Effects of Zr, Hf and Ta Additions on Properties of in situ Cu–20%Nb–Sn Superconductors

By Akihiko Nagata*, Kazuhiko Hayashi**, Toru Hanano*** and Osamu Izumi*

Improvements of high-field properties of in situ Nb3Sn superconductors were studied by additions of 2%Zr, 2%Hf and 2%Ta to Cu–20 mass%Nb melts. The eutectic structures around Nb dendrites were observed in all as-cast materials, and some difficulties arose from the structures in drawing the ingots with Zr and Hf into wires. The critical current densities were measured up to 15 T after various heat treatments.

Additions of Zr and Hf affected a little Jc in the high magnetic field region and H*c2 of in situ Cu–20%Nb–Sn superconductors. On the contrary, additions of Ta improved appreciably the high-field performance of in situ Cu–20%Nb–Sn superconductors in spite of the fact that Ta was not soluble in the Nb dendrites in the as-cast state. The highest Jc of (1-2)×10^8 A/m^2 at 12 T and H*c2 of 17.5 T were obtained on the in situ Cu–20%Nb–2Ta–Sn superconductors.

(Received February 22, 1985)

Keywords: in situ Nb3Sn superconductor, Nb3Sn superconductor, copper-niobium alloy, critical current density, zirconium, hafnium, tantalum, in situ superconducting composite

I. Introduction

The so-called bronze process has been commercially established to produce multifilamentary Nb3Sn superconductors for high-field magnets. In situ process is, however, thought to be an alternative process because of its simple and economical processing(1). Compared with the conventional bronze processed Nb3Sn superconductors, in situ Nb3Sn superconductors seem to have some merits such as the high critical current densities, Jc, superior strain tolerance(2)(3), high strength(4)(5) and relatively low heat treatment temperature(1). There are, however, some disadvantages in in situ Nb3Sn superconductors such as difficulty of making homogeneous ingots(1), higher ac losses(6)(9) and the rapid degradation of Jc in high magnetic fields(9)(10). Therefore, improvements of critical current densities of in situ Nb3Sn superconductors in high magnetic fields are required for their high-field applications.

In the case of the bronze processed Nb3Sn superconductors, there are extensive studies on improvements of their high-field performance by alloying various kinds of additives to Nb cores and/or matrix(11)(13) and superior results are obtained by additions of Ti(14)(16) and Ta(17)(19). There are, however, a few studies on improvements of high-field properties of in situ Nb3Sn superconductors(10)(20)(22), in which additives are Ta(10)(20)(21), Ti(22), Ga(21)(23)(25), Be(21), Al(21) and Zn(21).

In the present study, for improving high-field current capacities of in situ Nb3Sn superconductors, Zr, Hf and Ta were selected in consideration of the results of bronze processed Nb3Sn superconductors and added to Cu–20% Nb melts by the nonconsumable electrode arc-melting. Although the critical current density of in situ Nb3Sn superconductors increases with an increase in the Nb concentration of Cu–Nb ingots(1)(26), Cu–20%Nb alloys were used for improving their high-field performance from viewpoints of mechanical properties and ac losses.

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II. Experimental

Starting materials were Cu of 99.99%, Nb of 99.5%, electron beam zone refined Zr, Hf of 95% and Ta of 99.9% in purity. First, Cu–20%Nb–2% additive alloys about 150 g in mass were arc-melted several times in a button-shaped copper hearth under argon atmosphere using a nonconsumable tungsten electrode. Then, they were cut into small pieces and finally arc-melted again into 15 mm square ingots 80 mm in length. These square ingots were turned to rods 10–13 mm in diameter and then drawn into wires 0.24 mm in diameter. The chemical compositions and the reduction ratio of the cross-sectional area of materials are listed in Table 1.

The wires were cut to 40 mm in length and plated electrically with Sn of about 7%. Some wires were plated with various amounts of Sn for studying the influence of Sn concentration on $J_c$ of materials. Sn-plated wires were then sealed into quartz tubes evacuated to less than $4 \times 10^{-3}$ Pa and subjected to the two-step heat treatment. The first step was done at 673 K for 86 ks for dissolving Sn into the Cu matrix, and the second was carried out at 823–923 K for 43 ks–1.38 Ms for formation of the Nb$_3$Sn compound.

