Effects of Cr Diffusion on RRR Values of Cr-Plated Nb_3Sn Strands Fabricated by Internal-Tin Process

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***Abstract*—Nb_3Sn strands which will be used for the ITER TF coils should be chrome plated thickness of 1.8 μm to reduce AC loss and improve the thermal stability of cable. During heat treatment, the RRR value can be affected by Cr diffusion. In this work, the effect of Cr diffusion was systematically studied, using the KSTAR and ITER candidate strands. For the KSTAR strand, the Cu/non-Cu ratio was systematically varied from 1.53 to 0.69 by chemical etching whereas the samples were heat treated by the same schedule. For the ITER candidate strand, on the other hand, the Cu/non-Cu ratio was fixed to the specification value of 1.0, and the variation of the RRR value was studied with respect to the heat treatment schedule, especially the retention time of the 650°C plateau was varied from 100 to 200 hours. It was also compared with the Cr diffusion distance obtained from EPMA (Electron Probe Microanalysis). We found that the RRR value of the ITER candidate strand becomes lower than the ITER requirement of 100, if the heat treatment at 650°C is longer than 200 hours. The RRR can be reached up to 161 when the duration of 650°C plateau is reduced to 100 hours, while satisfying all other ITER requirements including the critical current density.**

***Index Terms*—Cu/non-Cu ratio, internal-tin processed Nb_3Sn, residual resistance ratio.**

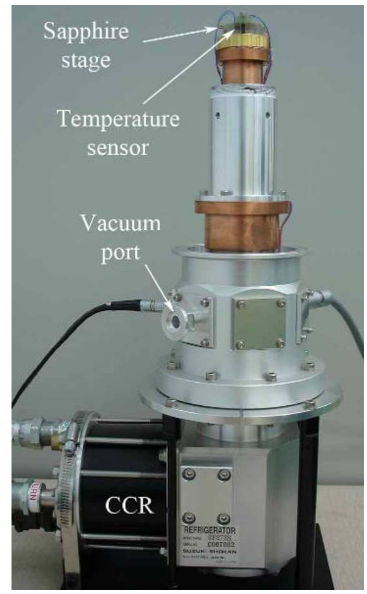

Fig. 1. A photograph of the RRR measurement system developed in this work.

I. Introduction

ONE of the stringent requirements for Nb_3Sn strands which will be used for the ITER TF coils is that the residual resistance ratio (RRR) should be larger than 100. The RRR for Nb_3Sn superconducting strand is usually defined as a ratio of the resistivity at 273 K to at 20 K. It is well known that the resistivity of metal without external magnetic field is influenced by three major contributions; thermal scattering, impurities and cold work (Matthiessen's rule) [1]. Since Nb_3Sn strands are used after heat treatment, the resistivity contribution from cold work can be neglected. At higher temperature, at 273 K, the resistivity of annealed metals will be dominated by the influence of thermal effects, whereas at 20 K, it will critically depends on impurity concentration. In other words, the RRR of Nb_3Sn will be mostly determined by the resistivity at 20 K, or by impurity concentration.

The impurities in the Cu stabilizer of the Nb_3Sn strand can be originated from the inherent impurities in the oxygen-free high-conductivity (OFHC) copper tube used or there might be tin leakage through broken Ta barrier from non-Cu region. But for Nb_3Sn strands used in the form of cable-in-conduit conductor (CICC), there is another source of impurities and the source can be a diffused Cr into the stabilizer [5]. Usually, Nb_3Sn strands used for large scale magnet applications are chrome plated to increase contact resistance or to reduce cable coupling loss [2]. In this work, a systematic study on the effects of chrome diffusion has been carried out using the KSTAR and ITER candidate Nb_3Sn strands. Detailed measurement procedures and sample preparations are described in Section II. The RRR measurement results with variations in Cu/non-Cu ratio or with different heat treatment schedule will be discussed in Section III.

