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Magnetization study of ITER-type internal-Sn Nb_3Sn superconducting wire*

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Through magnetization measurement with a SQUID magnetometer the heat treatment optimization of an international thermonuclear experimental reactor (ITER)-type internal-Sn Nb_3Sn superconducting wire has been investigated. The irreversibility temperature $T^*(H)$, which is mainly dependent on A15 phase composition, was obtained by a warming and cooling cycle at a fixed field. The hysteresis width $\Delta M(H)$ which reflects the flux pinning situation of the A15 phase is determined by the sweeping of magnetic field at a constant temperature. The results obtained from differently heat-treated samples show that the combination of $T^*(H)$ with $\Delta M(H)$ measurement is very effective for optimizing the heat reaction process. The heat treatment condition of the ITER-type wire is optimized at 675 °C/128 h, which results in a composition closer to stoichiometric Nb_3Sn and a state with best flux pinning.

Keywords: Nb_3Sn superconducting wire, internal-Sn process, irreversibility temperature, hysteresis width
PACC: 7470C, 7470P, 7430C, 7460G

1. Introduction

Nb_3Sn superconducting materials have become the first selection for high-field magnets such as those for nuclear fusion, next-generation accelerator, large hadron collider (LHC) etc. The international thermonuclear experimental reactor (ITER) project, as an example, really requires high-quality Nb_3Sn superconducting wires with medium non-Cu critical current density (J_{cn}) but rather lower hysteresis loss. For this special requirement, high Cu composite design, restack rod process (RRP) internal-Sn method and a smaller number of sub-elements with non-reaction diffusion barrier (Ta) are usually the best choice for multifilament wire design and manufacturing.[1]

It is known that the wire composite design and heat treatment process are two key factors of high-quality wire fabrication. Obviously, for a specially designed ITER Nb_3Sn wire the most important task is the heat treatment optimization, i.e. to choose the most suitable reaction temperature and time to obtain J_{cn} (4.2 K, 12 T) a value as high as possible at a high field. The J_{cn} is usually dependent on A15 phase composition and grain-size-related flux pinning situation. That is to say, optimizing the heat process of Nb_3Sn wire is practically to promote the A15 composition closer to the stoichiometric Nb_3Sn, and to obtain the best flux pinning property at the same time.

Over the past decade, much research work has been made on Nb_3Sn superconductors.[2] Some researchers focused their work on heat treatment. Naus *et al*[3] mainly studied various heat treatment conditions, including Cu-Sn alloying and A15 phase formation, of modified jelly roll (MJR) processed internal-Sn Nb_3Sn wires. Fischer *et al*[4] systematically studied the heat reaction of A15 phase of powder-in-tube (PIT) wires. They all obtained very valuable results for heat treatment selection.

The optimization of heat treatment can be made through several ways, of which the magnetization measurement by means of a SQUID magnetometer is a practical and reliable method. With SQUID one

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can make two kinds of measurement. One is the irreversibility temperature ($T^*(H)$) and the critical temperature (T_c) measurements which are determined by a warming and cooling cycle at a fixed field. These two superconducting properties are mainly dependent on the A15 phase composition of Nb_3Sn wire and are useful to optimize the heat reaction process from the viewpoint of A15 composition. The other is the hysteresis width (ΔM) measurement which is obtained by cycling the magnetic field at a constant temperature. The hysteresis width versus field can be used to estimate the heat treatment process because ΔM reflects the flux pinning situation of the A15 phase.

Suenaga *et al*[5] first studied the irreversibility temperature of a multifilament Nb_3Sn wire. The lower boundary of the temperature region below the upper critical field line $H_{c2}(T)$ (or critical temperature line $T_c(H)$) of the Nb_3Sn wire during a temperature cycle was called the irreversibility temperature $T^*(H)$. In Ref.[5] a SQUID magnetometer was used for measurement and the $T^*(H)$ was taken as the point of onset of reversible magnetization at an applied magnetic field. A similar SQUID measurement is used also in our study.

Cycling magnetic field at a constant temperature with a SQUID magnetometer was adopted by the authors of Refs.[3] and [4]. Fischer *et al* not only obtained the Kramer irreversibility field (H^*_{Kramer}) but also calculated the flux pinning force and even critical current density J_c for their PIT wire. However, owing to the complexity of wire configuration and fabrication it is not practical to calculate the J_{cn} from magnetization measurement for internal-Sn wire.

