Title

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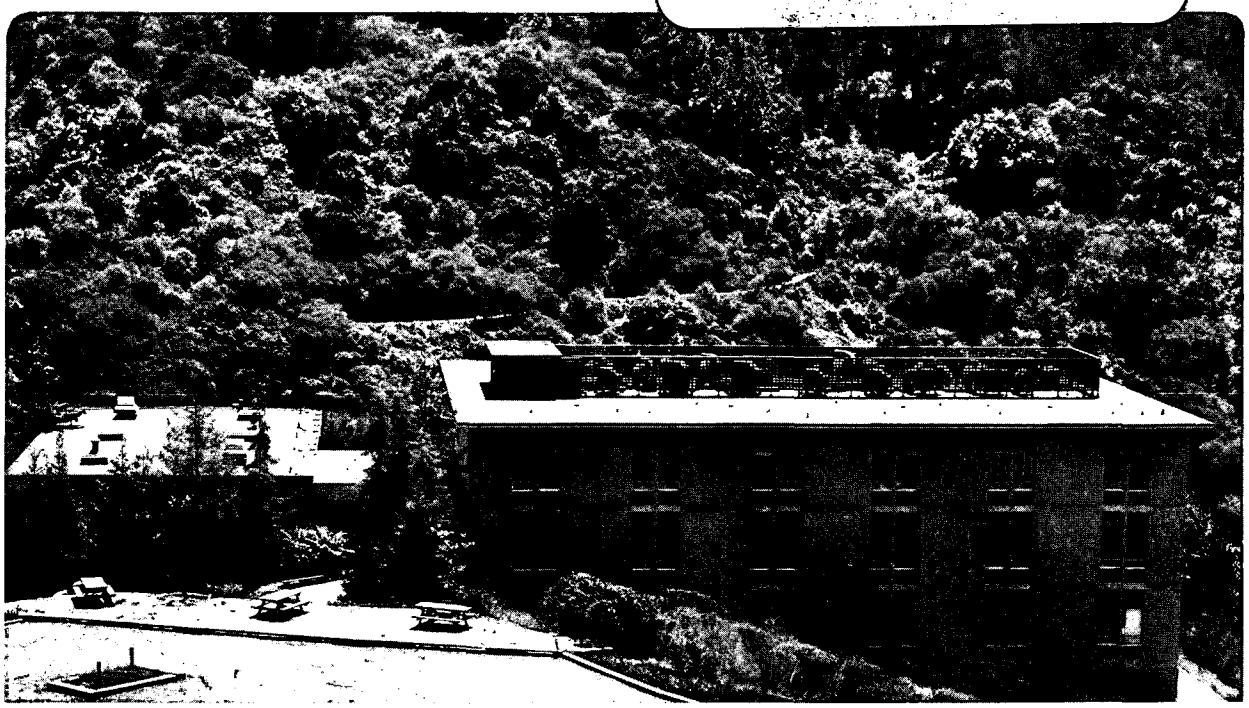

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THE CRITICAL CURRENT DENSITY AND MICROSTRUCTURAL STATE OF AN INTERNAL TIN MULTIFILAMENTARY SUPERCONDUCTING WIRE

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ABSTRACT

The critical current density (J_c) of internal tin wires is increased when low-temperature diffusion heat treatments are performed prior to a high temperature reaction. To determine the variation of J_c with pre-reaction heat treatments a copper-stabilized IGC internal tin wire with an outside diameter of 0.267mm was studied. The wire has 2 to 2.5μm diameter filaments, and within the Ta barrier, the area ratio of the copper matrix and Sn core to Nb is about 2.2. Due to the character of the Cu-Sn phase diagram, heat treatments at a series of temperatures below the Nb_3Sn reaction temperature affect the local Sn concentration in the matrix about the Nb filaments. The variation in J_c resulting from these heat treatments is a consequence of the microstructural state of the conductor and the morphology of the Nb_3Sn layer produced. The results of this work show that the internal tin and bronze-processed wires have different $J_c(H)$ characteristics. The two processes have comparable critical currents at high fields, suggesting the same H_{c2}, while at low fields the internal tin wire is superior, suggesting a better grain morphology.

INTRODUCTION AND SUMMARY

There are two methods for increasing the critical current of a conductor under specified operating conditions of temperature and magnetic field. One is to increase the amount of Nb_3Sn in the wire cross section. The second is to improve the quality of the Nb_3Sn layer produced. Various fabrication techniques have been developed to increase the amount of Nb_3Sn in a conductor [1]. One technique, the high tin or internal tin process [2], starts with a Cu-Nb-Sn composite that is deformed to final size and heat treated. Since copper and tin (or Sn-Cu alloys) are introduced in near elemental forms that are ductile and co-deform well, more tin can be added than a homogeneous solution of tin in copper would permit. This additional tin allows complete conversion of Nb to Nb_3Sn to occur at a lower matrix (Cu+Sn) to niobium ratio. As a result, it is possible to introduce more Nb_3Sn into the cross section and thereby increase the critical current.

