Investigation of the Cu based binary alloys and the internal matrix reinforcement bronze processed Nb$_3$Sn wires

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Abstract. Mechanical strength improvement on Nb$_3$Sn wire is the most important research subject to realize high field magnet applications operated under higher electromagnetic force environment. Recently, we approached to the internal matrix reinforcement technique due to the solid solution mechanism using ternary bronze alloy matrix on the bronze processed Nb$_3$Sn wire. In this study, the effect of the solute element on the mechanical property of the matrix after Nb$_3$Sn synthesis heat treatment was evaluated. Several Cu based binary alloys were casted, and these alloys were sintered in order to demonstrate the matrix after Nb$_3$Sn synthesis. We confirmed that the both 0.2% proof stress and ultimate tensile stress of the Cu-In alloy was higher than those of the pure Cu and Cu-Zn alloy. The mechanical strength improvement due to the internal matrix reinforcement using Cu-Sn-In ternary alloy matrix was caused by (Cu, In) solid solution formation. The comparisons of mechanical property between several Cu alloys were also investigated for the further mechanical strength improvement.

1. Introduction

The mechanical strain sensitivity of critical current density ($J_c$) property in Nb$_3$Sn wire is essentially higher than that of other A15 superconducting wires. Therefore, mechanical strength improvement on Nb$_3$Sn wire is the most important research subject to realize high field magnet systems operated under higher electromagnetic force environment. Recently, we approached to the internal matrix reinforcement technique due to the solid solution mechanism using ternary bronze alloy matrix on the bronze processed Nb$_3$Sn wire. In this technique, the matrix after the Nb$_3$Sn phase is formed is strengthened using a metallurgical solid solution strengthening mechanism, and the Nb$_3$Sn phase is mechanically protected by the strengthened matrix. This technique seemed to become simpler compared with the other high strength processes, and also realize the mechanical strength improvement without the decrease of over-all $J_c$ (engineering $J_c$) property. We fabricated the Nb$_3$Sn precursor wires using Cu-Sn-Zn and Cu-Sn-In ternary alloys matrices [1, 2].

The comparisons of the critical transport current ($I_c$) dependence as a function of the axial tensile stress on the internal matrix reinforced Nb$_3$Sn multifilamentary wires using Cu-Sn-Zn and Cu-Sn-In...
ternary alloy matrices is shown in figure 1 [2]. We confirmed that the peak stress obtained to the maximum $I_c$ value on the Nb$_3$Sn wire using Cu-Sn-Zn and Cu-Sn-In alloy matrices were shifted to higher tensile stress compared with the conventional Nb$_3$Sn wire. Furthermore, we also found that Cu-Sn-Zn and Cu-Sn-In ternary alloy matrices transformed to the (Cu, Zn) and (Cu, In) solid solution phase after Nb$_3$Sn synthesis heat treatment using the Micro-focused XRD analysis [1, 2]. These suggested that the peak tensile stress shifting was caused by these high mechanical strength (Cu, Zn) and (Cu, In) solid solution transformations after Nb$_3$Sn synthesis heat treatment.

Here, it should be noted that the Cu-Sn-In ternary alloy matrix sample showed a higher peak stress than the Cu-Sn-Zn ternary alloy matrix sample shown in Fig. 1. This mentioned that the degree of mechanical strength improvement by the solid solution formation depended on the solute elements in the ternary bronze alloy. We thought that the influence of the solute element in the ternary alloy matrix was one of the important factor for further mechanical strength improvement due to the internal matrix reinforcement on the bronze processed Nb$_3$Sn wire.

In this study, several Cu based binary alloys to demonstrate the in-situ state of the internal matrix after Nb$_3$Sn synthesis heat treatment were casted, and uniaxial tensile testing at room temperature were performed. Based on the tensile testing at room temperature, the effect of the solute element on the mechanical property of the internal matrix after Nb$_3$Sn synthesis heat treatment was investigated.

### 2. Sample preparation and experiments

In this study, the various Cu based binary alloys such as Cu-Sn, Cu-Zn, Cu-In and Cu-Ti were made from metal Cu (> 99.96 %), Sn (> 99.9 %), Zn (> 99.95 %), In (> 99.99 %) and Ti (> 99.43 %). These Cu based binary alloys were casted by the unidirectional melt-solidification process in Osaka Alloying Works Co., Ltd [3]. The binary alloy ingot size was obtained 80 mm in a diameter and 150 mm in a length. Figure 2 shows that the photograph of the melt-solidification operation and schematic illustration in the unidirectional melt-solidification process. In this process, a high-temperature

| Cu-X alloy | The composition of the solute element (mass%) |
|------------|---------------------------------------------|
| Cu-Sn      | 0.5 / 1.0 / 3.0                             |
| Cu-Zn      | 1.0 / 5.0 / 10.0                            |
| Cu-In      | 0.5 / 1.0 / 3.0 / 5.0                        |
| Cu-Ti      | 0.5 / 1.0 / 2.0                             |
Graphite crucible heated by a high-frequency coil is directly and rapidly cooled with water. The oxidation of the ingot is avoided as much as possible because the molten metal is not directly exposed to the air. Furthermore, the graphite crucible is moved at a constant speed and the molten metal is solidified unidirectionally by the direct water-cooling, thereby, the metal ingot made by this process obtains a uniform microstructure longitudinally. This unique process is so-called the "MIZUTA method" from the name of the principle inventor in Osaka Alloying Works Co., Ltd, and also usually fabricate and supply the high quality bronze alloy ingot for the commercial bronze processed Nb₃Sn wire in worldwide.

