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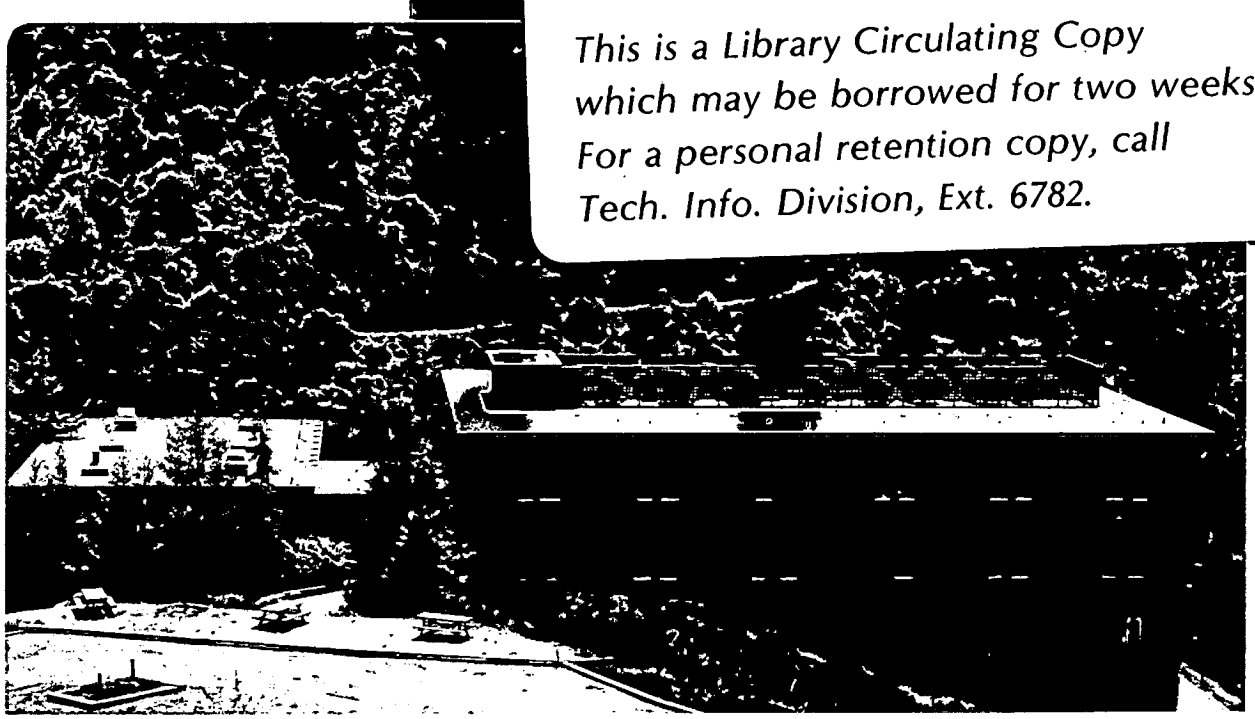

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DISCLAIMER

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INTRODUCTION AND SUMMARY

Prior work by Tachikawa and coworkers [1,2] has shown that the addition of magnesium to the bronze matrix prior to the formation of bronze-processed Nb_3Sn tape causes a significant increase in the critical superconducting current density at 6.5 tesla, and that this increase is associated with a decrease in the apparent A15 grain size. The present work was undertaken to determine whether a similar improvement in J_c would follow the addition of Mg to multifilamentary Nb_3Sn wires and to identify the microstructural and mechanistic sources of any beneficial effects. To accomplish this, multifilamentary wires were drawn in the laboratory. They contained 133 filaments of pure Nb embedded in bronze with various concentrations of Sn and Mg. Their critical current densities were measured as a function of bronze composition, heat treatment, and transverse magnetic field at 4.2K. The reacted A15 layers were subsequently examined using a variety of microscopic and microanalytic techniques. The work is still incomplete, but the results presented below seem sufficient to justify three major conclusions:

(1) Magnesium additions to the bronze increase the attainable critical current density in bronze-processed multifilamentary Nb_3Sn wire at all fields tested (8-15T). The increase is large enough to be of technological interest.