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The Nb_3Sn that is included in the cross section of an internal tin wire also appears to have an exceptionally high critical current density, J_c, in the 10-12T range, which further enhances the overall critical current (Fig.1) [3,4,5]. The high critical current density in this range suggests the presence of a superior A15 morphology to that produced by the bronze process. However, the maximum critical current has been obtained in previous work only after elaborate multi-step heat treatments [4] that include long-term aging at relatively low temperatures. Simpler heat treatments have been studied on similar wires [5,6], but these result in some loss of critical current. The high critical current shown in Fig. 1 of the internal tin conductor agrees favorably with previous work on a similar material which had no Ta barrier or Cu stabilizer [4].

The present work was undertaken to confirm the high critical current density of internal tin wire that is properly heat treated, to investigate the multi-step heat treatment used and to simplify it if possible, and to clarify the microstructural source of the high critical current density. The principal results of the work confirm the exceptional properties of the A15 phase, show that those properties can be realized without extensive low-temperature heat treatment, and suggest that the microstructural source of the good properties is the fine, uniform A15 grain size.

EXPERIMENTAL PROCEDURE

An internal tin wire which is manufactured by Intermagnetic General Corporation was used in this investigation [7]. Most of the Cu-Sn diffusion observations were performed on a 61 sub-element wire. Intermetallic phase determination was done with a scanning electron microscope equipped with a KEVEX energy dispersive x-ray analyser (SEM/EDS).

Critical current measurements were done on an individual sub-element that had been deformed to a diameter of 0.267mm, so that its internal dimensions and filament size were comparable to the large conductor. The sub-element had a Ta barrier and Cu stabilizer which accounted for 15% and 60% of the cross sectional area of the wire respectively. The area of the active core inside the Ta diffusion barrier ($1.36 \times 10^{-2} mm^2$) was used to determine the critical current density. All critical current measurements were done in a transverse magnetic field with the samples supported such that the Lorentz force produced no bending of the sample. Strains induced by the differential thermal contraction of the sample and probe were minimized by selection of appropriate probe materials 8]. The standard four point probe technique was used on 30mm samples that had been cut from longer sections. The voltage leads were placed 5mm apart in the center of the sample. A 0.1μV/mm criterion was used in most of this work. In cases where different criteria were used the sensitivity is indicated.

The wires were cut into 150mm lengths for heat treatment. The ends of the wires were sealed by melting until a small alloy bead was created. At least 20mm from each end is discarded prior to I_c measurements. The low temperature heat treatments used to homogenize the tin are given in the table below.

HEAT TREATMENT NOTATION

	A	1A	CA
HEAT TREATMENT	200°C/200h + 375°C/33h + 580°C/218h	200°C/120h + 380°C/24h + 580°C/233h	---------- 380°C/48h + 580°C/233h

RESULTS AND DISCUSSION

Influence of Pre-Reaction Heat Treatments on Microstructure

The IGC three-step heat treatment (A), 200°C for 200h, 375°C for 33h followed by 580°C for 216h was taken as the reference heat treatment for a metallurgical study of the wires, since measurements showed it produced a 15-20% better J_c at 10T for a 700°C final treatment temperature than wires heat treated directly at 650 and 700°C. A better understanding of the overall microstructure in the conductor that results from the Cu-Sn inter-diffusion led to shortened heat treatments, that retained the peak J_c.

The 200°C heat treatment produces two intermetallic layers around the tin core (fig. 2a). Each layer is about 5-6μm thick. Before the reaction the copper layer between the tin center and first row of niobium filaments is about 10μm. After the reaction a 5μm layer of unreacted copper remains, the tin has not diffused to the niobium filaments. The two intermetallic layers have been tentatively identified as the $\varepsilon(Cu_3Sn)$ and $\eta(Cu_6Sn_5)$ phases by SEM/EDS. It is assumed that the compositions observed correspond to the equilibrium phases. X-ray diffraction analyses are in progress to determine the crystal structure of each phase.

The second step, 375°C for 33h, produces an all ε core. The ε-Cu interface is 10-15μm or 5-10 rows into the filaments (Fig. 2b). Porosity is observed at this stage of the diffusion heat treatment. Most of the porosity is at the periphery of the core and in the filament region. The pore size in the filament region was kept small apparently due to the growth restraint presented by the filament array. This porosity could originate from two sources, a volume difference between the initial phases (Cu and Sn) and final phase(ε), and/or the Kirkendall effect.

The temperature of the third step is 580°C. After 48h at this temperature α phase (Cu-Sn solid solution) is produced throughout the filament region with a high tin phase(s) in the core (Fig. 2c). There also appear to be isolated islands of a high tin phase in the filament region. The composition of the high tin region corresponds to the γ phase, but the microstructure of these regions appears two phase. The

lath-like appearance of the microstructure may be a result of a phase transformation on cooling in which the γ phase decomposes to the α and δ phases. The porosity which was in the core region and first few rows of filaments has now moved to the outer filaments leaving the core region void free (Fig. 2c).

