BNL-26391

CONF-790815--9

# SUPERCONDUCTING PROPERTIES OF $(Nb,Ta)_3Sn$ WIRES FABRICATED BY THE BRONZE PROCESS

M. Suenaga, K. Aihara, K. Kaiho, and T. S. Luhman
Brookhaven National Laboratory
Upton, New York 11973

MASTER

Form 2075

BNL-26391

# Superconducting Properties of $(Nb,Ta)_3Sn$ Wires Fabricated by the Bronze Process*

M. Suenaga, K. Aihara,† K. Kaiho,†† and T. S. Luhman
Division of Metallurgy and Materials Science
Brookhaven National Laboratory
Upton, New York 11973

## ABSTRACT

Measurements of the superconducting critical temperature $T_c$, critical current density, $J_c$ ($8<H<22.5$ T), and the critical magnetic field $H_{c2}$ were made on bronze processed $(Nb,Ta)_3Sn$ monofilamentary wires. Ta content in the $Nb_3Sn$ compound was varied by alloying the Nb core prior to a reaction heat treatment. Core compositions were 0, 3, 7, 10, and 20 wt% Ta and heat treatments for the reaction were 16, 64, and 120 h at 725°C. For the 120 h heat treatment $T_c$ decreased monotonically with Ta content from 17.5 to 15.7 K while $H_{c2}$ increased from 19.8 to 24.6 T. With increasing Ta content $J_c$ (16 T) increased from $0.7 \times 10^5$ A/cm$^2$ to a maximum value of $1.3 \times 10^5$ A/cm$^2$ at 7 wt% Ta. Further increases in the Ta content produced a decrease in $J_c$(16 T). At 10 T $J_c$ decreased with increasing Ta content. An important aspect of this work is the observation that alloying with Ta did not hinder wire ductility during drawing. It appears therefore that the improvements in $J_c$(16 T) can be incorporated into commercially manufactured conductors.

---

*Work performed under the auspices of the U.S. Department of Energy.

†A visiting scientist from Hitachi Research Laboratory, Ibaraki, Japan.

††A visiting scientist from Electrotechnical Laboratory, Tokyo, Japan.

# Superconducting Properties of $(Nb,Ta)_3Sn$ Wires Fabricated by the Bronze Process*

M. Suenaga, K. Aihara,† K. Kaiho,†† and T. S. Luhman
Division of Metallurgy and Materials Science
Brookhaven National Laboratory
Upton, New York 11973

## INTRODUCTION

Because of the growing interest in the use of multifilamentary superconducting $Nb_3Sn$ composites for the magnets used to magnetically confine plasma in fusion reactors, various attempts were made to increase the superconducting critical current density of $Nb_3Sn$.(1-7) Since these conductors are made by the "bronze process",(8-10) i.e., by reaction of Nb filaments with a Cu-Sn matrix to form $Nb_3Sn$ filaments, alloying elements are required which form solid solutions with either Cu-Sn or Nb. Solid solutions are required so that the conductors mechanical ductility is not significantly reduced.

All previous attempted modifications of $Nb_3Sn$ except one by Livingston(7) were made by substituting Al, Ga, In, etc. for Sn in $Nb_3Sn$. All of these elements when added to the matrix or the core, tend to reduce their ductility. Livingston, however, alloyed Nb with Ta, a substitution that did not reduce the drawability of the composites. He showed that the critical current measured up to 9 T increased above that of the pure $Nb_3Sn$ when the Ta addition was limited to less than 10 at.%. $T_c$ of the alloyed wires was lower than for the pure $Nb_3Sn$ wires by 1.0 K at the 10 at.% Ta addition.

Since Livingston's critical current measurements were limited to 9 T and the magnetic field range of interest for the application of this material to magnetic fusion reactors could be above 10 T, we prepared a set of wires with

---

*Work performed under the auspices of the U.S. Department of Energy.

†A Visiting Scientist from Hitachi Research Laboratory, Ibaraki, Japan.

††A Visiting Scientist from Electrotechnical Laboratory, Tokyo, Japan.

pure and Ta-alloyed Nb cores. The critical temperatures, the critical currents up to 22.5 T, and the critical magnetic fields for these wires were measured. The results of these measurements are reported here.

## SPECIMEN PREPARATION

Five monofilamentary composite wires were fabricated with a matrix and a core having nominal compositions of Cu-13 wt% Sn and Nb-0, 3, 7, 10, and 20 wt% Ta. All Nb-Ta alloys were arc melted in an argon atmosphere, homogenized for 1.5 h at 1800°C, and swaged to rods of a 6.35 mm diameter. After these alloys were annealed at 1200°C for 1.0 h under vacuum, they were inserted into a bronze matrix with a 12.7 mm diameter. Then, the composite rods were cold drawn to 0.635 mm wires using several intermediate annealing steps at 500°C. These composite wires were then vacuum encapsulated in quartz tubing and heat treated at 725°C for periods of 16, 64, and 120 h.

For determination of the thickness and the cross sectional areas of the compound layers, cross sectional optical micrographs at 150 and 1000 times magnifications were taken at the center of each 38 mm long wire which was tested for $I_c$. The areas of the compound layers were determined by multiplying the perimeter of the core (measured using an opisometer) by the thickness of the layers. In thicker layers (>2 μm) the width was irregular around the circumference of the compound. Thus, the thickness was determined by measuring the areas of the compound using a planimeter for four micrographs, which were taken at a magnification of 1000, and dividing these areas with the length of the layer in these micrographs. When the layers were thin (<2 μm), the layers were uniform enough to make accurate measurements of the thickness with a magnifier scale.