II. Experimental

For the RRR measurement, our own measurement system was set up using a closed cycle refrigerator (CCR) manufactured by Suzuki Shokan, model RF50D with maximum cooling power of 4.7 W (Fig. 1). To increase thermal conduction and for an electric insulation, the sample stage is made of sapphire and can accommodate two 24 mm-long sample at a time. The distance between the voltage taps is about 11 mm. After sample mounting, the samples were covered with Apiezon N grease to improve temperature homogeneity. Between the samples, a silicon diode sensor is attached with Stycast epoxy and the temperature is controlled by a Lake shore 331 temperature controller, which enables stable temperature control from 300 K down to 10 K. Current is supplied by using Keithley 6221 current source and the voltage is measured with Keithley 2182A nano-voltmeter. During the resistance measurements, the polarity of 0.1 A

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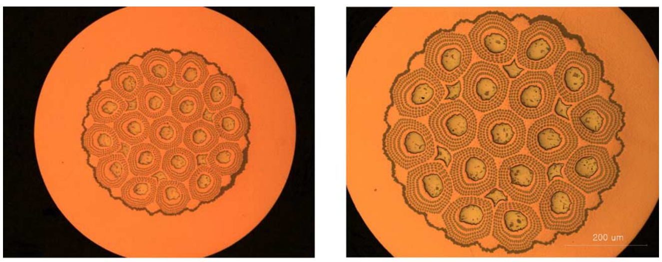
TABLE I
THE RRR MEASUREMENTS COMPARISON

Sample name	RRR PPMS	RRR CCR	Error (%)
R1	204	199	1.0
R2	79	78	2.5



(a) (b)

Fig. 2. Optical microscope images of the Nb3Sn strands studied in this work. (a) KSTAR strand; (b) ITER strand.

TABLE II
BASIC SPECIFICATIONS OF THE Nb_3Sn STRANDS

	KSTAR	ITER
Diameter(mm)	0.778	0.816
Cu/non Cu ratio	1.53	1.0
Thickness of Ta barrier(μm)	7.0	6.6
Thickness of Cr-layer(μm)	1.8	1.8
Twist pitch(mm)	10	15

DC current was alternated to get rid of any constant thermoelectric noise. The RRR results measured by our system were compared with measurements using a commercial Quantum Design PPMS (Physical Properties Measurement System) with an AC transport option. As is listed in Table I, both measurement results are in agreement within 3% error.

Nb_3Sn strands used in this work were manufactured by Kiswire Advanced Technology (KAT) and cross-sectional photograph images are shown in Fig. 2. The KSTAR type strand corresponds to Fig. 2(a) and an ITER candidate strand is Fig. 2(b). The basic specifications of each strand are listed in Table II. Since the Cu/non-Cu ratio of the KSTAR type strand is larger than that of the ITER strand, the KSTAR strand was used for a study on the RRR dependence of the Cu/non-Cu ratio. The Cu stabilizer of the KSTAR strand was etched by using HNO_3 based etchant. With longer etching time, the Cu stabilizer became thinner and the Cu/non Cu ratio was reduced Fig. 3. The etched strands were plated with 2 μm thick Cr-layer. The thickness of Cr-layer was measured by a coulometric thickness tester manufactured by Yamamoto. After chrome plating, the ends of strands were folded to prevent tin leakage from the edges during the heat treatment, and then the samples were heat treated as follows; 210°C for 50 hours, 340°C for 25 hours, 450°C for 25 hours, 575°C for 100 hours, and finally at 650°C for 200 hours, with the temperature ramp rate of 5°C/hour.

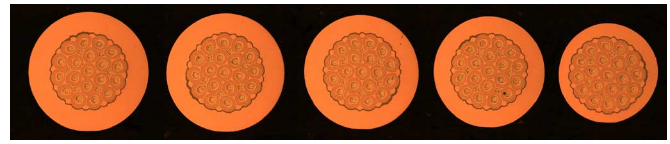


Fig. 3. Decrease of the Cu/non Cu ratio with increased etching time. From left to right, the Cu/non-Cu ratio is 1.38, 1.22, 1.12, 1.05 and 0.69, respectively.