The critical current, $I_c$, was measured using a four-probe method in liquid helium (4.2 K) and in the external field, $H$, up to 15 T which applied vertically to wires. $I_c$ was determined by the appearance of the voltage of 1 $\mu$V across about 10 mm-length of wire specimens. $J_c$ was calculated by dividing $I_c$ by the cross-sectional area of wires. Therefore, it is the overall critical current density in the present study.

The microstructures of as-cast materials and wire specimens were observed by optical microscopy and SEM. The chemical composition of the Nb dendrites and the Cu matrix of as-cast materials and the Sn distribution on the cross-sectional area of heat treated wires were studied by using EPMA.

III. Results and Discussion

1. Critical current density up to 8.5 T

Critical currents, $I_c$, were measured in the magnetic field up to 8.5 T produced by a 9 T superconducting magnet for all heat treated specimens. First, $J_c$ at 8.5 T will be discussed as a function of heat treatment condition for each material, since the main purpose of this study is the improvement of high-field properties of in situ Nb$_3$Sn superconductors.

Figure 1 shows the change in $J_c$ at 8.5 T of in situ Cu–20Nb–2Zr–Sn superconductors with the heat treatment time and temperature. For the 823 K-heat treatment, $J_c$ increases with increasing time, which is, however, lower than that for the heat treatments at 873 and 923 K. $J_c$ at 8.5 T on all samples heat treated at 873 and 923 K are in the range of $(3-4) \times 10^8$ A/m$^2$. The highest $J_c$ at 8.5 T is $4.3 \times 10^8$ A/m$^2$ for in situ Cu–20Nb–2Zr–Sn superconductors after

![Graph showing critical current density](image)
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Figure 2 shows the change in $J_c$ at 8.5 T of in situ Cu-20Nb-2Hf-Sn superconductors with the heat treatment condition, which is almost the same as that of in situ Cu-20Nb-2Zr-Sn superconductors. $J_c$ of in situ Cu-20Nb-2Hf-Sn superconductors after the heat treatment at 873 and 923 K lies in the range of $(3-5) \times 10^8$ A/m$^2$. The highest $J_c$ is $5.0 \times 10^8$ A/m$^2$ after heat treating for 0.69 Ms at 873 K.

Figure 3 shows $J_c$ at 8.5 T of in situ Cu-20Nb-2Ta-Sn superconductors heat treated at 823, 873 and 923 K as a function of time. Even heat treated at 823 K, relatively high $J_c$ at 8.5 T is obtained after a long time heat treatment, which differs from the previous two materials. For the heat treatments at 873 and 923 K, $J_c$ first increases with increasing heat treatment time, reaches maximum for 173 and 86 ks, respectively, and then decreases gradually. The highest $J_c$ at 8.5 T of in situ Cu-20Nb-2Ta-Sn superconductors is $5.6 \times 10^8$ A/m$^2$ after the heat treatment for 173 ks at 873 K. Thus, the highest $J_c$ at 8.5 T was obtained by additions of Ta to in situ Cu-20Nb-Sn superconductors in this study. But these $J_c$ values are a little lower than those of the in situ Cu-20Nb-Sn superconductors without additives which showed $J_c$ of $6 \times 10^8$ A/m$^2$ at 8.5 T after the optimum heat treatment at 873 K for 346 ks in our previous study(27).

In comparison among the variations of $J_c$ for the heat treatment at 823 K in Figs. 1, 2 and 3, the diffusion of Sn into the Cu matrix and the formation of Nb$_3$Sn seem to be faster in in situ Cu-20Nb-2Ta-2Sn superconductors than others. Therefore, Sn distributions on the cross-sectional area of wires with reaction were studied by EPMA. Figure 4 shows the diameter of regions without reaction of the in situ Cu-20Nb-Sn superconductors with 2Zr, 2Hf and 2Ta and without additives (marked “None” in the figure) after the heat treatments for 346 ks at 823 and 873 K. It is clearly observed that additions of Zr, Hf and Ta retard the diffusion of Sn in the Cu matrix of wires.

Figure 5 is SEM microstructures of in situ Cu-20Nb-2Hf-Sn and Cu-20Nb-2Ta-Sn superconductors after the heat treatment for 0.69 Ms at 923 K, showing the Nb$_3$Sn filaments in the longitudinal section of wires. The grain growth of Nb$_3$Sn filaments is well developed in in situ Cu-20Nb-2Ta-Sn superconductors, but the coarsening of Nb$_3$Sn can not be observable in in situ Cu-20Nb-2Hf-Sn superconductors.