Growth of the layer thickness as a function of duration of heat treatments, t, are shown in Fig. 1. The growth for all compounds was faster than

$t^{1/2}$. (If the mechanism for the growth was controlled by the bulk diffusion of either Nb or Sn, or both atoms simultaneously through the compound, then $t^{1/2}$ growth is expected.) In the thick layers (64 h and 120 h), several cracks in the compound running radially through the layer were observed in optical micrographs. These cracks would presumably cause faster diffusion of Sn atoms through the compound layer, short circuiting the bulk diffusion, and resulting in a growth of the compound faster than $t^{1/2}$. In addition, as shown in Fig. 1, alloying cores with Ta also increased the growth rate over that for the unalloyed core.

The compositions of the cores and the compounds were measured by a microprobe using a ZAF correction. To avoid extra x-ray counts from the matrix, the matrix was chemically etched with a $H_2O$-$HNO_3$ solution after the specimens were mounted and polished. The nominal compositions of the cores are listed in Table I together with their measured compositions and the measured compositions of the $(Nb,Ta)_3Sn$ compound layers. As found earlier,(7) the relative percent of Ta in the core was also found in the compound. The amount of Cu in the compound increased with Ta additions from 0.4 to 2.1 at.%. The significance of the increased Cu in the compound to the superconducting properties will be discussed elsewhere. A 1 μm step scan across the compound layer was made in a Nb-7 wt% Ta specimen heated for 120 h at 725°C. There were no observable variations in Nb, Ta, or Sn concentrations across the layer.

Scanning electron microscopy was employed to observe grain sizes in fractured layers of $(Nb_3Sn)$, $(Nb\text{-}7\ wt\%\ Ta)_3Sn$, and $(Nb\text{-}20\ wt\%\ Ta)_3Sn$ specimens which were heated for 64 h at 725°C. Although the grain sizes for the unalloyed $Nb_3Sn$ appeared to be somewhat smaller than those in $(Nb\text{-}20\ wt\%\ Ta)_3Sn$, it was difficult to assess a quantitative difference in the grain sizes between these compounds. Most of the grains were in the range of 1000 to 2000Å but a few grains 5 to 10 times larger were found on the surface of the cores in all wires.

## SUPERCONDUCTING CRITICAL TEMPERATURES

After each heat treatment, two 6.35 mm long pieces of the wires were cut and were used for the measurements of the critical temperature, $T_c$. An ac technique at 220 Hz was used to observe the superconducting transition and the temperature was measured using a calibrated Ge thermometer. Accuracy of the measurement is ±0.1 K. Midpoint critical temperatures of these wires are shown in Fig. 2 as a function of alloying content of Ta in the cores. As was observed earlier,(7) $T_c$ of the compound decreased with increasing Ta content in the compound. The midpoint $T_c$ of the wires for this study were lower than for the earlier study(7) by 0.2 to 0.8 K depending upon the composition of Ta. These discrepancies can be attributed to the difference in the measuring methods of $T_c$. The resistive technique used for the earlier study tends to measure a higher transition temperature for a given specimen than does the ac inductive technique used in the present investigation.

In contrast to the earlier study,(7) which reported that $T_c$ of the wires did not change with reaction time from 1 day to 14 days at 750°C, the critical temperatures of the present wires were found to increase with heat treating time. The functional dependence is $t^{1/2}$ where t varies from 16 to 120 h at 725°C. In one case (Nb-10 wt% Ta), $t^{1/2}$ dependence on the reaction time was observed for reaction times from 8 to 256 h. The source of this discrepancy is not clear. A compressive strain which results from the difference in thermal contraction between the matrix and the A15 compound is known to decrease the critical temperature of the compound.(11,12) Thus, the observed increases in the critical temperatures are perhaps related to decreases in the compressive strains in the compounds due to the softening of the bronze matrices in those specimens which were heated longer than 64 h. Softening occurs by Sn depletion of the matrix. Increases in $T_c$ due to the atomic ordering appear to be less significant in these heat treatments since the increases in $T_c$ with the increased heating time for these wires after the matrix is removed is substantially less than those with the matrix.$^{(13)}$

## SUPERCONDUCTING CRITICAL CURRENTS AND MAGNETIC FIELDS

Superconducting critical current densities, $J_c$, for these wires were measured as a function of applied magnetic fields up to 19 T for most cases and to 22.5 T for a limited number of the specimens. For those measurements of $J_c$ up to 19 T approximately 38 mm long wires were used. The voltage leads were ∿15 mm apart and a 1 μV was used as the criteria for the critical current, $I_c$. For the measurements to 22.5 T, approximately 1.0 cm long wires were cut out from the central section of the specimens tested to 19 T and the separation of the voltage leads were approximately 5 mm. Again, 1 μV was used as the criteria for the critical current. The critical currents measured in the 22.5 T magnet were approximately 20% higher at 19 T than those which were measured in the 19 T magnet. Thus, all critical currents which were measured in the 22.5 T magnet were reduced to match at 19 T with the critical current measured in the 19 T magnet. Critical current densities were determined by dividing critical currents by the cross sectional areas of the compounds for each wires. Examples of variations in the critical current densities with applied magnetic fields are shown in Fig. 3 for the wires with the (Nb-3 wt% Ta) core. Three heat treating periods (16, 64, and 120 h) are given. The high field (H>12 T) critical current densities for all wires increased with heat treating periods, although $J_c$ for $Nb_3Sn$ at low fields usually decrease with the increased heat treating time.$^{(14)}$

Another and perhaps a more illustrative way of presenting the influence of heat treatment time and alloying effects on the critical current densities of these wires is to employ Kramer's$^{(15)}$ formulation for the flux pinning strength, $F_p$, at high magnetic fields, e.g.