When the A treatment is completed after 218h at 580°C, the high tin phase disappears leaving only the α phase. A ring of porosity through the filament region develops in some of the sub-elements but not in all. This porosity could have a strong effect on the strain sensitivity of the conductor. A deep etched cross section of the wire seen in Fig. 3 reveals the extent of the Nb_3Sn formation. The filaments near the core are close to complete reaction while those at the sub-element periphery are not. Figure 3 also shows that the filaments near the core are somewhat flattened. This flattening occurred during wire fabrication.

A different overall wire microstructure is obtained when the conductor is taken directly to the reaction temperature. Figure 4 shows a wire that has been heat treated 2 days at 700°C. Substantial porosity is seen in the core regions but not in the filaments. The porosity is present as early as 3h into the heat treatment when a high-tin phase is still observed in the core.

Critical Current and Microstructure

The high critical current of the internal tin conductor has two origins. The first is the increased amount of Nb_3Sn in the wire cross section over other conductors. The second is the superior morphology of the A15 produced. Figure 1 shows that the Nb_3Sn in the internal tin process carries substantially more current in the 10-12T range than the Nb_3Sn produced in a bronze-processed conductor. In an attempt to determine the source of this J_c improvement the A15 grain structure of the internal tin wire was characterized.

Prior work on a bronze-processed wire showed that the Nb_3Sn layer could be subdivided into three distinct layers [9]. Columnar grains appear at the Nb-A15 interface while coarsened grains appear near the bronze. Between these two regions is a layer of fine equiaxed grains. The transmission electron microscopic (TEM) study of the internal tin wire that is in progress reveals that the A15 layer produced is fine grained and uniform. The wire seems to have few columnar grains and few coarse grains. The aspect ratio of the few columnar grains observed is about 2, which is substantially less than the value of 5 reported for the bronze process. The average A15 grain size is at least as small as that reported for the equiaxed grains in the bronze process (~70nm, 700°C aging temperature) [9]. TEM observations by Scanlan, et al. [10] give a range of Nb_3Sn grain sizes for a 700°C aging temperature (100-150nm).

The results shown in Figs. 1 and 5 agree favorably with previous results by Schwall, et al. However, the $J_c(H)$ characteristic for their conductor appears to be steeper than those produced in this work. At present the more rapid drop of the $J_c(H)$ curves is not clear, e.g. testing method differences or intrinsic conductor properties. The

stress states which develop in the conductor for different heat treatments and wire configurations are currently being studied. It is hoped that a better understanding of the high field properties of the wire will result.

The critical current density was always higher in samples that received a low-temperature diffusion heat treatment prior to reaction (Figs. 5,6). Figure 5 presents the results (10T,4.2K) for pre-heat treatment 1A along with data for wires that received no low-temperature heat treatment. Pre-heat treatment 1A reached peak J_c of 1620 A/mm^2 after one day at 700°C. The wires taken directly to the reaction temperature (650, 700, and 730°C) all had lower peak critical current densities. The relatively low temperature, 650°C for 6 days treatment, produced the best J_c of the three, 1410 A/mm^2. The critical current density of treatments 650°C/6 days and 700°C/4 days are 15% and 20% lower than treatment 1A + 700°C/1 day, respectively. Wires that received pre-reaction heat treatments also had a less rapid degradation in J_c with overaging.

The wires taken directly to high temperature also had a greater scatter in J_c. This scatter implies non-uniformity along the length of the wire. Figure 4 shows the microstructure in the bronze resulting from a high-temperature treatment. Near the inner ring of Nb_3Sn filaments large voids have developed. As mentioned earlier their presence as early as 3h into the heat treatment would tend to inhibit tin diffusion outward. Niobium filaments adjacent to regions of the core without viods react quickly since radial diffusion of tin into the copper is unrestricted while the niobium filaments adjacent to voids require longer range axial diffusion of tin before the reaction can commence. This inhomogeneous distribution of tin causes the A15 morphology to vary along the length of the filaments.

The highest $J_c(H)$ characteristics were obtained using pre-heat treatment 1A and CA followed by 700°C for one day (Fig. 5). Also plotted in Fig. 5 is treatment 700°C/4 days. Pre-heat treatments 1A and CA followed with 700°C/1day produce the same J_c at low fields with only a slight difference at high fields (CA higher). These results show that a long 200°C treatment is not required. The 380°C for 2 days produces an equivalent microstructure to that seen in Fig. 2b (200°C/200h+375°C/33h).

CONCLUSIONS

1. The internal tin process yields a very high critical current in magnetic fields in the range of 10-12T. The high critical current reflects both the increased amount of Nb_3Sn in the wire cross section and an improved critical current density within the A15.

2. The improved critical current density is associated with a more uniform and fine-grained A15 phase in the superconducting filaments.

3. The heat treatments previously used to achieve exceptional properties in internal tin wires are more complex than needed. The long time initial aging at temperatures below 380°C does not appear to be necessary. However, some homogenization heat treatment, e.g. at 380°C +

580°C, is useful before the high temperature reaction treatment. Heating the wire directly to the reaction temperature causes a 15-20% loss in critical current.

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REFERENCES

1. M. Suenaga: Metallurgy of Continuous Filamentary A15 Superconductors, Superconductor Materials Science, S. Foner and B. Schwartz, (eds.) New York, Plenum Press, 1981, pp. 201.