All as-cast materials showed almost similar dendritic structures by a micrographic observation, and the size of Nb dendrites was about 10 $\mu$m for all materials independent of alloying...
elements. The distribution of additives in the as-cast material is shown in Table 2. In the present study, small pieces of Zr, Hf and Ta metals were arc-melted together with Cu and Nb metals without using master alloys of Zr, Hf and Ta. As is seen in Table 2, only 0.2% Zr exists both in the Cu matrix and the Nb dendrites, and Hf is 0.4% in the Cu matrix and 0.1% in the Nb dendrites. Ta is located by 1.5% in the Cu matrix and could not be detected in the Nb dendrite, which was different from other studies. It is concluded, however, that the presence of a small amount of additives in the Cu matrix and in the Nb dendrite affects considerably the diffusion of Sn in the Cu matrix, resulting in the effect of formation and coarsening of Nb3Sn filaments.

2. Variation of \( J_c \) with Sn content

For studies of effects of the Sn concentration on \( J_c \), wires were plated with various amounts

<table>
<thead>
<tr>
<th>Material</th>
<th>Nb dendrite</th>
<th>Cu matrix</th>
<th>Eutectic</th>
</tr>
</thead>
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<td></td>
<td>Nb Additive</td>
<td>Nb Additive</td>
<td>Nb Additive</td>
</tr>
<tr>
<td>Cu-20Nb-2Zr</td>
<td>0.6 0.2Zr</td>
<td>0 0.2Zr</td>
<td>0 8.3Zr</td>
</tr>
<tr>
<td>Cu-20Nb-2Hf</td>
<td>0.6 0.1Hf</td>
<td>0 0.4Hf</td>
<td>0 14.2Hf</td>
</tr>
<tr>
<td>Cu-20Nb-2Ta</td>
<td>0.4 0Ta</td>
<td>0 1.5Ta</td>
<td>0 34.2Ta</td>
</tr>
</tbody>
</table>

Table 2 Chemical composition of Nb dendrite and Cu matrix in as-cast materials.
of Sn and subjected to the heat treatments which gave the highest \( J_c \) at 8.5 T for each material, that is, 873 K–346 ks for the Zr addition, 873 K–0.69 Ms for the Hf addition and 873 K–173 ks for the Ta addition, followed by \( J_c \) measurements up to 8.5 T. As a typical result of the effect of the Sn concentration on \( J_c(H) \) curves, the change in \( J_c(H) \) with Sn content for in situ Cu–20Nb–2Zr–Sn superconductors is shown in Fig. 6. The increase in \( J_c \) and the decrease in the slope of \( J_c(H) \) curves with increasing Sn concentration are seen in Fig. 6. The latter implies that the critical field, \( H_{c2}^z \), becomes higher if these \( J_c \) values are used for the Kramer’s plot(11). Figure 7 shows the variation of \( J_c \) at 8.5 T with Sn concentration of in situ Cu–20Nb–2Zr–Sn superconductors. A simple calculation gives that the Sn concentration necessary to transform the Nb filament to Nb3Sn completely is about 10% for in situ Cu–20Nb–2Zr–Sn superconductors, but the increase in \( J_c \) becomes sluggish around 8%Sn. The highest \( J_c \) at 8.5 T of in situ Cu–20Nb–2Zr–Sn superconductors is \( 6.3 \times 10^8 \) A/m², which is obtained by the Sn concentration of 14.5%. Almost similar results were obtained in the case of additions of Hf and Ta.

The increase in \( J_c \) with increasing Sn concentration is thought to be due mainly to the increment of the amount of Nb3Sn formed. The Sn distributions on the cross-sectional area of wires with reaction with different Sn concentrations were tested by using EPMA. For example, in the case of in situ Cu–20Nb–2Ta–Sn superconductors heat treated at 873 K for 173 ks the diameter of region without reaction was about 70 µm for the wire with 7%Sn and about 30 µm for that with 12.4%Sn. It is considered that the enhancement of Sn diffusion with increasing Sn concentration is due to a steeper gradient of Sn profiles at the diffusion front.

Since, with increasing Sn concentration, \( J_c \) at 8.5 T increases and the slope of \( J_c(H) \) curves in the high magnetic region becomes sluggish as shown in Fig. 6, the improvement of the high-field properties is expected by the high Sn amount. In the case of the conventional bronze processed Nb3Sn superconductors, it was reported that superior Nb3Sn layers were produced by using the high Sn bronze matrix(11). In the present study, it is considered that Nb3Sn filaments with high \( H_{c2} \) are expected to form by deposition of the high Sn concentration.

