Abstract. The reactive diffusion between Ta and a bronze was experimentally examined using sandwich diffusion couples consisting of Ta and a Cu–9.3Sn–0.3Ti alloy. The diffusion couples were isothermally annealed at a temperature of \( T = 1053 \) K for various times up to \( t = 1200 \) h. During annealing, a layer of \( \text{Ta}_9\text{Sn} \) is formed at the interface in the diffusion couple. The mean thickness of the \( \text{Ta}_9\text{Sn} \) layer increases in proportion to a power function of the annealing time. The exponent of the power function is equal to unity at \( t < 167 \) h but smaller than 0.5 at \( t > 167 \) h. This means that the transition of rate-controlling process occurs at \( t = 167 \) h. For the reactive diffusion between Ta and the bronze at \( T = 1053 \) K, the growth of \( \text{Ta}_9\text{Sn} \) is controlled by the interface reaction at \( t < 167 \) h but by the volume and boundary diffusion at \( t > 167 \) h.

1. Introduction
In the electronics industry, a bronze method has been conveniently used to manufacture superconducting \( \text{Nb}_3\text{Sn} \) composite-wires with multifilamentary structure [1–12]. Here, \( \text{Nb}_3\text{Sn} \) is an intermetallic compound with the A–15 type crystal structure. In the bronze method, a ductile rod of Nb is embedded in a Cu–Sn alloy matrix and then extruded into a filament form. A bundle of filaments is inserted into a Ta tube covered with a Cu tube and then protruded in a wire. The resultant multifilamentary wire is annealed at an adequate temperature. Owing to reactive diffusion during annealing, a layer of \( \text{Nb}_3\text{Sn} \) is formed at the interface between the Cu–Sn alloy and Nb. The Cu–Sn alloy is called bronze, and thus this technique is denominated the bronze method. The growth behavior of the \( \text{Nb}_3\text{Sn} \) layer in the bronze method was investigated by many researchers [5–12]. However, monofilamentary and multifilamentary diffusion couples were adopted in most of the investigations. In such diffusion couples, interdiffusion takes place in rather complicated manners, and hence the \( \text{Nb}_3\text{Sn} \) layer with a uniform thickness cannot be formed easily. As a consequence, the filamentary diffusion couples are not appropriate to observe the growth behavior of the \( \text{Nb}_3\text{Sn} \) layer.

Instead of the filamentary diffusion couples, sandwich \((\text{Cu–Sn})/\text{Nb}/(\text{Cu–Sn})\) diffusion couples were used to study experimentally the growth behavior of the \( \text{Nb}_3\text{Sn} \) layer in the bronze method [13, 14]. In the sandwich diffusion couple, interdiffusion occurs along the direction perpendicular to the interface, and hence the \( \text{Nb}_3\text{Sn} \) layer with a rather uniform thickness is formed during the interdiffusion. In the experiment by Osamura et al. [13], sandwich diffusion couples were prepared from Nb and a binary Cu–Sn alloy containing 7.4 at% of Sn, and then isothermally annealed in the temperature range of \( T = 973–1073 \) K. Different sandwich diffusion couples were prepared from Nb
and a binary Cu–8.3Sn alloy and then isothermally annealed at \( T = 923–1053 \) K in a previous study [14]. To improve the superconducting properties of NbSn, a small amount of Ti is added into the Cu–Sn alloy. The influence of Ti on the growth of NbSn was experimentally studied by Osamura et al. at \( T = 973–1073 \) K using \((\text{Cu–7.5Sn–}1\text{Ti}/\text{Nb}/(\text{Cu–7.5Sn–}1\text{Ti}))\) diffusion couples [13]. The influence of Ti was also experimentally examined at \( T = 923–1053 \) K using sandwich diffusion couples consisting of Nb and a Cu–8.1Sn–0.3Ti alloy in a previous study [15]. According to these experiments [13, 15], the addition of Ti into the Cu–Sn alloy considerably accelerates the growth of NbSn at higher annealing temperatures but hardly at lower annealing temperatures.