2. Y. Hashimoto, K. Yoshizaki, and M. Tanaka: Processing and Properties of Superconducting Nb_3Sn Filamentary Wires, London ICEC Proceedings, IPC Science and Technology Press, pp. 332, 1974.

3. K. Yoshizaki, O. Taguchi, F. Fujiwara, M. Imaizumi, Y. Hashimoto, K. Wakamoto, T. Yamada and T. Satow: Properties of Multifilamentary Nb_3Sn Wires Processed by Internal Tin Diffusion, Adv. Cryog. Eng., vol. 28, p. 380, 1982.

4. R.E. Schwall, G.M. Ozeryansky, D.W. Hazelton: Properties and Performance of High Current Density Sn-Core Process MF Nb_3Sn, IEEE Trans., vol. MAG-19, pp. 1135, May, 1983.

5. S.F. Cogan, J.D. Klein, S. Kwon, H. Landis and R.M. Rose: On the Mechanical Properties of Sn-Core Processed Nb_3Sn Filamentary Composites, IEEE Trans., vol MAG-19, pp. 917, May, 1983.

6. N. Higuchi, K. Tsuchiya, C.J. Klamut, and M. Suenaga: Superconducting Properties of Nb_3Sn Multifilamentary Wires Fabricated by Internal Tin Process, Colo., Adv. Cryog. Eng., vol. 30, pp.739, 1984.

7. B.A. Zeitlin, G. Ozeryansky, K. Hemachalam: An Overview of the IGC Internal Tin Nb_3Sn Conductor, IEEE Trans., in press.

8. L.F. Goodrich and F.R. Fickett: Critical Current Measurements: A Compendium of Experimental Results, Cryogenics, pp. 225, May, 1982.

9. I.W. Wu, D.R. Dietderich, J.T. Holthuis, M. Hong, W.V. Hassenzahl, and J.W. Morris, Jr.: The Microstructure and Critical Current Characteristic of a Bronze-Processed Multifilamentary Nb_3Sn Superconducting Wire: J. Appl. Phys., 54 (12), pp. 7139, 1983.

10. R.M. Scalan, W.A. Fietz and E.F. Koch: Flux Pinning Centers in Superconducting Nb_3Sn: J. Appl. Phys., vol. 46, pp. 2244, 1975.

