Influence of heat treatment excursion on critical current and residual resistivity ratio of ITER Nb$_3$Sn strands

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Abstract
Heat treatment is critically important to the performance of Nb$_3$Sn superconducting strands. For very large Nb$_3$Sn magnet coils, such as the International Thermonuclear Experimental Reactor (ITER) central solenoid (CS) coils, heat treatment carries the risk of temperature and time excursion, which may result in performance degradation. Therefore, it is prudent to study the effect of possible excursion on Nb$_3$Sn performance. In this study, Nb$_3$Sn strands used for ITER CS coils are heat treated at different temperatures for different times. Their critical current, residual resistance ratio and hysteresis losses are measured. It is found that in the range we studied, critical current and hysteresis losses do not change significantly. Residual resistance ratio, however, decreases with increasing heat treatment temperature and time. This is attributed to the diffusion of metallic elements from the plated Cr layer to the copper stabilizer. Based on a model of metallic elements diffusion, a numerical code is developed to predict residual resistance ratio as a function of heat treatment temperature and time.

Keywords: Nb$_3$Sn, heat treatment, critical current, RRR, Cr diffusion

(Some figures may appear in colour only in the online journal)

1. Introduction

A Nb$_3$Sn strand is a composite of Cu, pure Nb, and Sn or Sn containing components, which requires a reaction heat treatment to form the A15 phase of superconducting Nb$_3$Sn. Obviously the superconducting properties of a Nb$_3$Sn strand is strongly influenced by the heat treatment schedule. In heat treatment, the Nb$_3$Sn reaction is limited by diffusion of Sn to Nb filaments [1]. So as the heat treatment advances, the thickness of the reacted A15 phase increases with temperature and time. At the same time, the Sn content of the A15 layer increases. Both lead to an increase in critical current ($I_c$). Heat treatment at too high a temperature for too long, however, results in a large Nb$_3$Sn grain size with fewer grain boundaries. This reduces the flux pinning ability by grain boundaries and consequently lowers the critical current. In order to maximize A15 layer thickness and its Sn content while minimizing its grain size, the heat treatment schedule is optimized for a specific strand manufacturing route and its architecture. Many studies have been carried out [2–16] on the optimization of Nb$_3$Sn heat treatment schedule to bring out the best possible superconducting properties. In principle, deviation from the optimized heat treatment schedule may lead to performance degradation. For large Nb$_3$Sn magnet coils, due to the challenges in achieving uniform temperature of large thermal mass, heat treatment temperature and time excursions are always possibilities, which might lead to coil performance degradation.

The central solenoids (CS) of the International Thermonuclear Experimental Reactor (ITER) are wound by Nb$_3$Sn cable-in-conduit conductors and need to be heat treated after coil-winding [17]. Such a large sized coil requires a very large heat treatment facility [18] which makes precise and uniform temperature control very challenging. In addition to the possible heat treatment interruption due to electrical power or other failures, temperature and time excursion during heat treatment are also possible. In order to minimize the risk of coil performance degradation, therefore, it is prudent to study
the effect of heat treatment temperature and time excursion from the optimized heat treatment schedule.

Moreover, it has been reported that residual resistance ratio (RRR) of Cr plated ITER strands decreases with increasing heat treatment time [19–23]. This has been attributed to Cr diffusion into the copper stabilizer. Nevertheless, despite the continuing efforts over recent decades by a number of research groups, a complete understanding of this phenomenon and ability of predicting strand RRR by its heat treatment schedule are still lacking. In this paper, we studied the effect of heat treatment temperature and time excursion on Nb3Sn critical current (Ic) and RRR. Our discussion is focused on the prediction of RRR of Cr plated strands based on their heat treatment schedule.

2. Experimental

The Nb3Sn strands used in this study are made by Japan Superconductor Technology Inc. (JASTEC) and Kiswire Advanced Technology (KAT). JASTEC and KAT strands are made by the bronze and internal-tin routes respectively. Both are Cr plated with nominal diameters of 0.82 mm and copper/non-Cu ratio of 1. Figure 1 shows their cross-sections.