(2) The magnesium segregates almost completely to the Nb_3Sn layer during the reaction. Mg resides predominantly within the A15 matrix; it is not a strong surfactant in Nb_3Sn.

(3) The most obvious effect of the Mg addition is to retard grain coarsening during growth of the A15 layer, yielding a uniformly fine-grained product. This effect accounts for much (if not most) of the improvement in J_c. Preliminary experimental results also suggest that Mg decreases the minimum A15 grain size, and that it may also improve the Sn distribution within the reacted layer to establish a more uniformly stoichiometric phase. It is not clear what, if any, effect Mg has on the inherent superconducting properties of Nb_3Sn.

EXPERIMENTAL PROCEDURE

1. Wire Manufacture. The multifilamentary wires used in this research

were manufactured in the laboratory from pure starting materials. They differed in composition of the bronze (Table 1) which was varied to measure the influence of Mg at two Sn levels. The initial bronze ingots were melted in quartz tubes under argon and cast into rods. The rods were doubly swaged and homogenized, and were then machined to 10mm outer diameter and bored to form tubes of 5mm inner diameter. Pure Nb rods were inserted into the tubes and the composite was drawn into wire. The monofilament wires were bundled in groups of seven, enclosed in a tube of the same bronze composition, and redrawn. The seven-filament wires were then rebundled in groups of nineteen (133 filaments) inside bronze tubes of identical composition and drawn to a final diameter of 0.5 mm. During drawing the wires were annealed at 450°C for 40 minutes after approximately each 50-80% reduction in area. Sample cross-sections of two finished and partially reacted wires are shown in Fig. 1. The filaments are reasonably uniform, though those near the periphery of the wire are noticeably flattened. Small differences in the drawing properties of the wires and the manufacturing procedure caused the final filament size to vary from wire to wire. The compositions and characteristics of the wires are listed in Table 1, where the composition of the bronze is given in atomic percent (the balance is Cu), D is the effective diameter of the filaments (determined from the cross-sectional area of the filament) and R is the volumetric ratio of bronze to Nb.

TABLE 1: COMPOSITION AND FILAMENT SIZE

comp. (at.%)	D	R
6.7Sn	11.4	14
6.7Sn-0.09Mg	13.4	10
6.7Sn-0.6Mg	12.5	12
7.8Sn	8.3	27
7.8Sn-0.09Mg	12.1	12

2. Heat Treatment. After manufacture the wires were sectioned into segments approximately 10 cm. in length and heat treated in sealed quartz tubes under argon to form the A15 phase. The heat treatment temperatures were 650, 700, 730, 750 and 780°C, and were chosen to bracket the optimum reaction temperature of the Mg-free wire [3,4]. The heat treatment times were one to fourteen days. The progress of the reaction during heat treatment was monitored by sectioning the wires after selected reaction times, taking scanning electron micrographs and measuring the area of the reacted layer with an image processing microcomputer. The consistency of measurements taken from serial sections showed that the reaction was uniform along the wire length.

3. Measurement of the Critical Current Density. The critical current (I_c) of the wires was measured at 4.2K in transverse magnetic fields of 8-15T at the National Magnet Laboratory. The tests employed a four-point probe technique on specimens 30mm long. The critical current was defined to be that giving a potential difference of 1 microvolt between voltage taps placed 5mm apart. The critical current density (J_c) was determined by dividing the critical current by the measured area of A15 phase in the

4. Materials Characterization. The characterization of the A15 phase employed microstructural and microchemical analyses in addition to the overall stereological examination of the reacted layer described above. The grain size of Nb_3Sn was estimated from scanning electron fractographs of broken wire specimens (the A15 phase always fractured in an intergranular mode) and measured more precisely from transmission electron micrographs of thin foil samples prepared by ion milling. The composition within the A15 layer was studied by electron microprobe analysis, which readily reveals the Mg, by scanning transmission electron microscopy, which offers greater spatial resolution but a less sensitive analysis of Mg, and by high resolution scanning Auger analysis, which was used to assess the degree of segregation of Mg to the Nb_3Sn grain boundaries.

RESULTS AND DISCUSSION

The work planned for this research project is only partly complete. The results obtained to date include the following.