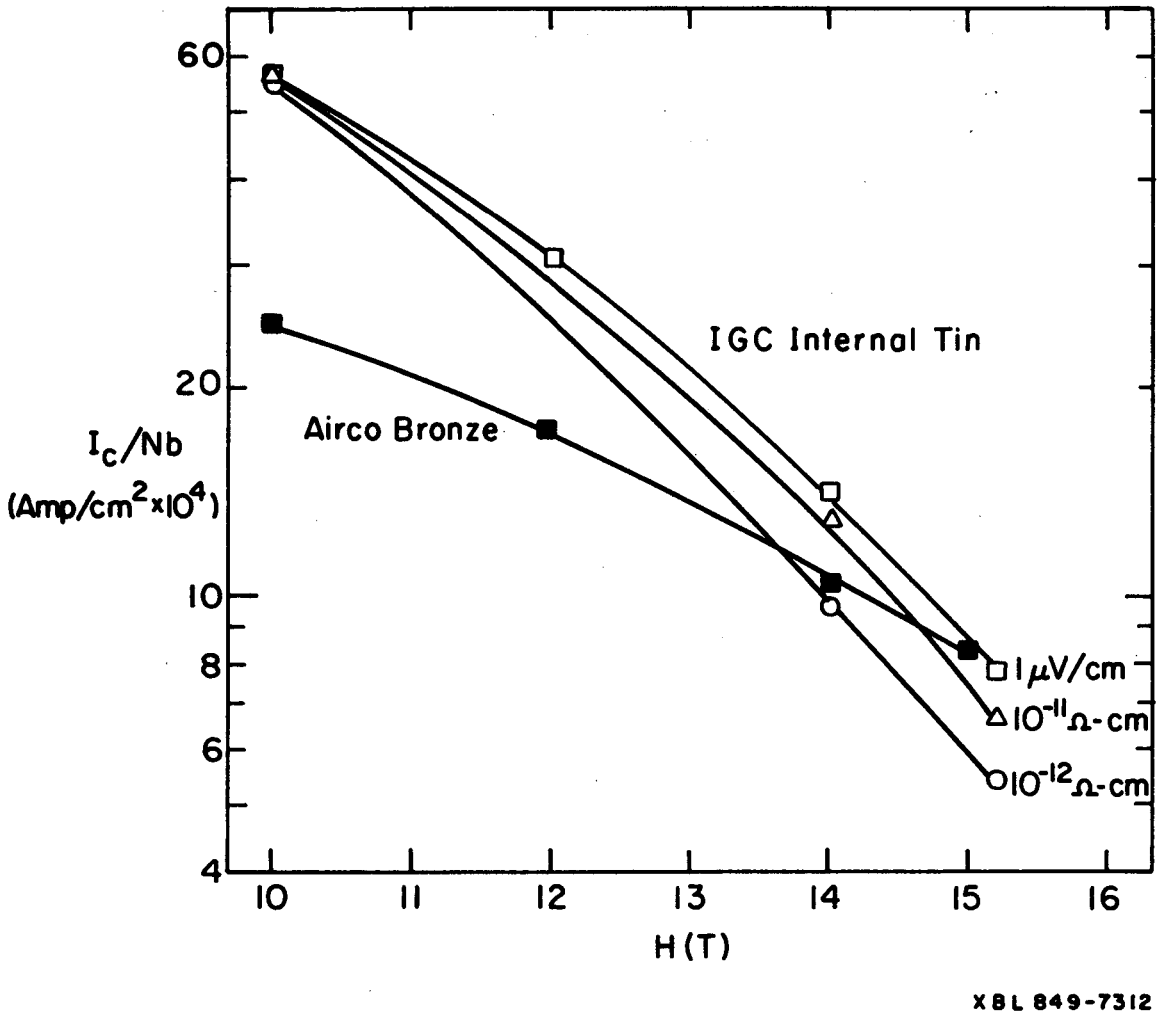

Fig. 1. Critical current density versus magnetic field in the internal tin wire (this work) is compared to that in a bronze-processed wire (ref. 9) by normalizing the critical current (I_c) to the initial niobium content in the wires. The superior 10–12T performance of the internal tin wire suggests a better layer morphology.

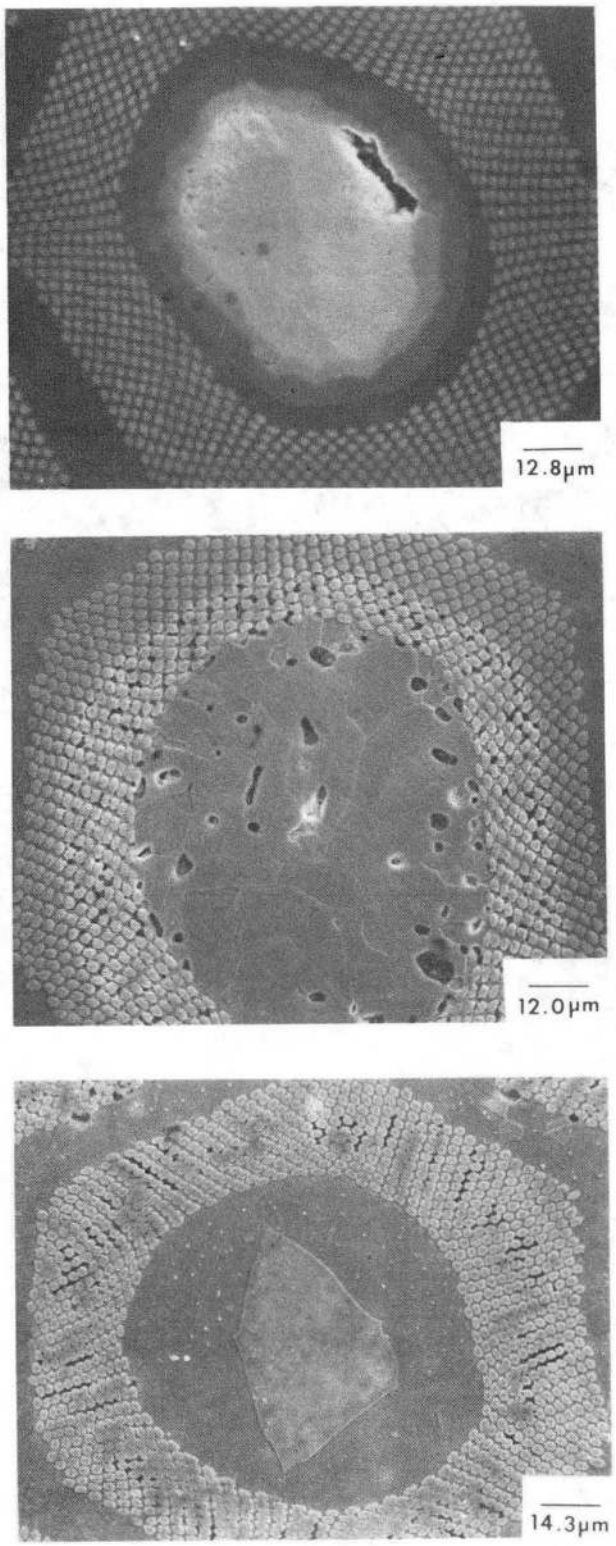

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Fig. 2. Micrographs showing the evolution of the microstructure during multi-step pre-heat treatment, (a)200°C/200h, (b)plus 375°C/33h, (c) plus 580°C/48h. (a) High tin center with η and ε intermetallic layers after step 1. (b) Epsilon phase center with porosity after step 2. (c) Central region of gamma phase surrounded by α phase. The α phase contains pores and isolated γ islands in the filament region.