For this study, heat treatments were divided into two steps as listed in table 1. For each strand, 36 sets of samples (each set includes one Ic, one RRR, and one hysteresis losses sample) were heat treated together in step one where temperature ramp rate to all levels was 5 °C h⁻¹. After each step two heat treatment, temperature was ramped up at 60 °C h⁻¹ to a level and held for a duration. Combinations of three temperatures and three or more durations were designed for step two heat treatments. Up to four samples were heat treated for each combination. After the step two heat treatment, the temperature was ramped down to 500 °C at 5 °C h⁻¹ followed by furnace cooling to room temperature.

Table 1. Heat treatment schedules.

|                | JASTEC          | KAT              |
|----------------|-----------------|------------------|
| Step one       | 570 °C for 250 h | 210 °C for 50 h, followed by 340 °C for 25 h, followed by 450 °C for 25 h, followed by 570 °C for 100 h |
| Step two       | 640 °C for 80, 100, 150 h | 640 °C for 100, 120, 150 h |
|                | 650 °C for 0, 10, 20, 40, 80, 100, 150 h | 650 °C for 100, 120, 150 h |
|                | 660 °C for 80, 100, 150 h | 660 °C for 100, 120, 150 h |

*After step one, samples were furnace cooled. The step two ramp up rate is 60 °C h⁻¹. After step two heat treatment, temperature is ramped down to 500 °C at 5 °C h⁻¹ before furnace cooling to room temperature.

**The ITER heat treatment schedule for JASTEC and KAT wires at step two is 650 °C for 100 and 120 h respectively.

Figure 1. Cross-section of Nb3Sn wires measured in this paper, left JASTEC, right KAT.

*Figure 1. Cross-section of Nb3Sn wires measured in this paper, left JASTEC, right KAT.*
After heat treatment, samples were tested for \( I_c \), hysteresis losses (\( Q_{\text{hyst}} \)) and RRR. \( I_c \) were measured at 4.2 K in 11, 12, and 13 T magnetic fields; a criterion of 10 \( \mu \)V m\(^{-1}\) was used to determine \( I_c \). RRR is defined as the resistance ratio between 273 K and 20 K. \( Q_{\text{hyst}} \) during a ±3 T field sweep were measured by a vibrating sample magnetometer at 4.22 K. For most heat treatment temperature and time combinations, multiple samples were heat treated and tested. In these cases, average property values are presented in this paper. More details of measurement techniques can be found in [24]. Cross-sections of some heat treated samples were polished and examined by a Zeiss 1540 electron microscope (FESEM). The backscattered electron intensity in the FESEM is sensitive to the atomic number of an element, so Sn exhibits brighter contrast than Cu or Nb. This is conveniently used to detect the Sn rich region in Nb\(_3\)Sn filaments.

3. Results and discussions

3.1. Cross-sections of reacted strands by FESEM

Figures 2(a)–(d) show cross-sections of JASTEC samples heat treated for 0, 10, 40, and 100 h at 650 °C. These filaments are about 2 \( \mu \)m in diameter with some minor bridging between the filaments. As heat treatment progressed from 0 to 100 h, the Sn content of each filament gradually increases, starting from the periphery of the filament. For the sample reacted for 40 h (figure 2(c)), a Sn deficient core is still clearly visible at the center of the filament. Whereas at 100 h (figure 2(d)), the reaction seems complete as indicated by the absence of the Sn deficient core.

3.2. Critical current and hysteresis losses

Figures 3(a) and (b) show 12 T \( I_c \) versus heat treatment temperatures for the JASTEC and KAT samples respectively. Evidently \( I_c \) is not sensitive to heat treatment temperature or time within the experimental uncertainty which can be up to 5% of \( I_c \) [25]. When the heat treatment time in step two is reduced to 20 h or less, however, \( I_c \) of the JASTEC strand reduces significantly as shown in figure 4(a) where data can be fitted (solid line) using an exponential function

\[
I_c = I_{c0} + A [1 - \exp(-t/\tau)]
\]

where \( t \) is heat treatment time and \( I_{c0}, A \), and a constant time \( \tau \) are fitting parameters. The best fit of \( \tau = 12 \) h suggests a relatively rapid reaction process compared with the optimized heat treatment schedule of 100 h. This exponential approach to an asymptotic level, as described by equation (1), is consistent with a Nb\(_3\)Sn growth where the growth rate decreases as Sn in the bronze matrix is being depleted.