1. The Influence of Mg on Wire Drawing and Reaction Rate. The wires containing Mg-bronze were noticeably more difficult to draw, presumably because of solution hardening by the Mg. However, the change in drawing response was minor, and was accommodated by slight alterations in the wire-drawing technique and annealing schedule. The Mg-bronze wires tended to have larger filament sizes after the completion of drawing to 0.5mm final diameter (Table 1), but it is not yet clear whether this difference reflects changes in the drawing properties of the wire or minor variations in the manufacturing procedure. The rate of the reaction forming A15 at the Nb-bronze interface also varied from wire to wire. However, the reaction rate depends on the filament size and shape as well as on the composition and temperature. Since the variation in reaction rate at given temperature was not large and the filament geometry was not constant, it is only possible to conclude that the Mg addition did not dramatically change the reaction rate.

2. The Influence of Mg on the Critical Current Density. The addition of Mg to the bronze-processed wire increased its maximum critical current density over the range 8-15T for all values of the reaction temperature. The increment in J_c increased with the magnesium concentration. Samples of the results are presented in Figs. 2 and 3. Fig. 2 shows the critical current characteristic, $J_c(H)$, for wires heat treated to essentially complete reaction (4 days) at 730°C. The increase in J_c following an addition of 0.6Mg to the bronze is much greater than that caused by the addition of 1.1Sn, and persists over the tested range of applied fields. Fig. 3 compares the J_c of the 6.7Sn-0.6Mg wire at 10T to those of the 6.7Sn and 7.8Sn wires in the most fully reacted condition for different aging temperatures. The data agrees with that of Tachikawa and coworkers [1,2] in showing an optimum temperature for the Mg effect, but suggests that the optimum temperature is lower for the multifilamentary wires (700-730°C) than it is for the tapes they studied (800°C). In fact, the Mg effect largely disappears when the aging temperature is raised to 780°C. The net improvement due to Mg is substantial. The addition of 0.6 Mg to the 6.7Sn bronze increases the maximum J_c by nearly 100%. The resulting current density is 60% higher than the maximum achieved in 7.8Sn.

3. The Distribution of Mg in the Reacted Wire. The available evidence shows that Mg segregates strongly to the A15 layer during the reaction, and suggests that it incorporates primarily in the bulk Nb_3Sn rather than in the grain boundaries. Fig. 4 presents data taken from electron microprobe studies of the reacted layer and gives the distribution of Mg in fully reacted 6.7Sn-0.6Mg aged at 750°C. Essentially all of the Mg has accumulated in the reacted layer. The measured Mg concentration profile through the reacted layer is nearly flat at a concentration of slightly more than 3%. The location of the Mg within the reacted layer was studied by high resolution Auger spectroscopy on fresh fracture surfaces, which reveal the Nb_3Sn grain boundaries, and on sputtered surfaces which represent the grain interior. The quantitative results of the Auger analysis are unreliable, since Mg does not have strong Auger peaks. However, the qualitative results are reasonably clear. No strong Mg peaks arise from fresh fracture surfaces and the peak height does not change consistently when the surface is sputtered away from the grain boundary; hence Mg does not segregate strongly to the grain boundary.

4. The Influence of Mg on the Grain Size. Previous work [3,4] on the grain size of reacted layers of Nb_3Sn has shown that the layer is divisible into three morphologically distinct regions: an inner layer of columnar grains growing out from the Nb interface, an intermediate layer of fine-grained material, and an outer layer of large, coarsened grains. It is hence important to consider the influence of Mg on both the minimum grain size and on the distribution of grain size. The grain size is best measured from TEM micrographs of the reacted layer. These measurements are in progress, and the preliminary results suggest that Mg does induce a consistent decrease in the minimum grain size, However, the most striking effect of the Mg addition is on the grain size distribution. As illustrated in Fig. 5, for example, the addition of Mg suppresses the growth of large grains in the periphery of the reacted layer, giving a much more uniform and fine-grained structure. This effect is most pronounced at intermediate reaction temperatures. At low temperature even the Mg-free material is reasonably fine-grained, while at high temperature even the Mg-bearing material coarsens. It is likely that the suppression of grain coarsening is responsible for much of the improvement in J_c. In a Mg-free wire aged at intermediate temperature, 30-50% of the total volume of the A15 phase is coarse-grained. Since the critical current density is a strong inverse function of the grain size, the grain refinement of this material is expected to yield a substantial improvement in J_c.