$$F_p = J_c\ H = K_s h^{1/2}(1-h)^2 \tag{1}$$

where $h=H/H_{c2}$ and $K_s=0.14\ H_{c2}^{5/2}\kappa_1^{-2}(1-a_o\sqrt{\rho})^{-2}$, and $\kappa_1$ is the Ginsburg-Landau constant ($\kappa=H_{c2}/\sqrt{2}H_c$), $a_o$ is the flux lattice spacing $a_o\simeq(\phi_o/H)^{1/2}$, and $\rho$ is the pinning center density. This equation can be rewritten as

$$F_p^{1/2}H^{-1/4} = J_c^{1/2}H^{1/4} = 0.37\ \kappa^{-1}(1-a_o\sqrt{\rho})^{-1}(H_{c2}-H) \quad . \tag{2}$$

As shown earlier$^{(16)}$ and noting the grain sizes are from 1000Å to 2000Å, it can be assumed that $(a_o\sqrt{\rho})<<1$ and thus, $F_p^{1/2}H^{-1/4}$ is linear with H. The influence of alloying the cores with Ta on the critical current densities is illustrated in Fig. 4 using this representation for those wires heat treated at 725°C for 64 h. As expected from Eq. (2), ($J_c^{1/2}H^{1/4}$) for all wires decreased linearly with applied magnetic fields until H approached the values close to the critical magnetic field of each wire. Then, the values of ($J^{1/2}H^{1/4}$) for all wires except that wire with a Nb-20 wt% Ta core, deviated up from the straight lines, while the values for the Nb-20 wt% Ta core sample deviated below the straight line.

An advantage of this method for presenting the variation in $J_c$ for different specimens is that the critical magnetic field, $H_{c2}$, can be determined by a linear extrapolation method. In many cases, as observed in Fig. 4, superconductivity exists beyond the $H_{c2}$ determined by this method. But for the discussion of $J_c$ at high magnetic fields, this $H_{c2}$ is particularly useful. For an example, from Fig. 4, two controlling factors on the values of $J_c$ at high magnetic fields ($H \gtrsim 10$ T) are evident. They are 1) $\kappa_1$ (since the slope $\Delta(J_c^{1/2}H^{1/4})/\Delta H$ is inversely proportional to $\kappa_1$) and 2) $H_{c2}$. For high $J_c$, small $\kappa$ and high $H_{c2}$ are required. The requirements are met only when high values of $T_c$ and the electronic specific heat coefficient accompanied by relatively low $\rho_N$ are simultaneously achieved. These conclusions are also described in slightly different ways by Kramer,$^{(15)}$ and D. U. Gubser et al.$^{(17)}$

The effects of Ta additions to the properties of the $Nb_3Sn$ at high magnetic fields are twofold: 1) increased $H_{c2}$ and 2) reduction in the slope of $(J^{1/2}H^{1/4})$ vs H plots. The slope $\Delta(J^{1/2}H^{1/4})/\Delta H$ is lowered by Ta additions to the compound. As mentioned above, since the slope is inversely proportional to $\kappa_1$ the result of the Ta addition is considered to be increased $\kappa_1$. The influence of Ta alloying on the $H_{c2}$ of the $Nb_3Sn$ is illustrated in Fig. 5 as a function of the core composition. $H_{c2}$ increased monotonically with increasing Ta contents although $T_c$ decreased with Ta. It is thought that this increase in $H_{c2}$ is due to the increased normal state resistivity of $Nb_3Sn$ by the addition of Ta to the compound. When the heat treatment duration was increased from 16 h to 64 h, approximately 2 T increases in the $H_{c2}$ were observed for the alloyed $Nb_3Sn$, but when it was further increased to 120 h, no increase in $H_{c2}$ was observed although $T_c$ increased with the additional heat treating time. Perhaps, this is due to two opposing effects on $H_{c2}$; 1) the decrease in the normal state resistivity and 2) the increased $T_c$ due to the reduction of compressive strains in $Nb_3Sn$ when the heat treatment time increases beyond 64 h.

In order to further illustrate the influence of the Ta alloying on $J_c$, the critical current densities at two magnetic fields ($H=10$ and 16 T) are shown in Fig. 6. The critical current densities at 10 T are slowly decreased with the Ta additions. A decrease of 40% is noted when the Ta content increases to 20 wt%. In contrast, $J_c$ at 16 T increased approximately by a factor of two for a 7 wt% Ta addition to the core and decreased to the original value of $J_c$ for the 20 wt% Ta addition. This increased $J_c$ at very high magnetic fields is considered to be very significant for the application of $Nb_3Sn$ conductors for magnets for fusion reactors.

Finally, as was mentioned above, the values of $(J^{1/2}H^{1/4})$ for the wires with the Nb-20 wt% Ta cores deviated below the straight line near the critical field. A similar behavior was also observed in a $(Nb\text{-}1\ wt\%\ Zr)_3(Sn_{1-x}Ga_x)$ monofilament wire.(18) We examined the possibility that these deviations are resulting from a paramagnetic limitation on the critical field. In Fig. 7, the values of $H_{c2}/T_c$ for the pure and alloyed $Nb_3Sn$ were compared with that for the paramagnetically limited critical magnetic field, $H_p$, using an equation, $H_p/T_c=1.84[1-(4.2\ K/T_c)^2]$. The values of $(H_{c2}/T_c)$ increased with the Ta content in the core and at the Ta concentration of 20 wt% the value of $(H_{c2}/T_c)$ approaches within 10% of $(H_p/T_c)$. Thus, this deviation of $(J^{1/2}H^{1/4})$ from linearity toward smaller values is taken as a evidence for the paramagnetic limitation on $H_{c2}$.

## ACKNOWLEDGMENT

The authors appreciate helpful discussions of Drs. D. O. Welch, C. L. Snead, Jr., and J. Bussiere during the course of this investigation. Careful microprobe measurements by Mr. R. Sabatini is especially acknowledged. Technical assistances by F. Iseli, D. Horne, F. Perez, C. Schnepf, and A. Cendrowski are also appreciated. The use of the high field magnets at the National Magnet Laboratory and very helpful assistances by its staff are greatly appreciated.