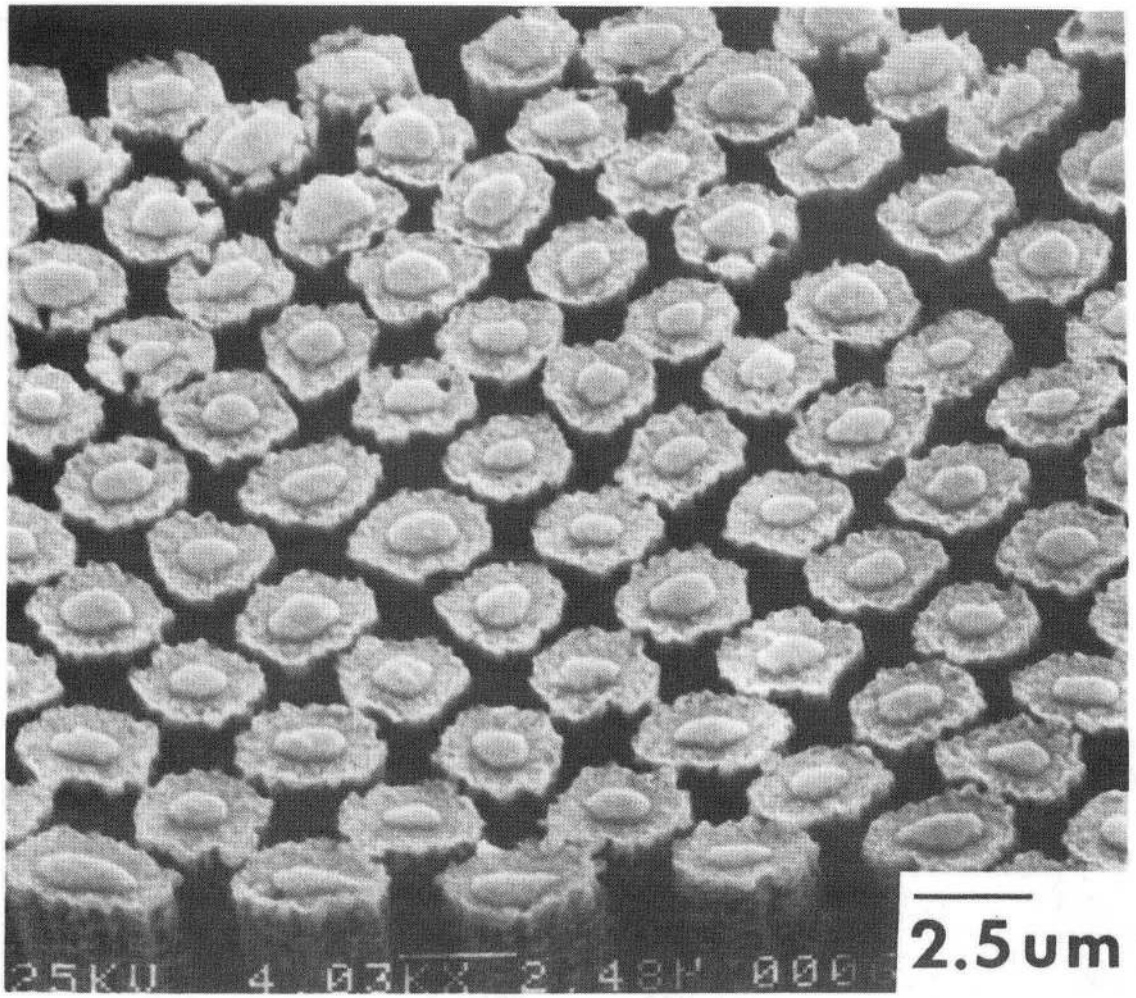

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Fig. 3. Scanning electron micrograph of etched filaments after heat treatment A. The filaments near the core are more reacted than those at the sub-element periphery.