5. The Influence of Mg on the Composition of the Reacted Layer. In previous work [3,4] scanning transmission electron microscopy was used to study the concentration profile of Sn within Nb_3Sn reacted layers. The results showed a gradient of Sn from a Sn-rich value at the bronze interface to a Sn-poor value at the Nb interface, with a band of nearly stoichiometric material near the center of the reacted layer. The initial results of similar studies of Mg-bearing material are presented in Fig. 6. The STEM analyses suggest that the Sn profile within the Mg-bearing layer is very flat relative to that in Mg-free wire [3,4]. Quantitative STEM analysis is difficult, and the results presented in Fig. 6 must be confirmed by further work before they can be accepted as true.

Nonetheless, the data taken to date indicate that Mg improves the composition as well as the grain size of the reacted layer.

CONCLUSION

The research reported here confirms the original work of Tachikawa and coworkers on the beneficial influence of Mg on the critical current density of bronze-processed Nb_3Sn. The results show that Mg may be used to improve J_c in multifilamentary wire, and that the increase is large enough (60-100%) to be technologically interesting. Chemical analysis reveals that the Mg segregates to the reacted layer, and resides principally in the bulk Nb_3Sn. The microstructural analyses suggest that its principal effect is to suppress coarsening of the Nb_3Sn grains and establish a uniformly fine-grained layer. Preliminary data also suggests that Mg decreases the minimum Nb_3Sn grain size and improves the overall stoichiometry of the reacted layer.

It should finally be recalled that, while the results obtained in this work are technologically interesting, the samples used had very high bronze to Nb ratios (R). Since the increase in J_c apparently depends on the concentration of Mg in the reacted layer, and since virtually all the Mg accumulates there, it may prove difficult to achieve comparable results at lower R values without substantially raising the Mg content of the bronze, or changing to an "external bronze" process. This question is under investigation.

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REFERENCES

1. K. Togano, T. Asano and K. Tachikawa, J. Less-Common Metals, 68, 15 (1979).

2. K. Tachikawa, Adv. Cryo. Eng., 26, 378 (1980).

3. M. Hong, I. W. Wu, J. W. Morris, Jr., W. V. Hassenzahl, W. Gilbert, and C. E. Taylor, Adv. Cryo. Eng., 28, 435 (1981).

4. I. W. Wu, M. Hong, W. V. Hassenzahl and J. W. Morris, Jr., Proc., ICEC9-ICMC, Kobe, Japan, 1982, Butterworth & Co., England, p. 388 (1982).