Table I

COMPOSITIONS OF THE CORES AND THE COMPOUND LAYERS

| Nominal Core Compositions | Ta Content in the Cores | | Compositions of the Compounds (at.%) | | | |
|---|---|---|---|---|---|---|
| (wt.%) | (wt.%) | (at.%) | Nb | Ta | Sn | Cu |
| Nb-0 Ta | 0 | 0 | 76.9 | 0 | 22.8 | 0.4 |
| Nb-3 Ta | 4.2 | 2.2 | 76.2 | 1.8 | 21.5 | 0.5 |
| Nb-7 Ta | 7.7 | 4.2 | 74.7 | 2.5 | 22.2 | 0.6 |
| Nb-10 Ta | 9.2 | 5.0 | 71.8 | 4.3 | 22.6 | 1.4 |
| Nb-20 Ta | 20.2 | 11.6 | 67.1 | 9.6 | 21.3 | 2.1 |

# References

1. O. Horigami, T. S. Luhman, C. S. Pande, and M. Suenaga, Appl. Phys. Letters, 28, 738 (1976).
2. D. Dew-Hughes, IEEE Trans. on Magnetics, MAG-13, 651 (1977).
3. R. Akihama, K. Yashukochi, and T. Ogasawara, ibid., p. 803.
4. R. Akihama, K. Yasukochi, and R. Roberge, IEEE Trans. on Magnetics, MAG-15, 629 (1979).
5. D. Dew-Hughes and M. Suenaga, J. Appl. Phys. 49, 357 (1978).
6. U. Zwicker, G. Müller, D. Park, K. Nigge, and H. Rolling, Mickrochim. Acta. Suppl. 7, 357 (1977).
7. J. D. Livinston, IEEE Trans. on Magnetics, MAG-14, 611 (1978).
8. M. Suenaga, W. B. Sampson, and C. Klamut, IEEE Trans. on Magnetics, MAG-11, 231 (1975).
9. O. W. Dies, IEEE Trans. on Magnetics, MAG-13, 447 (1977).
10. W. Fietz, IEEE Trans. on Magnetics, MAG-15, 67 (1979).
11. T. S. Luhman and M. Suenaga, Appl. Phys. Letters, 29, 319 (1976).
12. K. Aihara, D. O. Welch, M. Suenaga, and T. S. Luhman, Bull Am. Phys. Soc. 24, 456 (1979).
13. K. Aihara and M. Suenaga, unpublished results.
14. M. Suenaga, T. S. Luhman, and W. B. Sampson, J. Appl. Phys. 45, 4049 (1974).
15. E. J. Kramer, J. Appl. Phys. 44, 1360 (1973).
16. T. S. Luhman, M. Suenaga, D. O. Welch, and T. Onishi, to be submitted to Journal of Appl Phys.
17. D. U. Gubser, T. L. Francavilla, D. G. Howe, R. A. Muessner, and F. T. Ormand, IEEE Trans. on Magnetics, MAG-15, 385 (1979).
18. C. L. Snead, Jr. and M. Suenaga, IEEE Trans. on Magnetics, MAG-15, 625 (1979).

# Figure Captions

Figure 1. $(Nb, Ta)_3Sn$ compound layers as a function of heat treating duration at 725°C.

Figure 2. The superconducting critical temperatures for the $(Nb,Ta)_3Sn$ layers as a function of the Ta concentration in the $(Nb_3Ta)$ core.

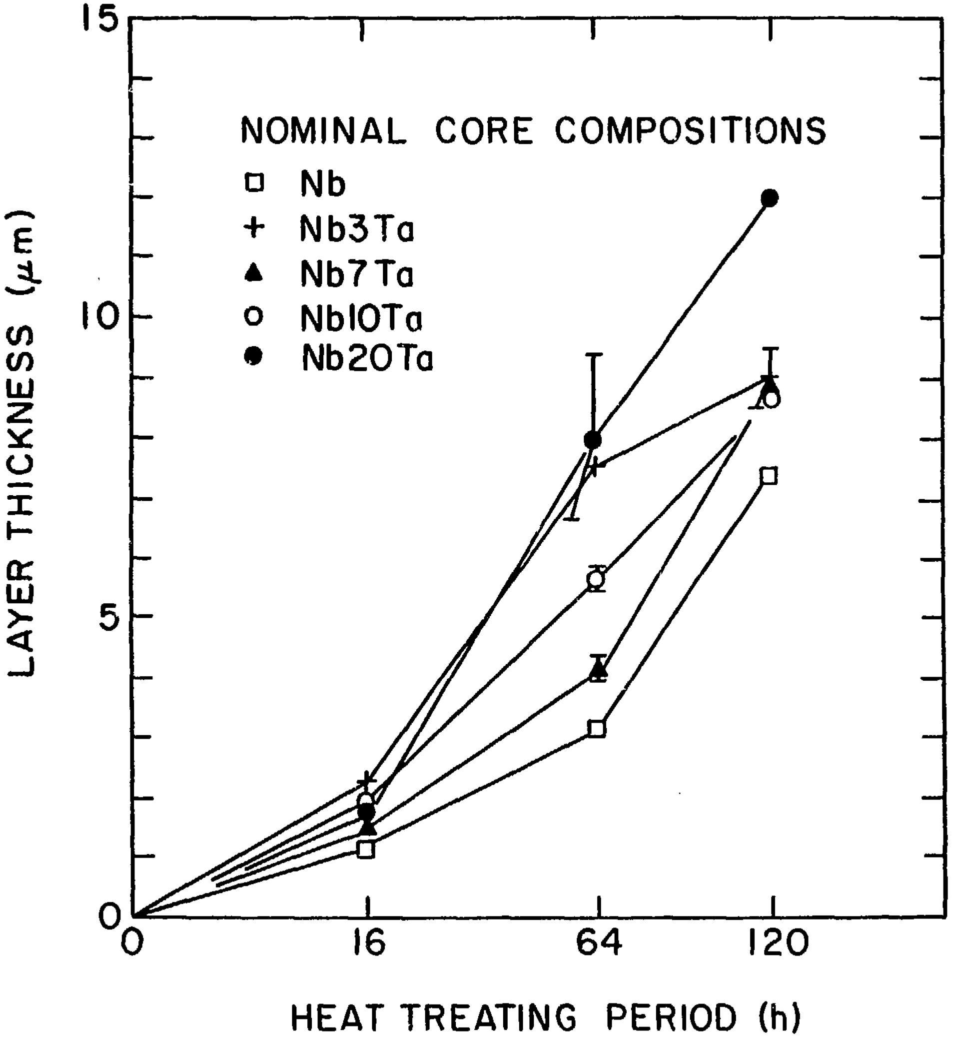
Figure 3. The superconducting critical current densities as a function of applied magnetic fields for the $(Nb\text{-}3wt\%\ Ta)_3Sn$ wires.