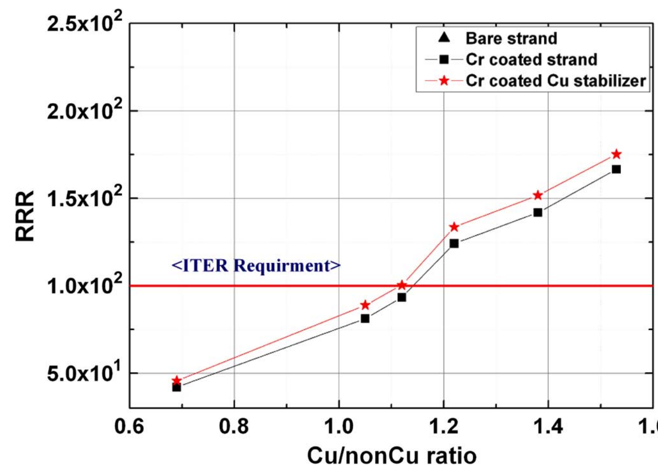


Fig. 4. The RRR as a function of the Cu/non-Cu ratio for the KSTAR strand.

During the heat treatment, the pressure in the furnace was kept under 1.0×10^{-6} Torr, and the temperature was controlled within ±5°C. After the heat treatment, the chrome layer at the ends was removed for soldering. For the ITER type strand, the Cu/non-Cu ratio was not varied but was set to the specification value of 1.0. On the other hand, the retention time at 650°C plateau region was varied from 100 to 200 hours. After the RRR measurements, the ITER type strands with different heat treatment schedule were also analyzed by EPMA (Electron Probe Microanalysis) to measure the chrome diffusion distance for each case.

III. RESULTS AND DISCUSSION

A. The Cu/non-Cu Ratio Dependence of the RRR

The RRR measurement results with variations of the Cu/non-Cu ratio for the KSTAR strand are shown in Fig. 4. The RRR of a bare strand without the 1.8 μm thick chrome plating was as high as about 220. It reduced to ~165 after the sample was chrome plated and the decrease of the RRR with the reduction of the Cu/non-Cu ratio can be clearly seen in Fig. 4. For the KSTAR strand, the ITER requirement of 100 cannot be satisfied if the Cu/non-Cu ratio is lower than about 1.1 under the heat treatment conditions described in Section II. The KSTAR strand was further etched until the Cu stabilizer region was totally removed, and the RRR of the non-Cu ratio region was measured directly as 8.44. It is lager than the reported value for a bronze processed strand [3] and is related to the difference in the area occupied by bronze.

Having measured the resistivity of the non-Cu region directly, the resistivity of the Cu stabilizer can be calculated from

$$R_{strand} = \frac{R_{Cu} \cdot R_{Non-Cu}}{R_{Cu} + R_{Non-Cu}}$$

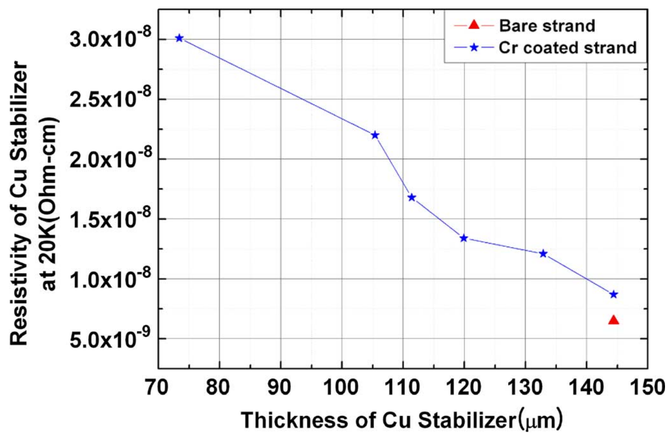


Fig. 5. Resistivity of the Cu stabilizer at 20 K as a function of the Cu stabilizer thickness for the KSTAR strand.