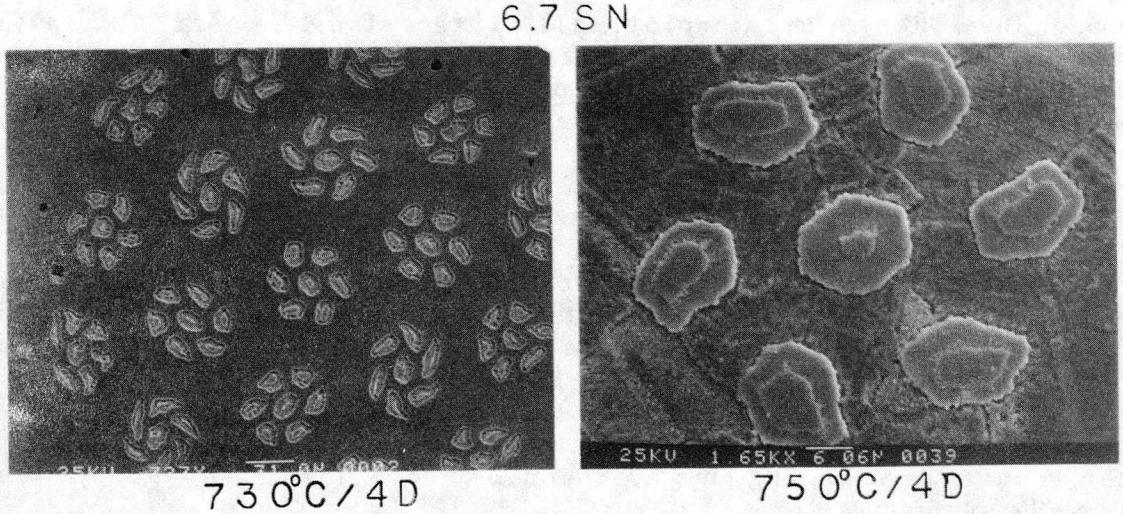

Figure 1. Sections of two partly-reacted wires. XBB 820-10448

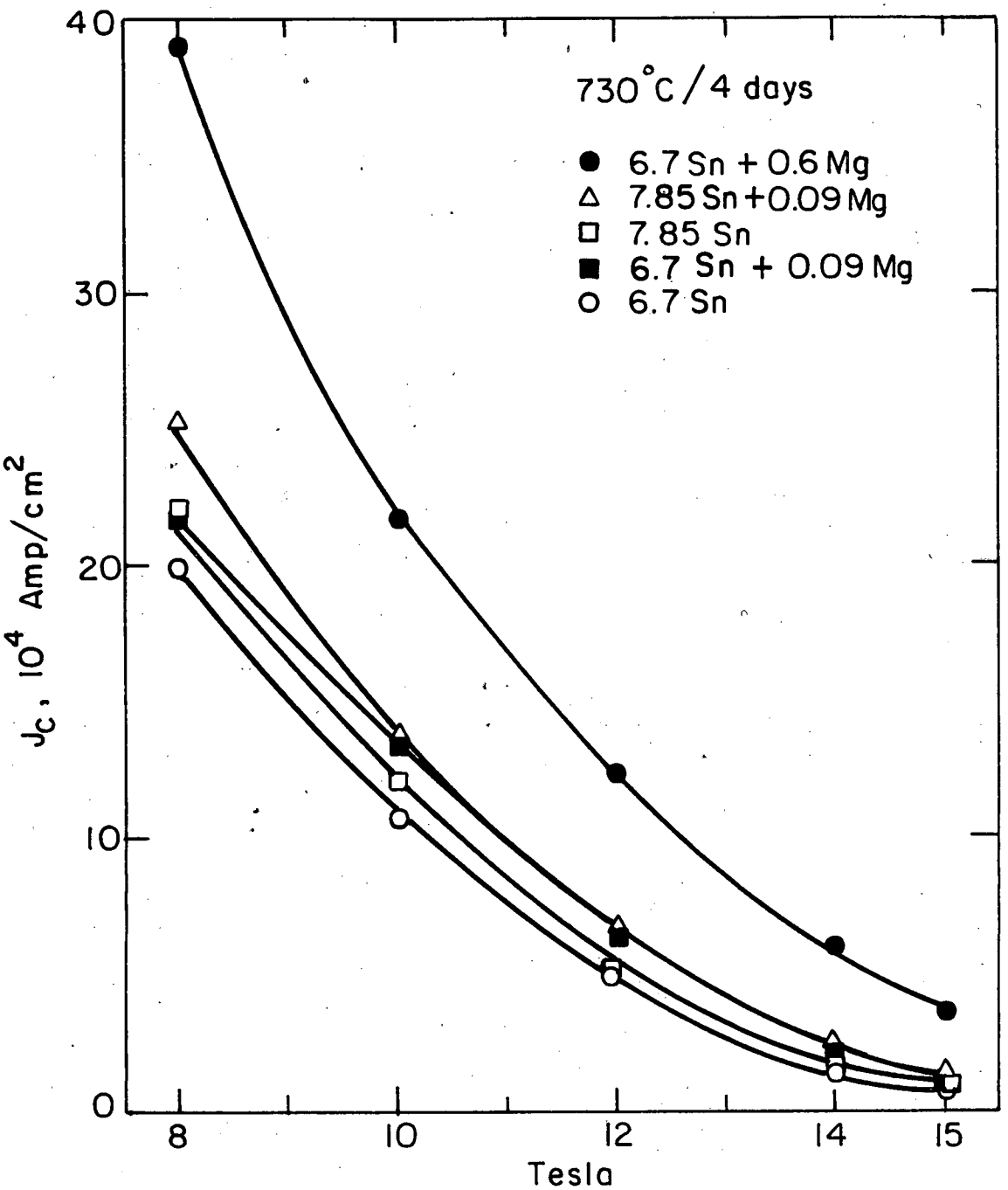

Figure 2. $J_c(H)$ for wires reacted at 730°C.