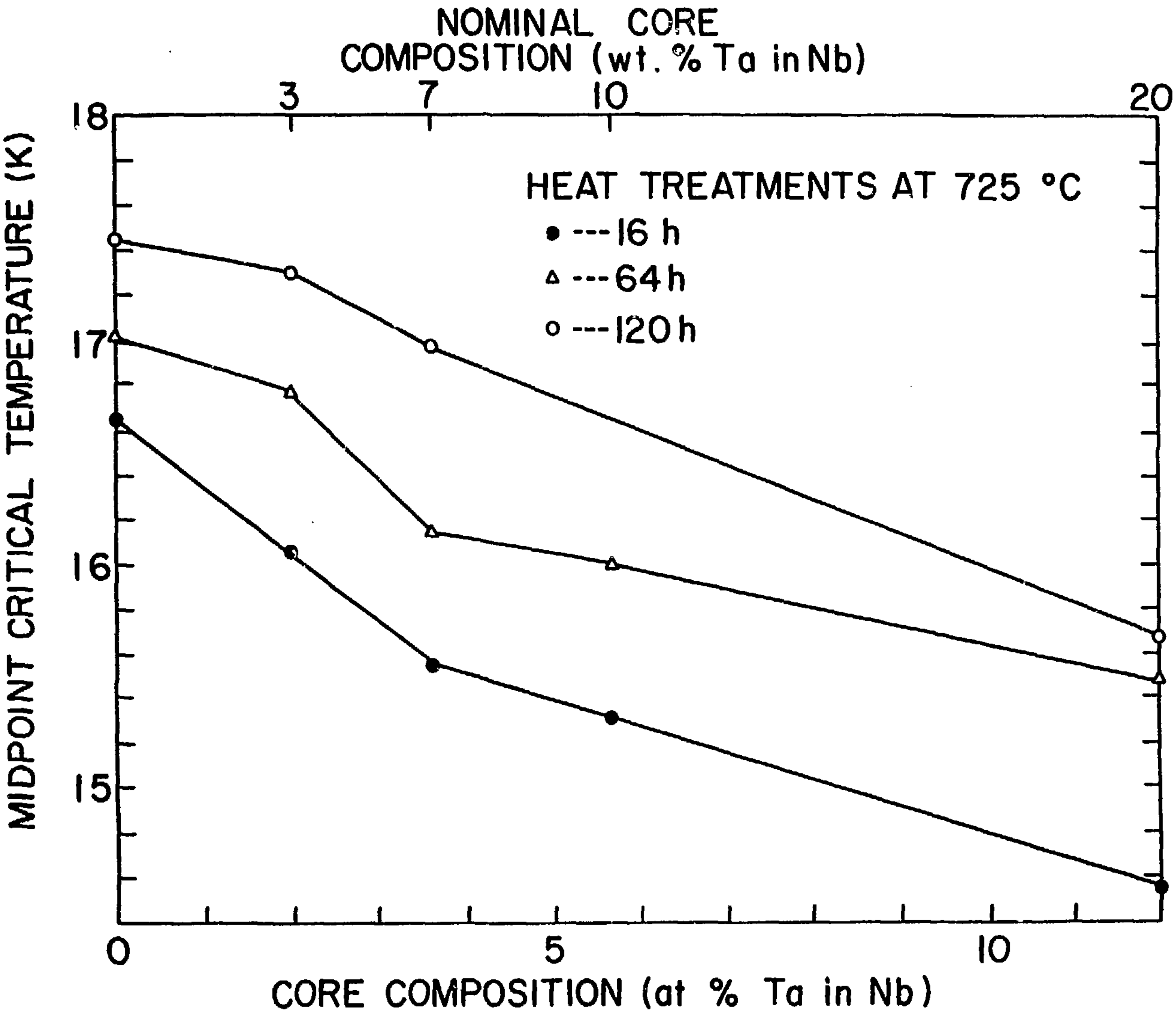
Figure 4. $(J_c^{1/2}H^{1/4})$ $(10^5\ A^{1/2}T^{1/4}/m)$ for the $(Nb,Ta)_3Sn$ wires as a function of applied magnetic fields.

