The microstructure and properties of J-R Nb3Al superconducting wires fabricated by diffusion method at an intermediate temperature

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Abstract. The precursor Nb-Al strands were fabricated by the method of Jelly-Roll. The effects of sintering temperature and time on the diffusion degree and superconducting property of the binary Nb-Al system were investigated under isothermal heat treatment at 1100 -1500 °C. The results show that the Tc of superconducting wires increased with the heat-treatment temperature rising at the isothermal region. Excessive heat-treatment time led to the decrease of the properties of Nb3Al wires under a certain heat-treatment temperature. The magnetic analysis results showed that the optimal Tc of J-R Nb3Al wires was about 16.8 K at a heat-treatment temperature of 1500 °C for 3 h.

1. Introduction
Since the low strain-stress property of Nb3Sn superconductors, the alternative Nb3Al superconductor has been deeply studied for the use of D-shapes coils in the International Thermonuclear Experimental Reactor (ITER) plan [1, 2]. Although the Nb3Al superconductor has a better property than Nb3Sn, the manufacture is still of a big problem up to now. Unlike the Nb3Sn superconductor, Nb3Al superconductor can’t be fabricated by...
the bronze process because of the easy formation of Cu-Nb-Al ternary compound [3]. In addition, according to the Nb-Al binary phase diagram [4], the stable stoichiometric phase of Nb₃Al can only exist at 1940 to 2060 °C, and the ratio of Al in the stable Nb₃Al is far away from the standard stoichiometry at a lower temperature, resulting in a bad superconductivity.

Nowadays, there are generally three kinds of methods for Nb₃Al superconductor fabrications. The first one is prepared via low temperature diffusion [5], such as the high energy ball milling method [6]; The second one is prepared via high temperature diffusion, such as the laser-irradiated method [7]; The third one is prepared via Rapid Heating Quenching and Transformation (RHQT) method [8, 9].

In the low temperature diffusion method, the $T_c$ value of samples is just around 15 K, which is far away from the theoretical value. As for the RHQT method, the precursor Jelly-Roll (J-R) Nb/Al wires were quickly heated by the ohmic heating and then quickly cooled down in a gallium liquid and eventually the nearly stoichiometric Nb₃Al superconducting wires were obtained with fine grains after the subsequent annealing treatment [10, 11]. Although the most popular method of fabricating Nb₃Al superconductor is RHQT, there still are some problems in making long superconducting wires. What’s more, the highest $T_c$ was about 18.5 K obtained by the laser-irradiated method, but the $J_c$ value was very low because of the coarse grains for this kind of high temperature diffusion method [12].

Attempts have been made to obtain the Nb₃Al superconducting wires with excellent properties. However, few investigations have been performed to clarify the effect of sintering temperature, sintering time on $T_c$ in total at an intermediate temperature region. Therefore, in order to further understand the detailed relationships, this study focuses on the influence of $T_c$ values in different sintering temperatures and time periods by the method of intermediate temperature diffusion.

2. Experimental
The J-R single-core Cu/Nb₃Al precursor wires, fabricated using Nb layer of 150 μm and Al layer of 50 μm [13, 14], were supplied by the WST Co., Ltd. The corroded Cu shell wires were annealed at a temperature ranging from 1100 to 1500 °C for 1 to 12 h. The diameter of wires was 1.3 mm. Each of the samples was heated by a heating rate of 100 °C/h and then cooled down to room temperature after switching off the furnace. During the annealing process, all samples were protected at the flowing Argon condition.

The surface of annealed wires was sanded and the phase composition was analysed by X-ray diffraction (XRD, Philips X’Pert MRD) using Cu Kα radiation. The microstructure and composition of the Nb₃Al wires were investigated by Field-emission scanning electron microscopy (FESEM, JEOL) and energy dispersive X-ray analysis (EDX), respectively. For all the Nb₃Al wires, Specimen of 1mm long were cut from each sample and the magnetization as a function of temperature (M-T) were measured by using the magnetic properties measurement system (MPMS, Quantum Design) under an applied field of 0.002 T and a temperature range of 9-25 K with a zero-field cooling (ZFC) process.
3. Results and Discussion