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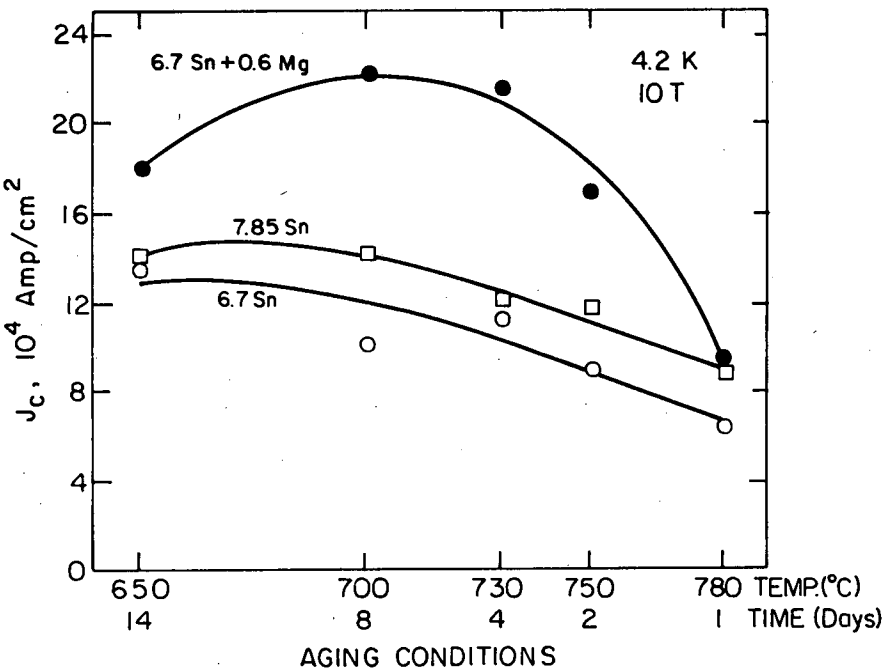


Figure 3.

J_c at 10T vs. composition and aging temperature.