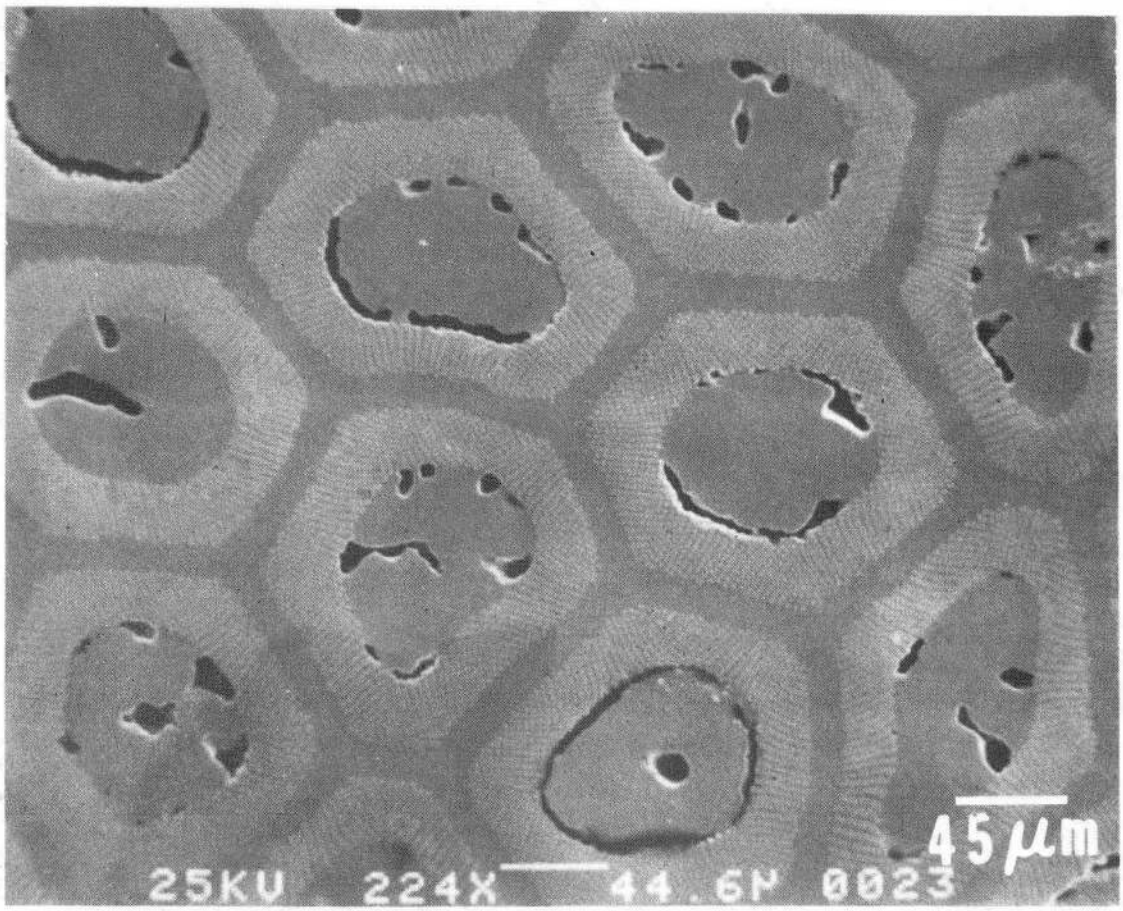

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Fig. 4. Scanning electron micrograph of a wire with no pre-heat treatment, 700°C for 2 days. Large voids have developed in the core region, predominantly at the first inner ring of niobium filaments.