The SQUID magnetization measurements of both the cycling temperature at a fixed field and the cycling field at a constant temperature are used to investigate the ITER-type internal-Sn Nb_3Sn superconducting wire. Combining $T^*(H)$ values with hysteresis width versus field is used to optimize the heat treatment process of the wire.

2. Experiment

2.1. Wire specimen preparation

The ITER-type Nb_3Sn wire has 19 uniformly distributed sub-elements (filament bundles) with 7.5wt% Ta-alloyed Nb filaments and pure Sn cores. Six tin inserts are allocated among the filament bundles. There are two layers of Ta and Nb as diffusion barrier with Ta at the inside. The outmost layer is the stabilizing Cu. It was fabricated with the RRP internal-Sn method through an extrusion-drawing process by Alstom in France. Figure 1 shows the SEM cross section of the wire.

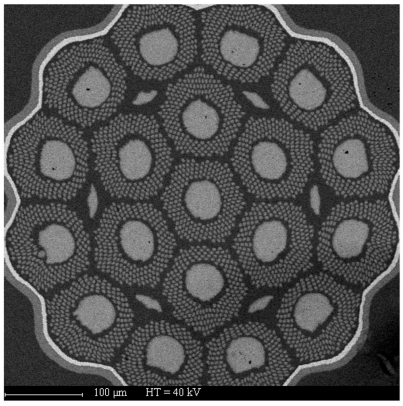

Fig.1. SEM photograph of the wire cross section.

The 0.81 mm (OD) wire was cut into ∼7cm samples and each of them was sealed in an evacuated quartz tube with ∼4Pa of Ar. All samples underwent 210 °C/50 h + 340 °C/25 h thermal treatment in horizontal tubular furnaces for Cu–Sn alloying prior to A15 phase formation heat treatment. Heat treatments at 650, 675, 700 and 725 °C were chosen to study the temperature influence on Nb-Sn A15 phase formation, and $8-200$ h dwelling time at 675 °C was used to observe the time effect.

2.2. Irreversibility temperature measurement

The $T^*(H)$ values were inductively measured using a SQUID magnetometer with a maximum magnetic field of 7 T. Each heat-treated wire sample was cut into short (∼6 mm) segments. Three of the segments were mounted together for one measurement on a clear plastic straw with their axis parallel to the applied field. Specimens were zero-field cooled to 10K and then a fixed magnetic field was applied. The magnetic moments were measured upon warming up to 20 K and then cooling back to 10 K in steps of 0.25 K. For temperatures far from the onset of reversible magnetization, steps of 1 K were adopted for measurement. At each temperature point the moment was taken two times to reduce noise. All the moments were normalized to the sample mass. The measurement magnetic field was in the range of 0.1 to 5 T.

From the normalized magnetic moment (M) as a function of temperature (T) going up and down, the irreversibility temperature $T^*(H)$ can be obtained as the onset value of the irreversible movement. Figure 2 shows a typical $M-T$ curve and the corresponding onset point.

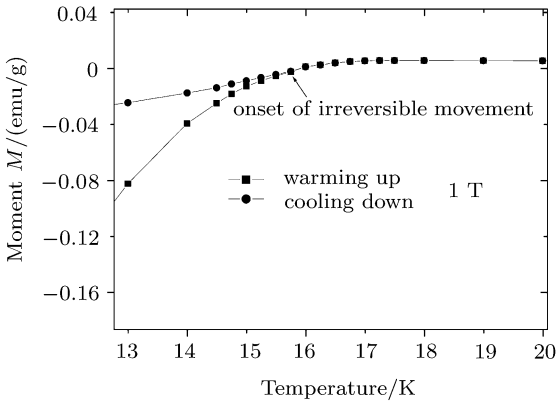

Fig.2. A typical $M-T$ curve and the onset point. This is a portion of the curve of a warming and cooling cycle of the wire sample heat-treated at 675 °C/128 h.

The temperature at which the moment difference (ΔM) upon warming and cooling tends to zero was taken to be $T^*(B)$. The $T^*(B)$ values were all determined using this criterion.