Recently, Cu–Sn alloys with the \( \alpha + \beta \) two-phase microstructure are preferentially used to manufacture the superconducting NbSn composite-wire. Here, \( \alpha \) is the primary solid-solution phase of Cu with the face-centered cubic structure, and \( \beta \) is the intermediate phase with the body-centered cubic structure. Since the concentration of Sn is higher in the \( \beta \) phase than in the \( \alpha \) phase, the amount of Sn supplied to NbSn is greater for the Cu–Sn alloy with the \( \alpha + \beta \) two-phase microstructure than for that with the \( \alpha \) single-phase microstructure. Hence, the influence of the \( \beta \) phase on the growth of NbSn was experimentally examined at \( T = 923–1053 \) K using sandwich diffusion couples composed of Nb and a Cu–9.3Sn–0.3Ti alloy in a previous study [16]. In these experiments [13–16], the mean thickness of the NbSn layer is expressed as a power function of the annealing time, and the exponent of the power function is typically close to unity. This means that the growth of NbSn is predominantly controlled by the interface reaction.

In the bronze method, Ta is used as a barrier against the diffusion of Sn from the bronze to the Cu tube. However, Ta may be gradually consumed by the reactive diffusion with the bronze during annealing. Unfortunately, no reliable information is available for the consumption of Ta during annealing. In the present study, the kinetics of the reactive diffusion between Ta and a bronze with the \( \alpha + \beta \) two-phase microstructure was experimentally examined at \( T = 1053 \) K using sandwich diffusion couples consisting of Ta and a Cu–9.3Sn–0.3Ti alloy.

2. Experimental

Plate specimens with a dimension of \( 2 \text{ mm} \times 5 \text{ mm} \times 12 \text{ mm} \) were prepared by spark erosion from a hot-rolled rectangular ingot of a ternary Cu–9.3Sn–0.3Ti alloy in a manner similar to a previous study [16]. Parallel surfaces with an area of \( 5 \text{ mm} \times 12 \text{ mm} \) of each Cu–Sn–Ti plate specimen were mechanically polished on 120–800 emery papers. One of the polished parallel-surfaces was again mechanically polished on 1500–4000 emery papers, and then finished using diamond with a size of 1 \( \mu \)m. Pure Ta sheet specimens with a dimension of \( 0.1 \text{ mm} \times 5 \text{ mm} \times 12 \text{ mm} \) were degreased in acetone with an ultrasonic cleaner. After degreasing, a Ta sheet specimen was immediately sandwiched between the finished surfaces of two freshly prepared Cu–Sn–Ti plate specimens in ethanol by a technique adopted in a previous study [16]. Each sandwich couple was completely dried, and then isothermally heat-treated for diffusion bonding in an evacuated silica tube, followed by air-cooling. The diffusion bonding was carried out at a temperature of \( T = 1053 \) K for 24 h. The diffusion couples were separately encapsulated in evacuated silica capsules, and then isothermally annealed at \( T = 1053 \) K for various times up to 1176 h. Hereafter, the summation of the heat-treating and annealing times is merely called the annealing time \( t \). Cross-sections of the annealed diffusion couple were mechanically polished using 1500–4000 emery papers and diamond with a size of 1 \( \mu \)m, and then finished with an OP-S liquid by Struers Ltd. The microstructure of the cross-section was observed with a backscattered electron image (BEI) by scanning electron microscopy (SEM). The observation was also conducted by optical microscopy (OM). Concentration profiles of Cu, Sn, Ti and Ta for various phases on the cross-section were measured by electron probe microanalysis (EPMA).