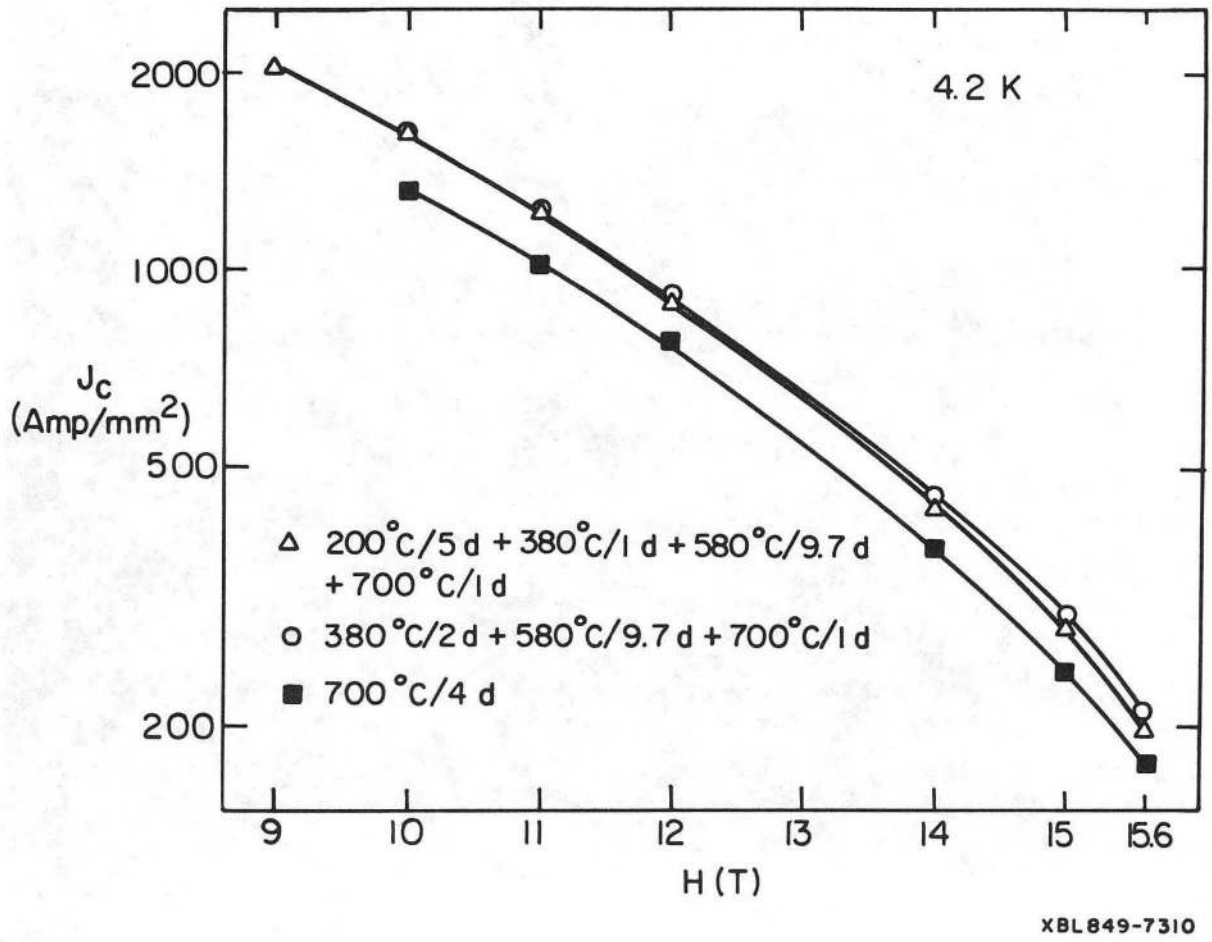

Fig. 5. Critical current density (for the area excluding Ta barrier and Cu stabilizer) versus magnetic field. A shortened heat treatment (circles) produces the same high J_c as the multi-step heat treatment with 200°C (triangles). Also presented is the J_c(H) curve for 700°C/4d.

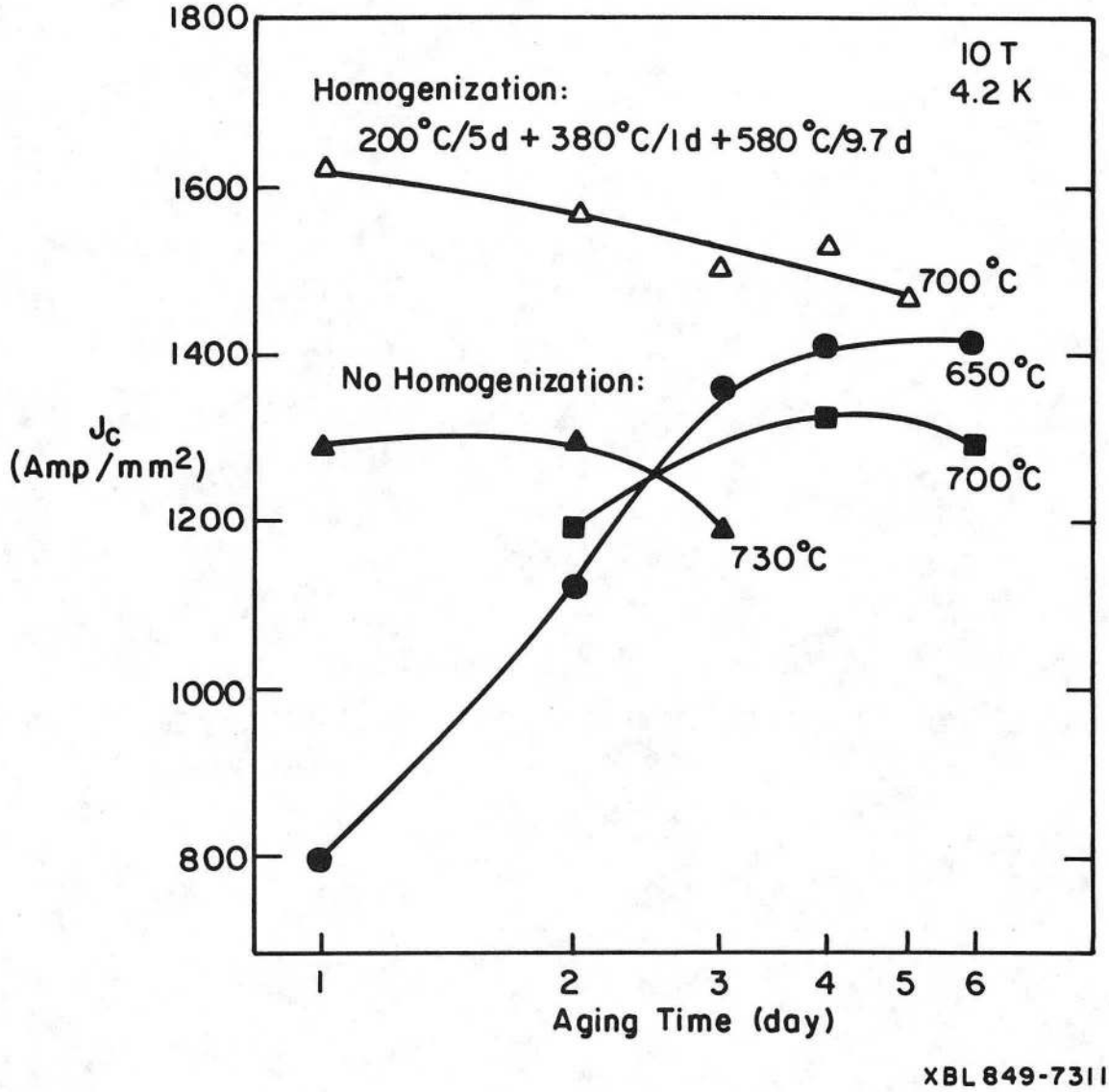

Fig. 6. Critical current density (for the area excluding Ta barrier and Cu stabilizer) versus aging time for wires given different heat treatments. The wires which received only a high temperature reaction treatment are represented by solid points, wires which received the multi-step homogenization heat treatment are represented by open points. points, w

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