Figure 4(a) also shows that even before the step two heat treatment (at time = 0 h in the figure), \( I_c \) is already appreciable at about 75% of the saturated value, thanks to 250 h at 570 °C in step one. After that, for only 20 h at 650 °C, the \( I_c \) reaches over 96% of the saturated value. Therefore the manufacturer optimized schedule of 100 h at 650 °C for the JASTEC strand is sufficiently long to avoid \( I_c \) degradation. The upper critical field \( B_{c2}^* \) (4.2 K) versus heat treatment time at 650 °C is plotted in figure 4(b). Here \( B_{c2}^* \) (4.2 K) values are obtained from \( I_c \) at 11, 12, and 13 T by linear extrapolation of Kramer plots [26]. The non-linearity of the Kramer plots for bronze wire observed at high field [27] is not apparent in the 11–13 T field range. In \( B_{c2}^* \) (4.2 K) calculations, self-field correction is not applied to \( I_c(B) \) data. An exponential function similar to equation (1) also provides a good fit for \( B_{c2}^* \) (4.2 K) versus time with a similar time constant of \( \tau = 13 \) h. Since \( B_{c2}^* \) (4.2 K) is related to Sn content in the A15 phase [28], the relatively rapid \( B_{c2}^* \) (4.2 K) rise in the beginning of the step two heat treatment indicates a relatively quick increase in Sn content of A15, in addition to the increase in A15 layer thickness. It should be noted that, although minor under-reaction does not cause significant \( I_c \) degradation, it might cause considerable \( I_c \) strain sensitivity which is detrimental to the performance of Nb\(_3\)Sn under high stress [3].

Since the hysteresis loss of a superconducting strand (\( Q_{\text{hyst}} \)) is proportional to its magnetization, and its magnetization is proportional to its \( I_c \), \( Q_{\text{hyst}} \) is directly linked to \( I_c \). Therefore, it is expected that \( Q_{\text{hyst}} \) increases with heat treatment time in a way analogous to \( I_c \) as shown in figure 5. The solid line in the figure is a fit by a function similar to equation (1) with a time constant of \( \tau = 12 \) h.

3.3. RRR experimental results and calculation

It is known that the RRR of Cr plated strands decreases with increasing heat treatment time [19–23]. In order to verify that the Cr layer is the main contributor to RRR degradation, the Cr layer is removed from a set of JASTEC samples by chemical etching with 37% HCl. These samples were heat treated together with a few Cr plated samples at 570 °C for various durations. As shown in figure 6, the RRR of samples without Cr have rather weak heat treatment time dependence; whereas the RRR of samples with Cr shows a clear downward trend with increasing heat treatment time. This experiment demonstrates very clearly that a plated Cr layer is largely responsible for the observed RRR degradation.

As for the effect of step two heat treatment, the RRR of JASTEC samples is plotted against heat treatment temperature and time and in figure 7, which shows a clear trend of degradation with increasing heat treatment temperature and time. This degradation in the RRR is consistent with a previously observed phenomenon which was attributed to the Cu contamination due to the diffusion of metallic elements in plated Cr. As depicted schematically in figure 8, Cr concentration distribution in Cu stabilizer at distance \( x \) from the Cr/Cu interface and at time \( t \) can be calculated by a complementary error function [19],

\[
C(x, t) = C_0 \left[ \text{erfc} \left( \frac{x}{2(Dt)^{1/2}} \right) \right]
\]

where \( C_0 \) is the initial Cr concentration at the Cr/Cu interface which, in this case, equals the solubility of Cr in Cu at the
heat treatment temperature, \( D \) is the diffusion coefficient which follows an Arrhenius equation,

\[
D = D_0 \exp\left(-\frac{E_a}{kT}\right) \tag{3}
\]

where \( D_0 \) is a constant, \( E_a \) is an activation energy, and \( k \) is the Boltzmann constant. For calculation of resistivity of contaminated copper, the resistivity \( \rho \) can be related to low level impurities concentration \( C(x, t) \) by Matthiessen’s rule,

\[
\rho(x, t) = \rho_0 + \alpha C(x, t) \tag{4}
\]