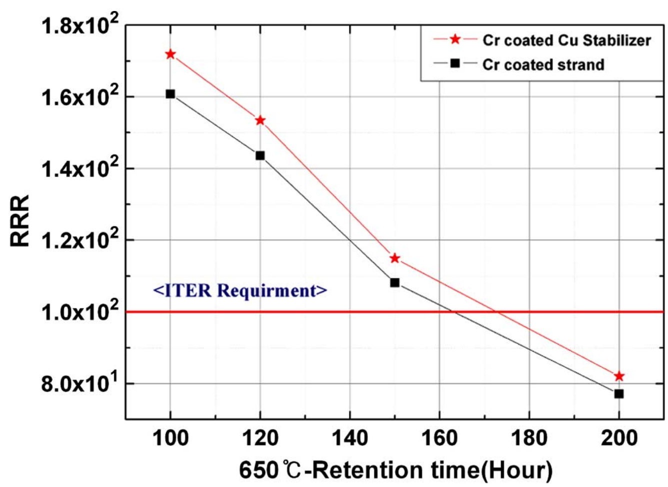


Fig. 6. The RRR of the Cr plated ITER strand as a function of the retention time at 650 °C plateau region during the heat treatment.

The RRR values for the Cu stabilizer as well as for the whole strand were decreased with the reduction of the Cu/non-Cu ratio as shown in Fig. 4. In Fig. 5, the resistivity of the Cu stabilizer at 20 K as a function of the stabilizer thickness is presented. The resistivity of the stabilizer at 20 K sharply increased as the thickness was reduced and the percentage increase of the resistivity at a thickness of 73 μm to that at 144 μm was as high as ~250%. On the other hand, the variations in the resistivity of the stabilizer at 273 K were within a range of empirical measurement error. This increase of the resistivity at 20 K is only depended on the Cu stabilizer thickness, because the samples had the same thickness of Cr plated layer and were heat treated at the same time. The resistivity of a metal at 20 K is mostly affected by the impurity concentration and it is the major cause for the observed reduction in the RRR value.

B. Heat Treatment Dependence of the RRR

Fig. 6 shows the variation of the RRR values with respect to the retention time in the 650°C plateau region during the heat treatment for the Cr plated ITER type strand with the specified Cu/non Cu ratio of 1.0. In the data we measured, the RRR decreases almost linearly as a function of the retention time at 650°C and it is expected to be lower than 100 if the retention time is longer than 160 hours. By the same way as described above, the RRR of the non-Cu region was directly measured and was equal to 7.79. The difference between the non-Cu RRR of the ITER and that of the KSTAR strands is about 8%, which is comparable to the 5% difference in the area occupied by bronze.

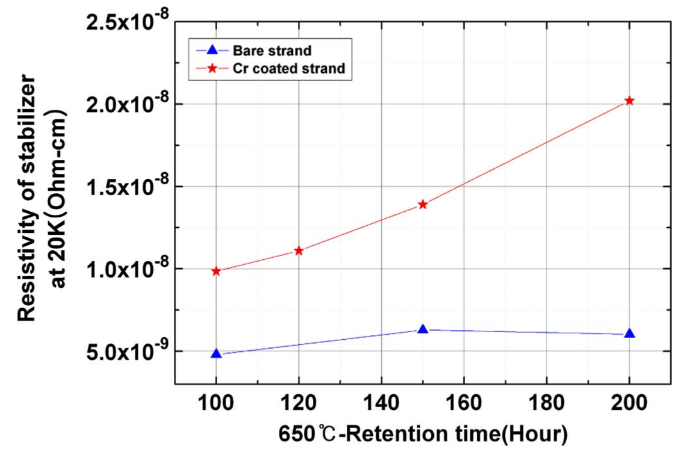


Fig. 7. Resistivity of the stabilizer for the Cr plated and bare ITER strand at 20 K as a function of the retention time at 650 °C.

The resistivity of the stabilizer at 20 K for the Cr plated and bare ITER strands was calculated and presented in Fig. 7. The resistivity of the stabilizer at 20 K for the Cr plated strand increased by almost twice as the retention time at 650°C increased from 100 to 200 hours while the RRR value reduced by almost half. Quite similar to the case of the RRR variation for the KSTAR strand with respect to the Cu/non-Cu ratio, the RRR values for the ITER strand are mostly affected by the impurity concentration. We also calculated the variation of the stabilizer resistivity at 20 K for the bare ITER strand, which are shown together in Fig. 7. Quite interestingly, the stabilizer resistivity at 20 K for the bare strand is almost independent from the retention time, which means that the impurities related to the 20 K resistivity are mainly due to the diffusion of chrome not due to the tin leakage through weak Ta barrier from the non-Cu region. The Ta barrier for the KSTAR strand was fabricated by the same way and we argue that the variation of the stabilizer resistivity at 20 K or the RRR values for the KSTAR strand is also due to chrome diffusion.