3. Results and discussion

Under the present annealing conditions, a layer of TaSn with a uniform thickness is formed at the interface in the diffusion couple. Concentration profiles of the constituent components across the
Ta₉Sn layer and the α phase of the Cu–Sn–Ti alloy were determined by EPMA along the direction normal to the interface. A typical result for the diffusion couple annealed at $T = 1053$ K for $t = 1200$ h is shown in Fig. 1. In this figure, the ordinate and the abscissa show the mol fraction $y_i$ of component $i$ and the distance $x$, respectively, and open circles, squares, triangles and rhombuses indicate the values of $y_{Cu}$, $y_{Sn}$, $y_{Ti}$ and $y_{Ta}$, respectively. As can be seen, $y_{Cu}$ monotonically decreases from the α phase to Ta, and $y_{Ta}$ from Ta to the α phase. On the other hand, $y_{Sn}$ is similar in Ta₉Sn and the α phase. However, $y_{Ti}$ is negligible in Ta₉Sn and Ta. Such a result was observed for all the annealed diffusion couples.

The mean thickness $l$ of the Ta₉Sn layer is plotted against the annealing time $t$ as open circles in Fig. 2. In this figure, the ordinate and the abscissa show the logarithms of $l$ and $t$, respectively. As can be seen, the thickness $l$ monotonically increases with increasing annealing time $t$. The open circles for shorter annealing times are located well on a straight line, and those for longer annealing times lie well on another straight line. Hence, in each annealing time range, $l$ is expressed as a power function of $t$ by the following equation:

\[
l = k \left( \frac{t}{t_0} \right)^n.
\]

Here, $t_0$ is unit time, 1 s. It is adopted to make the argument $t/t_0$ of the power function dimensionless. The proportionality coefficient $k$ has the same dimension as the thickness $l$, but the exponent $n$ is dimensionless. From the open circles in Fig. 2, $k$ and $n$ were estimated by the least-squares method in each annealing time range. The estimated values are shown in Fig. 2. Using these values of $k$ and $n$, $l$ was calculated as a function of $t$ from equation (1). The results are indicated as two solid lines in Fig. 2. These two lines are intersected each other at $t = 167$ h. The exponent $n$ is equal to unity at $t < 167$ h but smaller than 0.5 at $t > 167$ h. When the interdiffusion across the Ta₉Sn layer is the rate-controlling process for the growth of Ta₉Sn and volume diffusion governs the interdiffusion, $n$ is equivalent to 0.5. If boundary diffusion contributes to the interdiffusion, however, $n$ becomes smaller than 0.5 [17]. On the other hand, $n$ is equal to unity for the growth of Ta₉Sn controlled by the interface reaction [18]. Consequently, the growth of Ta₉Sn is controlled by the interface reaction at $t < 167$ h but by the volume and boundary diffusion at $t > 167$ h. The corresponding result for Nb₃Sn at $T = 1053$ K in a previous study [16] is indicated as open squares in Fig. 2. As can be seen, $n$ is rather close to unity for Nb₃Sn. Therefore, the growth of Nb₃Sn is predominantly controlled by the interface reaction.
Figure 2. The thickness $l$ of Ta$_9$Sn versus the annealing time $t$ at $T = 1053$K shown as open circles. The corresponding result for Nb$_3$Sn at $T = 1053$ K in a previous study [16] is indicated as open squares.

However, the growth rate is one order of magnitude smaller for Ta$_9$Sn than for Nb$_3$Sn. This means that Ta works as an effective diffusion barrier in the bronze method.

4. Conclusions

The kinetics of the reactive diffusion between Ta and the Cu–9.3Sn–0.3Ti alloy was experimentally examined at a temperature of $T = 1053$ K. During isothermal annealing at $T = 1053$ K, Ta$_9$Sn is produced as a layer at the flat interface between Ta and the Cu–Sn–Ti alloy. The thickness $l$ of Ta$_9$Sn is proportional to a power function of the annealing time $t$. The exponent of the power function is equal to unity at $t < 167$ h but smaller than 0.5 at $t > 167$ h. Hence, the growth of Ta$_9$Sn is controlled by the interface reaction at $t < 167$ h but by the volume and boundary diffusion at $t > 167$ h.

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