where \( \rho_0 \) is the resistivity of pure copper at a certain temperature and \( \alpha \) is a constant which represents resistivity increase per atomic percent of impurity. In the RRR calculation, for convenience we consider the Nb\textsubscript{3}Sn strand as a Cu stabilizer region and non-Cu core region connected in a parallel circuit. So the RRR can be calculated by

\[
\text{RRR} = \frac{K_{\text{Cu}-20\text{K}} + K_{\text{Core}-20\text{K}}}{K_{\text{Cu}-273\text{K}} + K_{\text{Core}-273\text{K}}} \tag{5}
\]

where \( K_{\text{Cu}-20\text{K}} \) and \( K_{\text{Cu}-273\text{K}} \) are conductances of the Cu stabilizer at 20 and 273 K respectively. \( K_{\text{Core}-20\text{K}} \) and \( K_{\text{Core}-273\text{K}} \) are conductances of the non-Cu core at 20 and 273 K respectively, which can be measured experimentally.

Using equations (2)–(4), we can calculate the conductance of Cu stabilizer \( K_{\text{Cu}} \) by radially integrating conductance over the entire Cu region,

\[
K_{\text{Cu}} = \int_{r_1}^{r_2} \frac{2\pi dr}{\rho(x)}
\]

\[
= \int_{r_1}^{r_2} 2\pi r \left[ \rho_0 + \alpha C_0 \text{erfc}\left(\frac{r_1 - r}{2\sqrt{D} t}\right)\right]^{-1} dr \tag{6}
\]
where $D$ is a function of temperature, following equation (3), and $r_1$ and $r_2$ are the inner and outer radii of the Cu stabilizer respectively as depicted in figure 8.

We developed a Microsoft Excel VBA code based on equations (5) and (6) to numerically calculate the RRR of a Cr plated strand as a function of heat treatment temperature and time. Parameters used in the code for the JASTEC strand are listed in table 2. Some of these parameters are explained as follows. The value of $\alpha = 4.0 \times 10^{-8} \text{Ω} \cdot \text{m} / \text{at%}$ is based on an experimental result by Linde [29]. A similar value is published by Gregory et al [30]. This value was also adopted by Novosilova et al [22] in their RRR simulation. The solubility of Cr in Cu, $C_0$, has considerable uncertainty according to a critical review by Chakrabarti and Lauphlin [31]. Due to this considerable uncertainty, we ignore its temperature dependence for simplicity, use 0.1 at% for 640 °C–660 °C temperature range based on data in [31]. It is also consistent with the $C_0$ value used by Novosilova et al [22] in their RRR calculations. Initial Cu RRR, $D_0$ and $E_0$ as free parameters are adjusted to best fit experimental data in figure 7. The calculated RRR

Figure 3. Critical current versus heat treatment temperature for (a) JASTEC strands and (b) KAT strands.

Figure 4. JASTEC strand data. $I_c$ as function of heat treatment time at 650 °C in 11, 12, and 13 T fields. The solid lines are simulations as described by equation (1) with $\tau = 12$ h.

Figure 5. Hysteresis losses of the JASTEC strand as a function of heat treatment time. The solid line is a fit with a function similar to equation (1) where time constant $\tau = 12$ h.
versus heat treatment time for all three temperatures are plotted in figure 7 as solid lines. The fitted values of these free parameters are listed in table 2 as well.

In the following, we discuss the significance of the values of free parameters, initial Cu RRR, $D_0$ and $E_a$. For simplicity, the value of initial Cu RRR takes into account the effect of step one heat treatment which is therefore not calculated separately. When the fitted initial Cu RRR of 540 is used to calculate the RRR of the strand, which includes both Cu and non-Cu regions, a strand RRR of 347 is obtained. This is in a reasonable agreement with the RRR measured after step one heat treatment as shown in figure 6.