From these results, the effect of additives on diffusion of Sn is not clear when large amounts of Sn were deposited, but it was observed that Sn diffused almost to the center of wires in the case of in situ Cu–20Nb–2Hf–Sn superconductors plated with 12.2% of Sn.

3. High-field properties

For studying higher field properties, \( I_c \) measurements from 8 T to 12 T were carried out on the wire samples which exhibited high \( J_c \) at 8.5 T by using a water-cooled Bitter type magnet. Figure 8 shows the variation of \( J_c \) on optimized in situ Cu–20Nb–Sn superconduc-
tors with 2Zr, 2Hf and 2Ta and without additives with the magnetic field, H. Additions of Zr and Hf improve Jc a little in a high field region and those of Ta improve more. Jc at 12 T is $5 \times 10^7$, $6 \times 10^7$, $8.5 \times 10^7$ and $1 \times 10^8$ A/m$^2$ for wires without additives, with Zr, Hf and Ta, respectively. LeHuy et al.\textsuperscript{(21)} reported that Jc at 12 T was $1 \times 10^8$ A/m$^2$ for in situ Cu-30\%Nb-1\%Ta-Sn superconductors, and Sue et al.\textsuperscript{(10)} reported Jc of $8 \times 10^8$ A/m$^2$ at 12 T for in situ Cu-30\%(NbTa)-Sn superconductors with various amounts of Ta. In the present study, Jc was obtained in the same grade as that by LeHuy et al.\textsuperscript{(21)} in spite of the lower Nb concentration. In the case of the bronze processed Nb$_3$Sn superconductors, high-field properties were improved by additions of Zr\textsuperscript{(29)(30)}, Hf\textsuperscript{(30)} and Ta\textsuperscript{(17)-(19)}, but the pronounced improvements of the high-field properties were not achieved successfully by addition of additives except Ta in this study. Figure 9 shows the as-cast structure of a Cu–20Nb–2Zr alloy revealed by SEM. Very fine eutectic-like structures are observable around the Nb dendrites beside the Nb dendritic structure. These structures were also observed in the as-cast alloys with Hf and Ta. The chemical compositions of those are determined by using EPMA and listed in Table 2. From the chemical compositions and the phase diagrams of Cu–Zr\textsuperscript{(31)}, Cu–Hf\textsuperscript{(32)} and Cu–Ta\textsuperscript{(31)(33)} systems, it is considered that the Cu–Cu$_3$Zr eutectic appeared in the Cu–20Nb–2Zr alloy and the Cu–Cu$_5$Hf eutectic in the Cu–20Nb–2Hf alloy though Cu–Nb–Zr and Cu–Nb–Hf phase diagrams are not known. In the case of the Ta-added alloy the fine eutectic-like structure around the Nb dendrites is considered to be the Cu–Ta eutectic since there are no intermetallic compound phases in the Cu–Ta phase diagram\textsuperscript{(31)(33)}. As for deformability of materials, it was not easy to draw the Cu–20Nb–2Zr and the Cu–20Nb–2Hf ingots into wires because of the presence of fine intermetallic compounds undeformable.

Fig. 8 Critical current density, Jc, of optimized in situ Cu–20Nb–Sn superconductors without additives and with Zr, Hf and Ta as a function of magnetic field, H, up to 12 T.

Fig. 9 SEM microstructures of the as-cast Cu–20Nb–2Zr ingot. Overall structure (a) and detail structure (b).
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at room temperature and the resultant work hardening. On the other hand, the Cu-20Nb-2Ta ingot was easily drawn into wires. Figure 10 shows the longitudinal structures of wire samples after optimum heat treatments. Very fine grains are observed between Nb3Sn filaments both in in situ Cu-20Nb-2Zr-Sn and Cu-20Nb-2Hf-Sn superconductors. Much larger particles were often observed and the alignment of Nb3Sn filaments was disturbed around them. On the contrary, no particles could be detected in in situ Cu-20Nb-2Ta-Sn superconductors as shown in Fig. 10.