Figure 1(a) shows the $M-T$ curves of Nb$_3$Al wires annealed at 1100-1500 °C for 3 h. It can be seen that all the samples have superconducting transition phenomena above the temperature of 12 K. In addition to the sample after annealing at 1200 °C, the diamagnetic signal and transition temperature of samples annealed at a temperature range of 1100-1450 °C gradually increased and their transition width becomes narrowed with the increase of annealing temperature. The results suggest that the diffusion rate of Al atoms is faster and the formation of Nb$_3$Al phase is increased with increasing the heat-treatment temperature, and that the Nb and Al atomic ratio of Nb$_3$Al phase is more close to the stoichiometric value of 3:1. The sample after annealing at 1200 °C has a narrow transition width and a low $T_c$ of about 14.3 K. It is indicated that the Nb$_3$Al phase of significantly deviated from the stoichiometric ratio of 3:1. As shown in Figure 1(a), the sample annealed at 1500 °C has a highest $T_{c\text{-onset}}$ of about 16.8 K, but the diamagnetic signal decreased and the transition width increased. It can be inferred that a small amount of Nb$_3$Al phase has formed with relatively close to the stoichiometric ratio when the heat-treatment temperature reached 1500 °C. Figure 1(b) shows the curves of the $T_{c\text{-onset}}$ against the annealing temperature. when the annealing time is 3 h, the $T_{c\text{-onset}}$ is improved with the increase of the heat-treatment temperature. At an annealing temperature range of 1100-1500 °C, a liner relationship formula can be drawn:

$$T_c = 3.85704 + 0.00862 \times T$$

Where $T_c$ and $T$ are the superconducting transition temperature and annealing temperature, respectively.

Figure 2 displays the XRD patterns of Nb$_3$Al wires annealed at different temperatures for 3 h. All the XRD lines in Figure 2 show diffraction peaks of Nb$_3$Al and Nb phases. When the heat-treatment temperature is 1100 °C, the XRD diffraction patterns of samples are mainly Nb diffraction peaks. A number of diffraction peaks of impurity phase appear at around $2\theta = 30^\circ$ with only a small amount of Nb3Al diffraction peaks in the XRD line. That is why the magnetic performance of the sample is very bad. With the increase of the annealing temperature, the diffraction peaks of the impurity phase decrease as (Figure 2), so the properties of the samples are gradually improved, indicating consistent performance results as shown in Figure 1(a). The XRD patterns are almost the same for the samples annealed at the temperature range of 1200-1500 °C, and the peaks of Nb$_3$Al, Nb phase and some impurity phases be detected. It is worth noting that the XRD pattern of the sample annealed at 1500 °C has no obvious peaks of impurity phases, but the transition width is very large. It is suggested that the Nb$_3$Al phase with different Nb/Al atomic ratios were formed in the sample.

Figure 3 shows the typical SEM images of the Nb$_3$Al wires annealed at 1100-1500 °C for 3 h. The precursor wire is Nb/Al single-core wire prepared by J-R method. As seen from Figure 3(a-1), (b-1), (c-1) and (d-1), there is still a coiled lamellar structure with Nb rod at the center in all the samples. Figure 3(a-2) shows that there are bright stripes, gray areas and holes: the bright stripes are the unreacted Nb, the gray region is the Nb/Al diffusion layer, and the holes are formed by the melting of the Al layer. There is a large
amount of unreacted Nb in the samples annealed at 1100 °C, which may be due to the poor superconducting transition performance. The Nb layer decreases obviously with the increase of the heat-treatment temperature as shown in figure 3(a-2), (b-2), (c-2) and (d-2), suggesting that the Nb and Al react more fully with increasing the heat-treatment temperature. It should be noted that there are two regions of dark gray and grayish white in the images as shown in figure 3 (b-1) and (c-1) with the heat-treatment temperature increasing to 1200 °C and 1450 °C. As indicated in Figure 3(d-2), there are only grayish white region after annealing at 1500 °C, and the grayish white region should be formed by grain growth at a high temperature.

Figure 1. (a) M-T curves of Nb3Al wires annealed at 1100-1500 °C for 3 h and (b) the Tc-onset against the annealing temperature.