2.3. Hysteresis width versus magnetic field

This experiment used the same SQUID magnetometer in the $T^*(H)$ measurement. The sample was zero-field cooled to a fixed temperature of 12 K and then a magnetic field was applied. The applied field was increased from zero to 7 T, back to zero, and then decreased to −7 T, back to zero again, in steps of 0.25 T. In the range of ±1 T the field was changed in steps of 0.1 T for the sharp variation of magnetic moment. The magnetic moments were tested during the whole field cycle and were normalized to the sample mass. A magnetization loop was obtained when the normalized moment was plotted as a function of field.

According to the origin-symmetry property of a hysteresis loop, the magnetization curve section of the second quadrant can be origin-symmetrically allocated in the fourth quadrant. The magnetization difference (hysteresis width ΔM) is then determined by the magnetization curves of the second and the fourth quadrants. Figure 3 shows the magnetization curves and the hysteresis width (ΔM) of a typical sample.

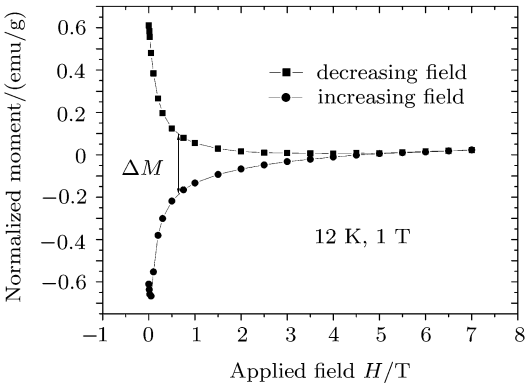

Fig.3. Magnetization curves and hysteresis width (ΔM) of the 675 °C/128 h sample tested at 12 K and 1 T.

The ΔM value plotted against field reflects the flux pinning situation of the wire sample at 12 K. The comparison between the $\Delta M-H$ curves of different samples is used to optimize the heat-treating process from the flux pinning aspect.

3. Results and discussion

The wire samples heat-treated at different temperatures of 650, 675, 700 and 725 °C for 128 h full time reaction and at 675 °C for various times of 8, 32, 98, 128 and 200 h, were measured of their $T^*(H)$ and $\Delta M(H)$ values. The obtained results can be used to study the temperature and time influence on heat treatment.

The $T^*(H)$ measurement results are described first and Table 1 lists the $T^*(H)$ values at different reaction temperatures. It can be seen that the $T^*(B)$ values show a small increase (less than 0.3K) from 650 to 675 °C and nearly no change for 675 to 725 °C treatments at the same applied field. To exhibit the details of the moment difference (ΔM) as a function of temperature, the data at 1 T of tested field for these three samples are shown in Fig.4, from which a small decrease of ΔM can be seen for the 725 °C/128 h sample.

Table 1. Temperature influence on $T^*(B)$(K).

Sample	0.1 T	0.5 T	1 T	2 T	3 T	4 T	5 T
650 °C/128 h	16.9	16.3	15.8	14.9	14.1	13.4	12.7
675 °C/128 h	17.0	16.4	15.9	15.0	14.2	13.5	12.9
700 °C/128 h	17.0	16.4	15.9	15.0	14.3	13.6	—
725 °C/128 h	17.0	16.4	15.9	15.0	14.2	13.5	12.8

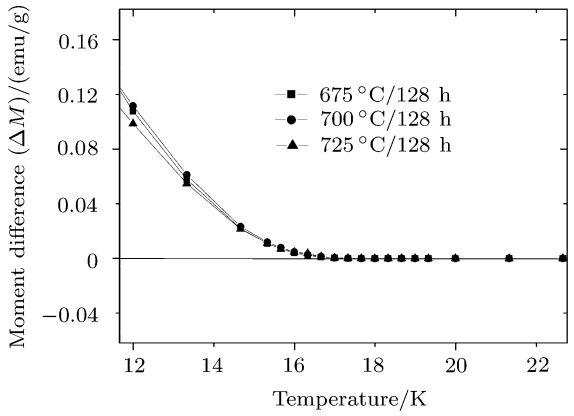

Fig.4. The moment difference (ΔM) as a function of temperature at 1T fixed field for the samples heat-treated in the temperature range of 675 to 725 °C.