In order to see the chrome diffusion more clearly, the Cr plated ITER strands with different retention time at 650°C were analyzed by using EPMA manufactured by Shimatsu. Cr diffusion distance is defined as a distance from the outer circumference to a point where we can observe the chrome impurities more than 0.1 wt.%. As can be seen in Fig. 8, the Cr diffusion distance is monotonically increased with prolonged retention time at 650°C. If the retention time at 650°C is longer than 200 hours, Cr diffusion distance is larger than the half of the stabilizer thickness. For a semi-infinite system, the diffusion distance can be approximated as, $2(Dt)^{1/2}$, where D is a diffusion coefficient and t is the retention time [4]. The obtained diffusion coefficient of $1.42 \times 10^{-11}\ \mathrm{cm}^2/\mathrm{s}$ is larger than the previous reported value [3]. The other thing to be noted is that we could not observe any tin impurities in the stabilizer by the EPMA we used.

We argued that to meet the ITER specification on the RRR value, the plateau time at 650°C should be shortened below 160 hours for the ITER candidate strand studied in this work.

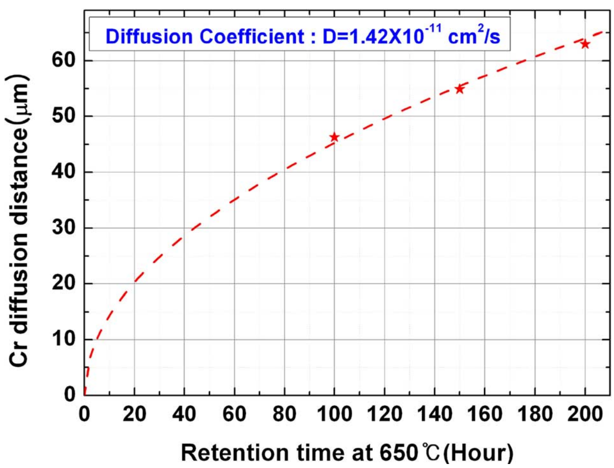


Fig. 8. EPMA analysis results for the ITER strand. Dotted line is calculated with an approximate diffusion distance expression for a semi-infinite system.

TABLE III
THE CHARACTERISTICS OF THE ITER TYPE STRAND

Parameter	value	
HT(650℃-Retention time) (hours)	100	200
Cu/non-Cu ratio	1.0	1.0
I_c (A)	234	242
J_c (A/mm^2)	895	926
n value	30	30
AC Loss (mJ/cc)	662	772
RRR	161	77

However, the reduction of the retention time at 650°C might degrade the other characteristics such as the critical current density. The overall performance characteristics were measured for the ITER candidate strand with different retention time at 650°C as listed in Table III. As can be seen in Table III, only the critical current density was slightly lowered about 3% as the retention time is reduced from 200 to 100 hours. On the other hand, all other characteristics are not affected or rather improved with a shortened heat treatment time.

IV. CONCLUSION

In summary, a systematic study on the effects of chrome diffusion has been carried out using the KSTAR and ITER candidate Nb_3Sn strands. It was shown that for the strands studied in this work, the RRR variation is mainly affected by the 20 K resistivity or by chrome diffusion. The retention time at 650°C strongly affects the RRR value and if we set the retention time to 200 hours, the RRR value larger than 100 can be obtained with the Cu/non-Cu ratio higher than 1.1 for the KSTAR strand. With the specified Cu/non-Cu ratio of 1.0, the RRR value larger than the ITER requirement is possible when the retention time at 650°C is less than 160 hours for our ITER candidate strand. The reduction of the retention time down to 100 hours increased the RRR up to ~161 with a slight reduction of the critical current density around 3%. The other characteristics are not degraded but rather improved. We suggest that for internal-tin processed Nb_3Sn strands due to their flexibility in the control of the total amount of the tin contents and relative easiness in the design change, it is possible to fabricate high performance strand with a reduced heat treatment time.

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