Figure 2. XRD patterns of Nb3Al wires annealed at 1100-1500 °C for 3 h

Figure 3. Typical SEM images of samples annealed at different temperatures for 3 h with 100x and 1000x magnifications. (a-1) and (a-2): 1100 °C; (b-1) and (b-2): 1200 °C; (c-1) and (c-2): 1450 °C; (d-1) and (d-2): 1500 °C.
Figure 4 shows the $M$-$T$ curves of Nb$_3$Al wires annealed at 1400 °C for different time. As shown in Figure 4, the properties of the samples are gradually improve with the increase in the heat-treatment time. As can be seen from the inset of figure 4, the sample annealed for 1 h has poor properties, suggesting that the reaction of Nb and Al is not sufficient, and there is only a very small amount of superconducting phase formed in the sample. The samples annealed at 1400 °C for 3, 6 and 12 h has a same $T_{\text{c-onset}}$ of about 15.8 K, but the superconducting diamagnetic signal increases with the increase in the annealing time, indicating that the formation of Nb$_3$Al phase increases. This suggest that the diffusion of Al and Nb atoms is more fully with the increase in the heat-treatment time, thus, the Nb$_3$Al phase content increases and the lattice defects decrease in samples after annealing at 1400 °C.

Figure 5 shows the XRD patterns of the samples annealed at 1400 °C for different time periods. The XRD lines of all samples have clearly peaks of Nb$_3$Al and Nb phases. The sample annealed for 1 h has formed Nb$_3$Al phase, but the superconducting property was not so good and the superconducting transition was almost invisible as shown in Figure 4, indicating that the reaction of Nb and Al is not sufficient at 1400 °C for 1 h. With the heat treatment time increasing from 3 to 12 h, there are obvious diffraction peaks of impurity phase at $2\theta = 35.1^\circ$ and $40.6^\circ$ in the XRD patterns. The Nb$_3$Al peak increases and the Nb peaks decrease obviously in the XRD line of the sample annealed for 12 h, indicating that the reaction of Al and Nb is more complete as the heat treatment time is prolonged.

In order to further illustrate the effect of heat-treatment time on the properties of Nb$_3$Al wires, the magnetization behavior have been investigated for Nb$_3$Al wires annealed at 1450 °C for different time. As shown in Figure 6(a), the sample annealed at 1450 °C for 3 h has a relatively good property, such as a higher $T_c$ and greater diamagnetic signal, comparing with those annealed for 1, 6 and 12 h. The sample annealed for 3 h has a higher $T_{\text{c-onset}}$ of about 16.4 K suggesting that the sample annealed at 1450 °C for 3 h can formed Nb$_3$Al phase with a relatively good quality. As seen from Figure 6(b), the properties of the
sample increased first and then decreased with the annealing time increasing from 1 to 12 h. It can be inferred by comparing the results of Figure 6(a) and Figure 4 that the optimization properties is obtained in a shorter annealing time with the increase in the heat-treatment temperature, and an excessive annealing deteriorates the properties of the sample.

Figure 7 shows typical EDX images of Nb$_3$Al wires annealed at 1400 °C for 6 h and 1450 °C for 3 h. As shown Figure 7(a), the Nb/Al atomic ratio of the sample annealed at 1400 °C for 6 h is about 5:1, much greater than the stoichiometric ratio of 3:1, thus resulting in a severe decrease in magnetic $T_c$ of about 15.8 K (Figure 4). A shown in Figure 7(b), the Nb/Al atomic ratio of the sample annealed at 1450 °C for 3 h is close to 3:1, resulting in higher $T_c$ of about 16.4 K than the sample annealed at 1400 °C for 6 h. It is suggested that the Nb/Al atomic ratio of the formation of Nb$_3$Al in the samples more close to the stoichiometric ratio of 3:1 when the sample annealed at higher temperature, and that increasing the annealing temperature is more beneficial to improve the properties of Nb$_3$Al wires than prolonging the annealing temperature.

![Figure 6](image1.png)

**Figure 6** (a) $M$-$T$ curves of Nb$_3$Al wires annealed at 1450 °C for 1, 3, 6, and 12 h. (b) The $T_{c\text{-onset}}$ versus annealing time at the annealing temperature of 1450 °C.

![Figure 7](image2.png)

**Figure 7** EDX images of Nb$_3$Al wires (a) annealed at 1400 °C for 6 h and (b) annealed at 1450 °C for 3 h.

4. **Conclusions**
In this study, a series of J-R single core Nb$_3$Al wires have been heat-treated at an intermediate temperature of 1100-1500 °C. The $T_c$ of the superconducting wires increases relevantly with the increase in the sintering temperature. There are some determined $T_c$ values in different sintering time when the sintering temperature is in a certain range. The optimal performance of samples is determined after sintering at 1500 °C for 3 h, and the obtained $T_c$ is about 16.8 K.

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