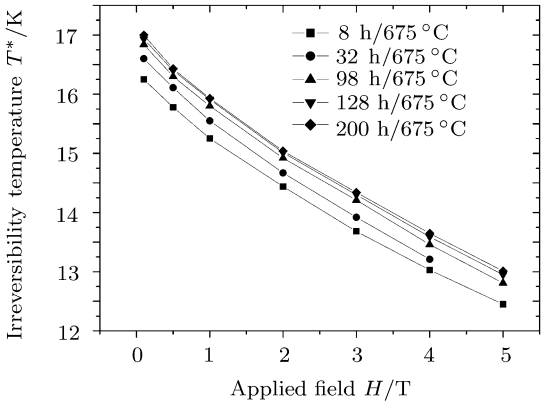

Fig.5. $T^*(H)$ as a function of the applied field.

Figure 5 exhibits the $T^*(H)$ values as functions of applied field for the five samples heat-treated for different times. It is noticed from Fig.4 that the irreversibility temperature decreases with the increase of applied magnetic field for each heat-treated wire. As the thermal reaction time increases, the $T^*(H)$ curve shifts upward and stays nearly at the same position after 128 h heat treatment. This is demonstrated more clearly in Fig.6 in which the $T^*(H)$ values versus the heat treatment time are plotted for the three fields of 1, 2 and 3 T. The three curves have nearly the same variation trend: as the heat-treating time increases from 8 h to around 128 h, the $T^*(H)$ first shows a continuous increase and then remains approximately a plateau after 128 h thermal treatment.

$\Delta M - H$ results are illustrated in Fig.7, which reveals the $\Delta M - H$ variation at different temperatures. It clearly shows that the $\Delta M(H)$ moves up to the highest position from 650 to 675 °C, and then has a small decrease at 700 °C and a rather large decrease at 725 °C.

The $\Delta M(H)$ values for various reaction times are displayed in Fig.8. It is found that the $\Delta M(H)$ also shows an increase from 8 to 128 h heat treatment, but a decrease after 128 h.

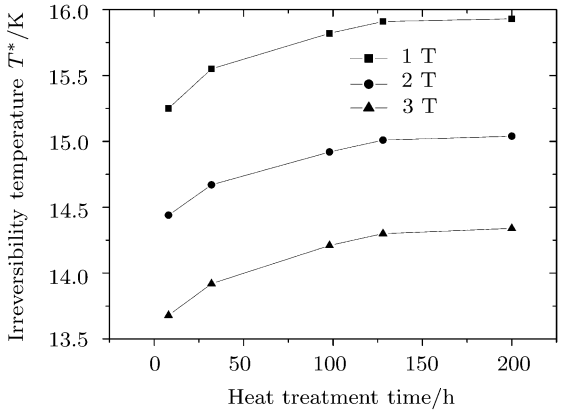

Fig.6. $T^*(H)$ as a function of heat treatment time at 1, 2 and 3 T tested fields.

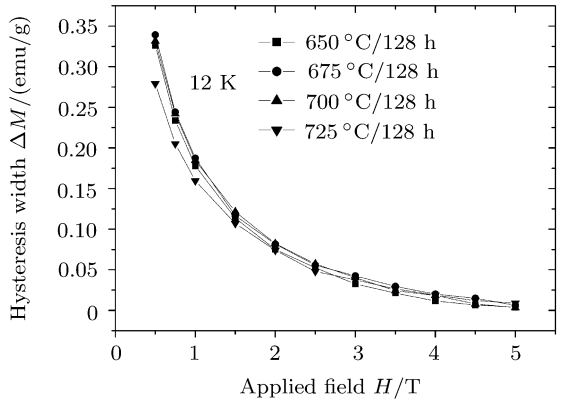

Fig.7. $\Delta M(H)$ variation at different heat-treatment temperatures.