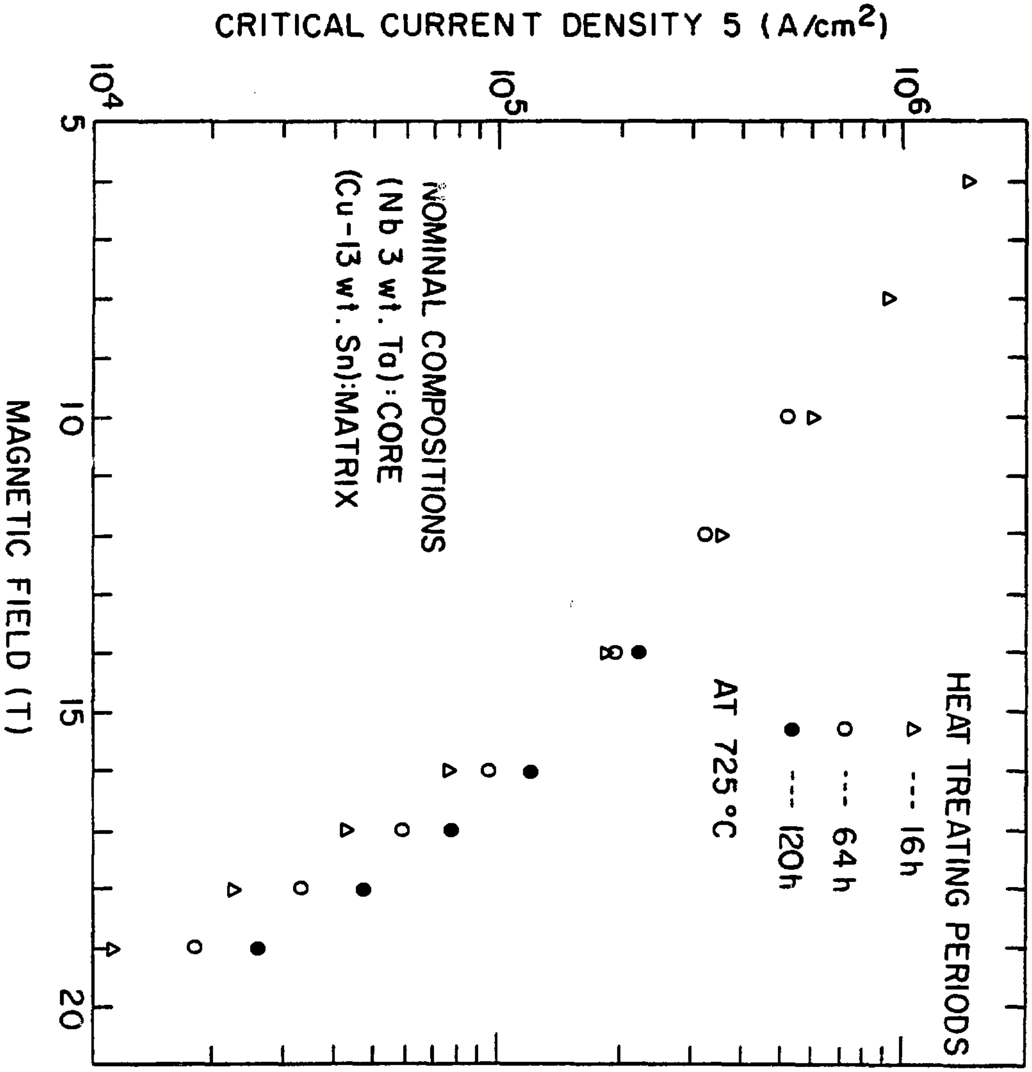
Figure 5. The superconducting critical magnetic fields of the $(Nb,Ta)_3Sn$ wires as a function of the Ta content in the $(Nb_3Ta)$ core.

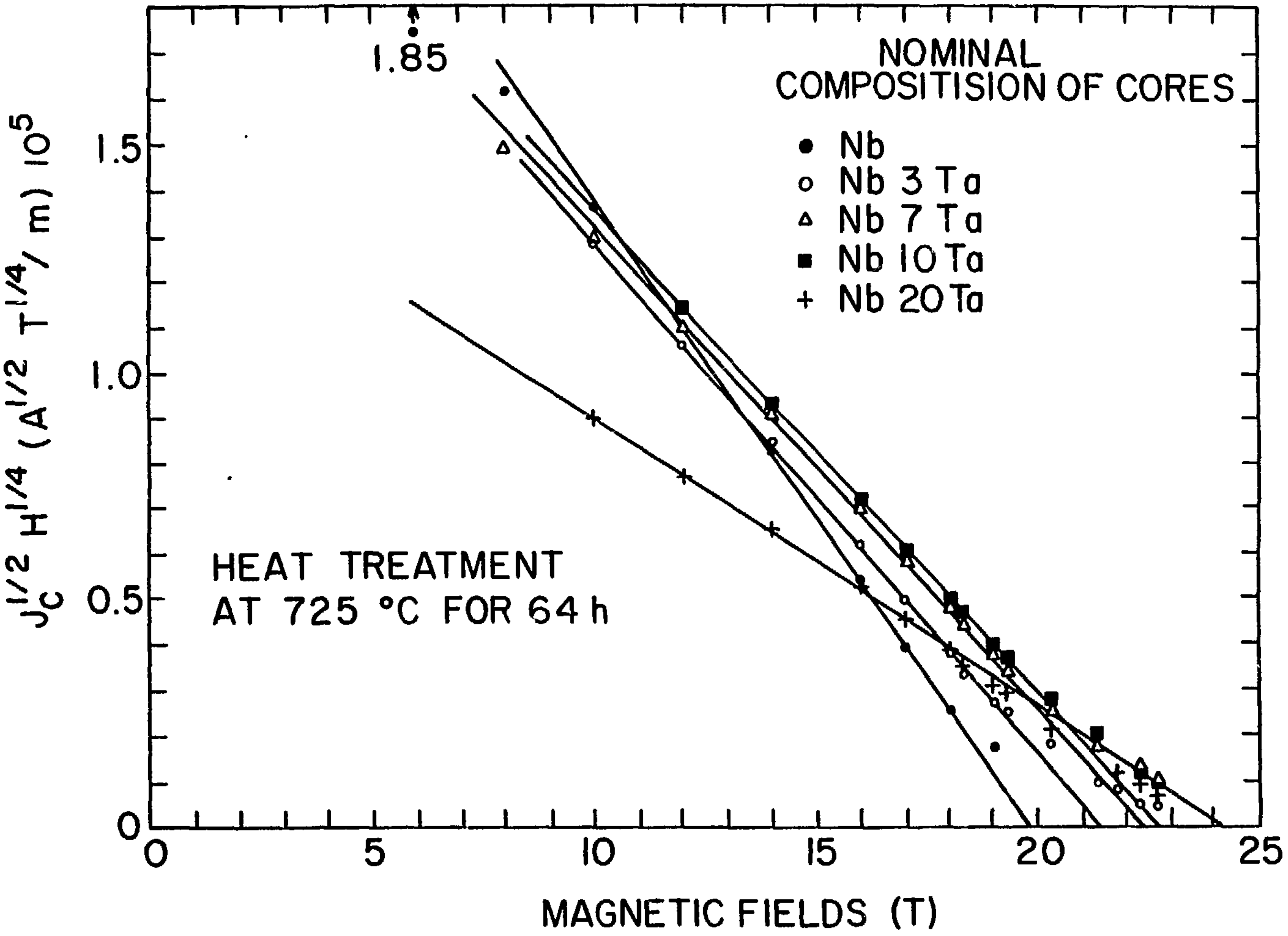
Figure 6. The superconducting critical current densities at 10 and 16 T as a function of the Ta content in the core.

