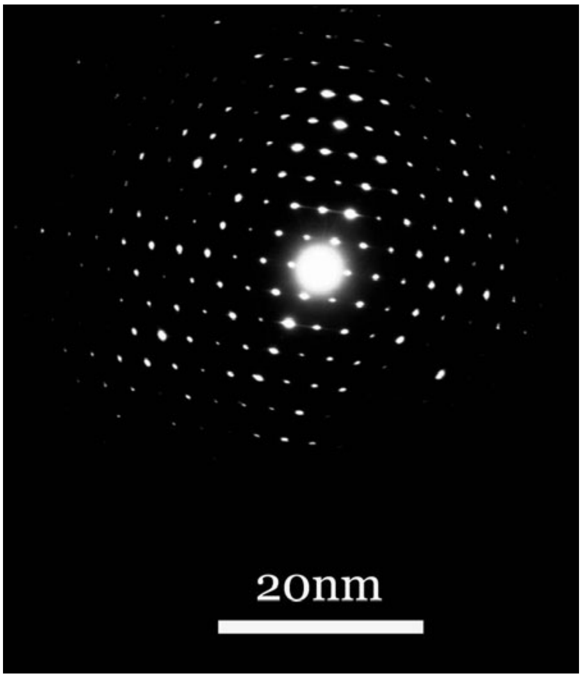


**Figure 10.** Electron diffraction pattern for $MgB_2$/Fe wire.

figure 10. The spots are consistent with $MgB_2$ and the shape of the spots implies that many crystal defects exist in this sample, which will contribute to the flux pinning. In other reports, a number of dislocations are observed in hot isostatic pressed samples and SiC-doped samples, leading to an improvement of $J_c$ in $MgB_2$ bulk samples. As discussed above, the combination effects of high density, small grains, precipitates and many crystal defects may be responsible for the high $J_c$ and large irreversibility field. However, the $MgB_2$/Fe wire has a low density as compared to the high quality bulk samples. Therefore, we can expect that $J_c$ can be further improved by increasing the density of the sample and introducing strong pinning centres.

## 4. Conclusion

We have successfully prepared dense single filamentary $MgB_2$/Ta/Cu wires and tapes with and without Ti-doping and $MgB_2$/Fe wires by the powder-in-tube technique. It is found that Cu has a serious reaction with $MgB_2$. By using Ta as a buffer layer, this reaction can be greatly suppressed. $J_c$ in $MgB_2$/Ta/Cu wires is higher than $10^5$ A cm$^{-2}$ at 5 K in 0.1 T and $10^4$ A cm$^{-2}$ at 20 K in 1 T. Furthermore, $J_c$ value is significantly increased to $1.5 \times 10^6$ A cm$^{-2}$ at 10 K in self-field and $2.7 \times 10^5$ A cm$^{-2}$ at 10 K in 1 T by Ti-doping, which may be due to the high density, fine $MgB_2$ particles and thin layer of $TiB_2$ in Ti-doped $MgB_2$/Ta/Cu tapes. Interestingly, $MgB_2$/Fe wires exhibit very high transport critical current densities at high temperatures and high fields. $J_c$ values achieve as high as $1.43 \times 10^5$ A cm$^{-2}$ (4.2 K, 4 T), $3.72 \times 10^4$ A cm$^{-2}$ (15 K, 4 T) and $2.34 \times 10^4$ A cm$^{-2}$ (25 K, 3 T). The small grains, fine precipitates and many crystal defects in the $MgB_2$/Fe wires may be responsible for the high $J_c$ and large irreversibility field.

## Acknowledgments

This work was supported by National '863' project of China and National Natural Science Foundation of China under Contract No 50172040.

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