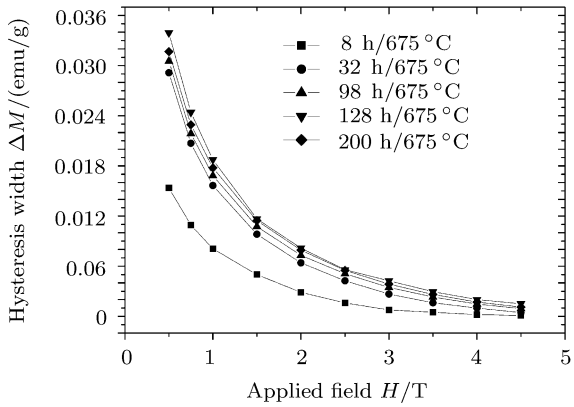

Fig.8. $\Delta M(H)$ values for various reaction times.

In order to interpret the variation of $T^*(H)$ as a function of heat-treatment time and temperature, the

variation of A15 phase composition of the wire during thermal reaction is investigated. It is known that the Nb filament in internal-Sn Nb_3Sn wire first develops a radial gradient layer of Nb-Sn A15 phase within which the Sn content is distributed with higher concentration at the outside of filament. With the progress of heat reaction the A15 phase gradient layer formed is continuously to grow and the Sn concentration gets enriched. Until the filament reacts completely, the gradient layer will flatten gradually and its composition becomes more and more homogeneous. Different reaction temperature causes different formation rate of A15 phase and different grain size distribution. The composition variation of A15 phase can be confirmed by the $T^*(H)$ measurement since irreversibility temperature is virtually a T_c-related property and thus dependent on the phase composition and crystal size.

From Figs.5 and 6 it is obvious that with the extension of heat reaction time from 8 to 128 h at 675 °C, the quantity of A15 phase increases continuously and its Sn content becomes more and more enriched. After about 128 h heat treatment, the A15 composition is much closer to the stoichiometric Nb_3Sn and has nearly no further increase of Sn concentration although the A15 grain size may become coarser.

The thermal influence on $T^*(H)$ (Table 1) indicates that for fully reacted wire samples of 128h heat treatment when the temperature is elevated from 650 to 725 °C, the A15 composition has no obvious change although the 650 °C/128 h sample shows a small shortage of Sn content. Comparatively, the best A15 composition can be achieved at the reaction temperature of 675 °C. The elevated temperature may make the grain size coarser and lower the ΔM value as indicated in Fig.4 for the 725 °C/128 h sample.

The $\Delta M(H)$ results can be analysed for the flux pinning variation. It is well known that the flux pinning centre of Nb_3Sn superconductor is the grain boundary. Smaller grain size means a larger boundary area and thus a larger flux pinning force. Therefore, a decrease of flux pinning is usually caused by coarsening. This is really detrimental to superconductivity enhancement of the Nb_3Sn wire. On the other hand, the flux pinning property is reflected by the hysteresis width ΔM. Because the critical current density J_{cn} is proportional to ΔM and flux pinning force $F_p = J_c \times H$, the F_p is also proportional to ΔM.

The $\Delta M - H$ curves obtained at different treatment temperatures (Fig.7) indicate that the flux pinning force is promoted to the highest value from 650 to 675 °C, and further elevating temperature deteriorates the flux pinning situation due to the grain coarsening and thus the decrease of boundary area. It is evident that the 725 °C/128h heat treatment is the worst condition.

Figure 8 shows the reaction time effect on flux pinning. It is apparent that the flux pinning force is the weakest for 8 h heat treatment and is enhanced to the highest with the reaction time prolonged to 128 h. The decrease of flux pinning after 128 h, as indicated by the lower $\Delta M(H)$ curve, is also due to grain coarsening.

The above interpretation demonstrates clearly that the 675 °C/128 h is the most favourable heat treatment process for the ITER-type internal-Sn Nb_3Sn superconductor wire due to the best A15 phase composition and grain size obtained.

4. Conclusion

From the above discussion it can be concluded as follows: The optimization of heat treatment process is one of the main factors for the fabrication of internal-Sn Nb_3Sn superconducting wire. This optimization requires systematic analyses of A15 phase composition and flux pinning property.

The irreversibility temperature $T^*(H)$ measurements under various heat treatment conditions mainly reflect the variation of A15 phase composition, while the hysteresis width $\Delta M(H)$ indicates the flux pinning situation. The combination of this two testing methods is very effective for heat process determination.

The heat treatment condition of our ITER-type wire is optimized at 675 °C/128 h from the view point of A15 phase having a composition closer to the stoichiometric Nb_3Sn and the best flux pinning situation.

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