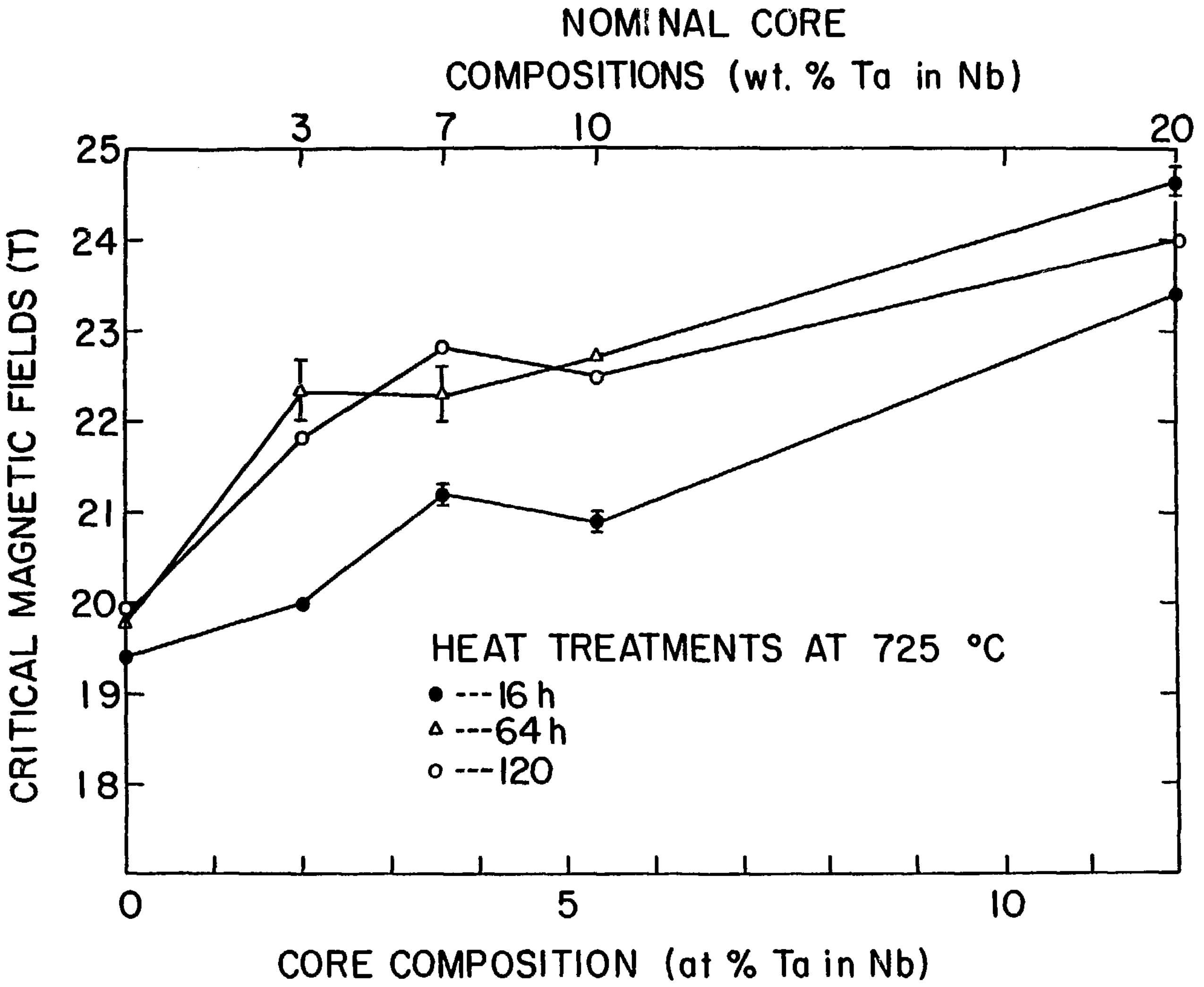
Figure 7. The value of $(H_{c2}/T_c)$ for the $(Nb,Ta)_3Sn$ wires are compared with the corresponding values of $(H_pT_c)$.