$D_0$ and $E_a$ obtained from fitting experimental data are compared with those in [32] and [33] and listed in table 3. It is evident that the diffusion coefficients obtained in this work are significantly higher than those in [32] and [33]. If we considered the possible precipitation of Cr during cooling from heat treatment temperature, as suggested by Alknes et al [23], to cause the measured low RRR, the diffusion coefficient would have been even higher. This discrepancy was also observed by Novosilova et al [22] who suggested that diffusion of other elements that co-exist in the Cr coating, such as oxygen, might be the cause. However, as Alknes et al [23] pointed out, oxygen as a main cause of RRR degradation is not likely.

| Table 2. Parameters used in the RRR calculation. |
|-------------------------------------------------|
| Parameters used in RRR simulation | Remark |
| Diameter (mm) | 0.82 | Measured |
| Core diameter (mm) | 0.591 | Measured |
| $\rho_{\text{Cu-273K}}$ (\(\Omega\)-m) | $1.54 \times 10^{-8}$ | [6] |
| Initial Cu RRR | 540 | Free |
| $\rho_{\text{Core-273K}}$ (\(\Omega\)-m) | $2.73 \times 10^{-8}$ | Measured |
| Core RRR | 3.98 | Measured |
| Solubility limit (at\%) | 0.1 | [31] |
| Resistivity increase per 1 at\% Cu (\(\Omega\)-m/at\%) | $4.0 \times 10^{-8}$ | [29, 30] |
| Cr diffusion $D_0$ (m\(^2\) s\(^{-1}\)) | $4.2 \times 10^{-2}$ | Free |
| Cr diffusion activation $E_a$ (eV) | 2.53 | Free |

Figure 6. RRR of the JASTEC strand as function of heat treatment time at 570 °C (first step) for samples with and without plated Cr.

Figure 7. RRR of the JASTEC strand as a function of step two heat treatment time at different temperatures. The solid lines are results of calculations for 640, 650, 660 °C using the parameters listed in table 2.

Figure 8. Schematic drawing of a strand cross-section and Cr distribution after heat treatment. $r_1$ and $r_2$ are the inner and outer radius of the copper stabilizer respectively.
This is because the diffusion coefficient of O in Cu (also listed in table 3) is about six orders of magnitude greater than that of Cr in Cu. So the RRR degradation would have been saturated very shortly after the start of heat treatment. In fact impurities of other metallic elements such as Ni, Fe, and Zn are commonly found in Cr plating electrolyte [35]. This presents another possible cause of RRR degradation. For example, Ni is completely soluble in Cu at Nb₃Sn heat treatment temperatures, and its diffusion coefficient in Cu [33] is higher than that of Cr in Cu as shown in table 3. Therefore even a low level of 0.1 at% Ni in Cr layer would be sufficient to cause significant contamination of Cu, despite the fact that the effect of Ni impurity on Cu resistivity is somewhat smaller than that of Cr [29, 30]. Therefore, we speculate that the combined diffusion of Cr and other metallic impurities in the Cr layer result in RRR degradation which advances with heat treatment time and temperature. Unfortunately, this low level of metallic impurities in the Cr layer is difficult to measure by conventional characterization techniques such as energy dispersive x-ray spectroscopy (EDS). Ultimately the complete understanding of this RRR degradation should be based on accurate measurement of Cr and other impurity content in the Cu stabilizer as a function of distance from the Cr/Cu interface. This is a very challenging measurement, due to the extremely high detection sensitivity needed. Previous measurements by laser mass spectrometer [20], and high sensitivity EDS [23] had only limited success.

In order to demonstrate the validity of our RRR calculation code, a few additional sets of RRR versus heat treatment time data are plotted in figure 9. These include RRR of KAT strand at 640, 650, and 660°C, as well as some data reproduced from the literature [21–24] where heat treatments were at 650°C only. A downward trend of RRR with heat treatment time is evident. The same calculated curves as presented in figure 7 is also plotted in figure 9. Despite the differences in strand manufacturer, testing labs and the step one heat treatment schedule, a universal trend of RRR versus heat treatment time is clear. It suggests the predictability of this phenomenon, and our RRR calculation code with the parameters listed in table 2 seems to be very useful in predicting the RRR of Cr plated strands.

4. Conclusion

Heat treatment sensitivity of JASTEC and KAT strands for ITER CS coils are studied by measuring I_c, Q_max and RRR of samples heat treated at various temperatures and times. We found that moderate variation in temperature and time of the step two heat treatment does not significantly change I_c. In the case of JASTEC strand, after the step one heat treatment, samples already have about 75% of their maximum I_c. The RRR decreases with increasing heat treatment temperature and time due to the diffusion of contaminants from the Cr layer into the Cu stabilizer. The RRR of a Cr plated Nb₃Sn strand can be predicted by a Cr diffusion model as demonstrated by our calculations in this paper.

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