Small amounts of Zr and Hf exist in the Cu matrix and the Nb dendrites as shown in Table 2, which is thought to improve the superconducting properties. On the other hand, the degradation of the alignment of Nb3Sn filaments by the presence of intermetallic compounds implies the decrease in $J_c$. Therefore, additions of Zr and Hf affect a little the high-field properties of in situ Cu-20Nb-Sn superconductors. In the case of Ta additions, no Ta could be detected in the Nb dendrites, but it is located mainly in the Cu matrix and in the region of the eutectic-like structure around the Nb dendrites ($\sim 10 \mu m$), where Ta precipitates are small ($\sim 0.1 \mu m$). After wire-drawing, these precipitates are considered to become very thin and fine and, furthermore, to come into contact with Nb filaments whose thickness is several 10 nm. Thus, Ta might be expected to react with Nb and Nb3Sn filaments during the heat treatment, and this might be the reason why additions of Ta improved $J_c$ in high magnetic field region in the present study.

Furthermore, $J_c$ measurements were carried out up to 15 T using a 16.5 T superconducting magnet on the optimized in situ Cu-20Nb-Sn superconductors without additives and with Zr, Hf and Ta, and the results are shown in Fig. 11. Addition of Ta is most effective for improving the high-field performance in this

![Fig. 10 SEM microstructures on the longitudinal section of optimized in situ Cu-20Nb-Sn superconductors with Zr(a), Hf(b) and Ta(c).](image)

![Fig. 11 High-field performance of optimized in situ Cu-20Nb-Sn superconductors without additives and with Zr, Hf and Ta up to 15 T.](image)
study. Addition of Zr improves $J_c$ slightly in a high field region and that of Hf does little.

Figure 12 shows the Kramer's plot using $J_c$ values in Fig. 11 for determining the upper critical field, $H_{c2}^*$. $H_{c2}^*$ values determined by the extrapolation of the $J_c^{1/2}H^{1/4}$ vs $H$ curves are 15.4, 16.8, 15.9 and 17.5 T for the optimized in situ Cu–20Nb–Sn superconductors without additives and with 2Zr, 2Hf and 2Ta, respectively. Thus, additions of these metals are said to improve $H_{c2}^*$, and the most effective one is Ta. Results of the bronze processed Nb$_3$Sn wires with Ta by Suenaga et al.\(^{(11)(17)}\) and in situ Nb$_3$Sn superconductors with Ta\(^{(10)(20)(21)}\) indicate that the enhancement of $H_{c2}^*$ is due to the substitution of Ta atoms for Nb sites in the Nb$_3$Sn compound. Therefore, it might be thought that Ta reacted with Nb and Nb$_3$Sn filaments during the heat treatment, as mentioned above, although Ta was not detected in the Nb dendrite after melting. Thus, it might be considered that the improvement of $J_c$ of in situ Cu–20Nb–2Ta–Sn superconductors in high field regions is due to the enhancement of $H_{c2}^*$. Finally, $J_c$ at 15 T of in situ Cu–20Nb–2Ta–Sn superconductors is $4.5 \times 10^7$ A/m$^2$, which is about 5 times as large as that of in situ Cu–20Nb–Sn superconductors without additives.

IV. Conclusion

The improvements of high-field properties of in situ Nb$_3$Sn superconductors were attempted by additions of 2%Zr, 2%Hf and 2%Ta to the Cu–20 mass%Nb melts.

Fine eutectic-like structures were observed in the as-cast materials with these additives, causing some difficulties in drawing the ingots into wires especially in the case of additions of Zr and Hf which produced the intermetallic compounds. Additions of Zr and Hf improved $J_c$ a little in the high field region and $H_{c2}^*$ slightly. On the other hand, addition of Ta improved markedly the high-field performance of in situ Cu–20Nb–Sn superconductors in spite of the fact that Ta was not located in the Nb dendrite. $J_c$ at 12 T of $(1-2) \times 10^8$ A/m$^2$ and $H_{c2}^*$ of 17.5 T were obtained on in situ Cu–20Nb–Sn superconductors by addition of Ta and were the highest superconducting properties in the present study.

Acknowledgements

The authors wish to thank Professors Y. Muto and Y. Nakagawa, Dr. K. Noto and the staffs of High Field Laboratory for Superconducting Materials at RISOM for their aid in use of the superconducting magnets and a water-cooled Bitter type magnet. Support of this work by the Grant-in-Aid for Fusion Research from the Ministry of Education, Science and Culture of Japan is gratefully acknowledged.

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