NOMINAL CORE COMPOSITIONS
□ Nb
+ Nb3Ta
▲ Nb7Ta
○ Nb10Ta
● Nb20Ta
LAYER THICKNESS (μm)
0
5
10
15
HEAT TREATING PERIOD (h)
0
16
64
120


NOMINAL CORE
COMPOSITION (wt. % Ta in Nb)
3
7
10
20
18
17
16
15
MIDPOINT CRITICAL TEMPERATURE (K)
HEAT TREATMENTS AT 725 °C
● ---16 h
△ ---64 h
○ ---120 h
0
5
10
CORE COMPOSITION (at % Ta in Nb)


CRITICAL CURRENT DENSITY J (A/cm$^2$)
$10^4$
$10^5$
$10^6$
MAGNETIC FIELD (T)
5
10
15
20
HEAT TREATING PERIODS
△ --- 16h
○ --- 64h
● --- 120h
AT 725°C
NOMINAL COMPOSITIONS
(Nb 3 wt. Ta):CORE
(Cu-13 wt. Sn):MATRIX


1.85
NOMINAL
COMPOSITISION OF CORES
● Nb
○ Nb 3 Ta
△ Nb 7 Ta
■ Nb 10 Ta
+ Nb 20 Ta
HEAT TREATMENT
AT 725 °C FOR 64 h
$J_c^{1/2} H^{1/4} (A^{1/2} T^{1/4}/m) 10^5$
0
0.5
1.0
1.5
0
5
10
15
20
25
MAGNETIC FIELDS (T)


NOMINAL CORE
COMPOSITIONS (wt. % Ta in Nb)
3
7
10
20
25
24
23
22
21
20
19
18
CRITICAL MAGNETIC FIELDS (T)
HEAT TREATMENTS AT 725 °C
● ---16 h
△ ---64 h
○ ---120
0
5
10
CORE COMPOSITION (at % Ta in Nb)

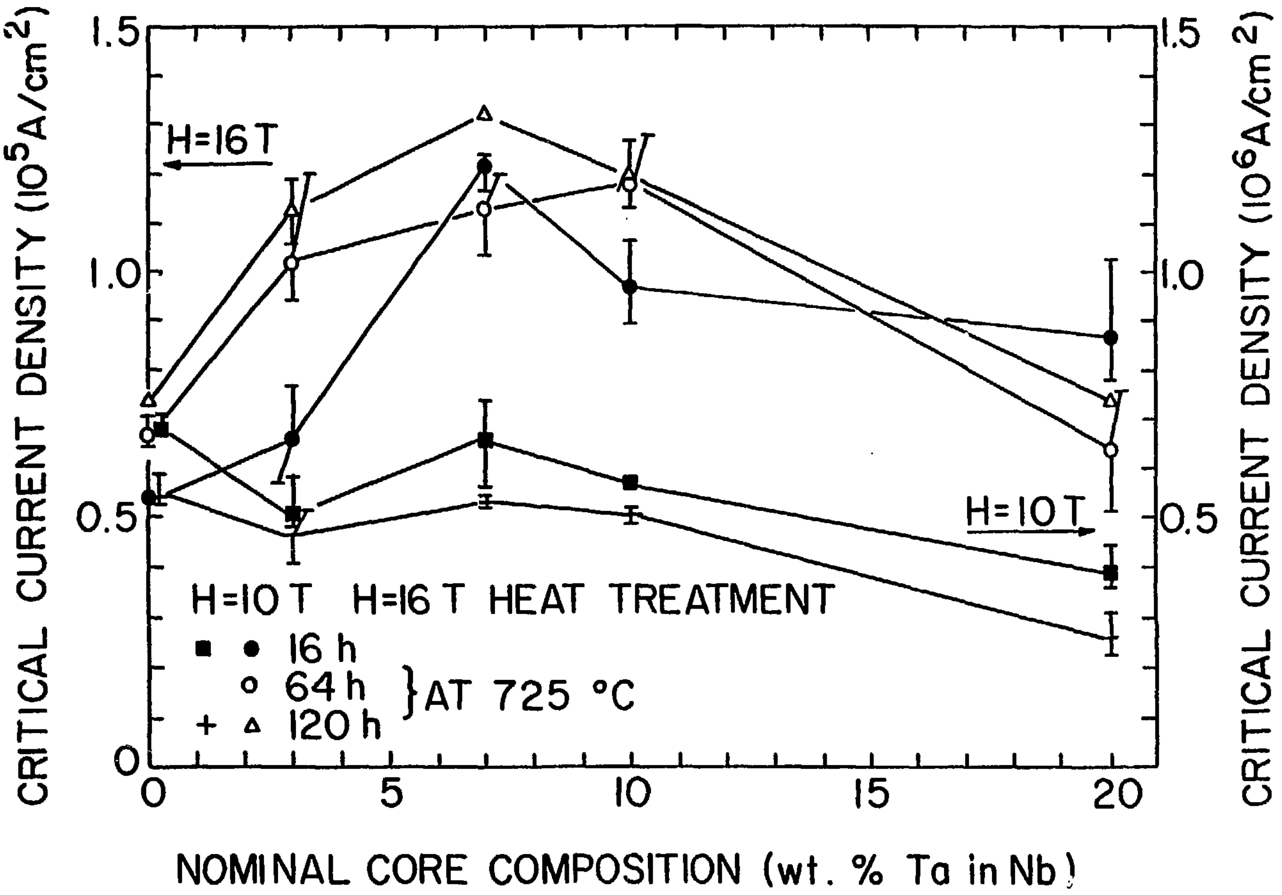

CRITICAL CURRENT DENSITY ($10^5$A/cm$^2$)
CRITICAL CURRENT DENSITY ($10^6$A/cm$^2$)
1.5
1.0
0.5
0
0
5
10
15
20
H=16 T
H=10 T
H=10 T H=16 T HEAT TREATMENT
■ ● 16 h
○ 64 h
+ △ 120 h
AT 725 °C
NOMINAL CORE COMPOSITION (wt. % Ta in Nb)

Fig. 7 this will be replaced with a glossie ma.