After the casting of various Cu based binary alloys, these alloys were sintered at 600 °C for 200 h in order to carry out the microstructure homogenizing and demonstrate the matrix after Nb₃Sn phase formation. Table 1 indicates that the nominal mass% composition of the several Cu based binary alloys in this study. In each Cu based alloy, three kinds of solute element mass% compositions were prepared. Any solute element composition is within the solid solubility limit on the binary equilibrium diagram. A part of the ingot was cut out in the radial direction, and a bar-shaped standard test piece of tensile testing was deformed from the center region. The bar-shaped standard test piece were prepared in accordance with the Proportion No. 14 of the Japan Industry Standard (JIS). The shape of the standard test piece was obtained to 7 mm in a diameter and 50 mm in a gauge length. The tensile testing was performed at room temperature. The tensile speed was fixed to 0.5 mm/min. The number of tensile test pieces in each alloy was three or four, and the 0.2% proof stress, ultimate tensile stress, and elongation of each Cu based binary alloys were average values of three or four samples. The maximum tensile stress was defined as the fracture stress.

![Figure 2](image-url). The photograph of the melt-solidification operation and schematic illustration in the unidirectional melt-solidification process (MIZUTA Method).

3. Results and Discussions

3.1. The 0.2 proof stress, ultimate tensile strength, and elongation of each Cu based binary alloys

Figure 3 shows that the mass dependence of solute element in various mechanical properties of Cu based binary alloys. The 0.2% proof stress, the ultimate tensile stress and the tensile elongation are shown in figure 3 (a), (b) and (c), respectively. Basically, it is well known that the mechanical properties of the Cu based binary alloys are improved by the alloying with various solute elements. In this study, improvement of mechanical strength such as 0.2% proof stress and ultimate tensile stress on the Cu-based binary alloy was confirmed by alloying with solute elements such as Sn, Zn, In and Ti. We concluded that the improvement of the mechanical strain sensitivity on the critical current property
of the Nb$_3$Sn wire using the ternary alloy matrix shown in Figure 1 was caused by the improvement of the mechanical strength of the matrix material after the Nb$_3$Sn formation. However, we also found that there was a difference in the mechanical property improvement depending on the kinds of the solute elements.

In the cases of the Sn and In solute elements, the 0.2% proof stress and the ultimate tensile stress were improved with a small amount of solute elements, and also increased remarkably with the increasing of the amount of solute element. Furthermore, the tensile elongation did not decrease even if the alloying with Sn and In solute elements. These suggested that the both Sn and In elements was effective solute element for the solid solution strengthening of the Cu based binary alloys.

In the case of the Zn solute element, the 0.2% proof stress and ultimate tensile stress were also improved by the alloying with Zn. However, the degree of these mechanical properties was overwhelmingly smaller compared with the alloying with Sn and In elements. It mentioned that the In element was more effective solute element for the solid solution strengthening of the Cu based binary alloys.

Figure 3. The mass dependence of solute element in various mechanical properties of Cu based binary alloys.
alloy. The superiority of the Cu-Sn-In ternary alloy on the mechanical properties of the Nb$_3$Sn wire shown in Figure 1 is due to the In solute element which is effective element for solid solution strengthening in the Cu based binary alloy.

In the case of the Ti solute element, the 0.2% proof stress and ultimate tensile stress were also improved by the alloying with Ti. Furthermore, Ti element was significantly effective solute element to improve mechanical strength of the Cu based binary alloy compared with Sn, In and Zn solute elements. Ti element was taken into the Nb$_3$Sn phase and was known as an additional element for the $J_c$ improvement under high magnetic field [4]. However, the excessive amount of Ti element decreases superconducting property [5]. In the other words, the increase of Ti element to improve the mechanical strength of the matrix material after Nb$_3$Sn formation was not suitable method from the viewpoint of the $J_c$ property.

3.2 Consideration of solid solution strengthening mechanism in Cu based binary

Generally, the solid solution strengthening mechanism of Cu based alloys is understood by the following as the strain field due to the difference in atomic size and the rigidity contributions. In the 1950s, it was experimentally shown that the 1.0% proof stress of metal copper was improved by alloying with various solute metals, and the mechanical strength behavior was difference between various solute metals [6]. R. L. Fleischer reported that the correlation between the increase of yield stress and the solute element on the Cu based binary alloy shown in Figure. 4 from the estimated contributions of the rigidity and the strain due to the difference of the atomic size among the solute elements [7]. As also shown in Figure. 4, Sn and In elements are effective factor for the improvement of the yield stress compared with Zn and the other element.

These results and discussions were similar to the experimental facts in this study, and clarified that the In element is the most suitable solute element for increasing the mechanical strength of bronze processed Nb$_3$Sn wires by using a ternary alloy matrix. On the other hand, Sn element was expected to contribute to high mechanical strength of the matrix material after Nb$_3$Sn formation. The active Sn remaining into the matrix were also became the internal matrix reinforcement technique. However, there was the critical risk that $J_c$ property was reduced.

4. Conclusions

The internal matrix reinforcement using ternary bronze alloy matrix was a simple and easy method for the mechanical strength improvement of Nb$_3$Sn wire, and was caused due to the solid solution
strengthening mechanism by a solute element. From the mechanical strength evaluations of the various Cu based binary alloys to demonstrate the matrix after Nb₃Sn formation, the In element had proven to become more effective solute element for the internal matrix strengthening compared with the Zn element.

Acknowledgement
This research was carried out by the financial supports of the Fusion Engineering Research Project (UFFF036-1), NIFS General Collaborative Research (KECF022) in National Institute for Fusion Science (NIFS), and the Grant-in-Aid for Scientific Research, KAKENHI ((B) 16H04621) from the Japan Society for the promotion of Science (JSPS).

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