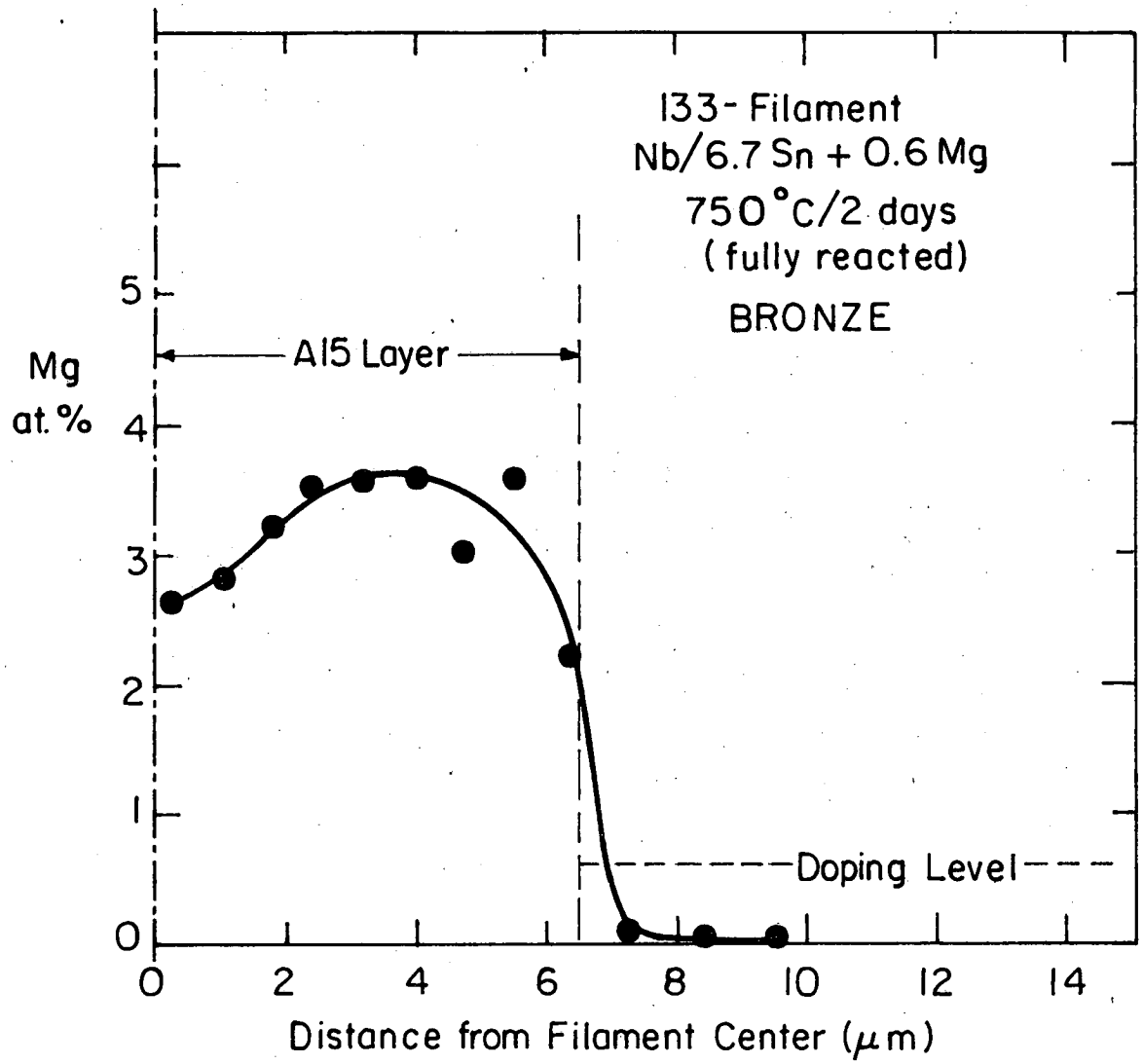
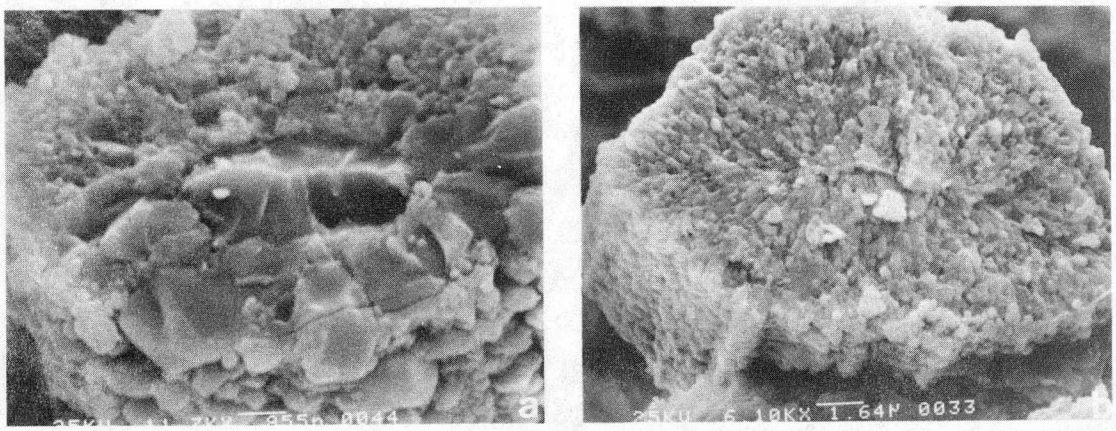


Figure 4. Electron microprobe composition profile for Mg.

XBL 8211-6825

750°C for 1 day



1 µm

7.85 % Sn

1 µm

7.85 % Sn + 0.085 % Mg

Figure 5. Scanning electron fractographs showing the Mg effect on the distribution of grain size.

XBB 820-9999

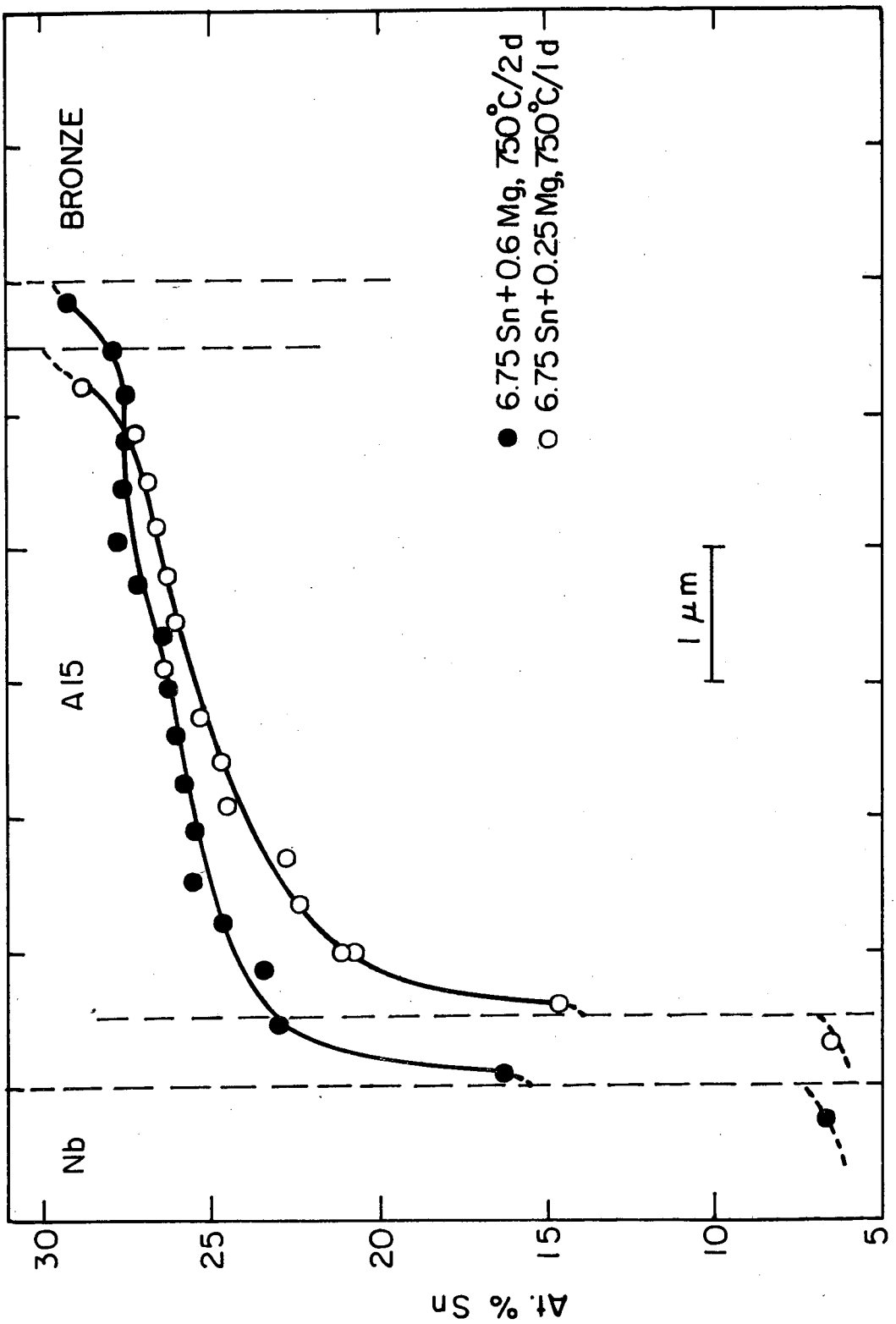


Figure 6. STEM/EDAX composition profiles for Sn within the reacted layer.

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