

A characteristic study of the superconducting phase in the niobium-aluminum-germanium system

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A study has been made of the time and temperature dependence of the growth of the superconducting A-15 phase and its grains in the Nb-Al-Ge system. In addition, changes in the microstructure and composition of the A-15 phase have been studied using energy dispersive analysis of x rays. The data obtained have been plotted and compared with theory. The results have been used to explain the variations in the superconducting properties of this system as observed in earlier work.

I. INTRODUCTION

Several superconducting materials have been developed over the years, each with its characteristic properties. The Nb-Al-Ge system is one of those with the optimal combination of critical temperature and upper critical field. However, the development of a commercially viable process to fabricate the Nb-Al-Ge superconductor, like all other superconductors with the A-15 structure, presents formidable problems, the reason being due to the brittleness of the A-15 phase.

One promising method that has been extensively studied by Pickus^{1,2} for producing multifilamentary superconductors, the infiltration technique, was used for this investigation. In this process, a compacted and sintered Nb rod is infiltrated with an Al-Ge alloy of eutectic composition and then deformed before being reacted to form the A-15 phase.

Work done by Pickus on multifilamentary wires and tapes of the Nb-Al-Ge superconducting system prepared by the infiltration method has shown that the critical temperature increases as the reaction temperature is increased.¹ Unfortunately, the critical current density was found to decrease at the same time, i.e., it increases as the reaction temperature is lowered. Furthermore, as was found from the current study, the volume fraction of the superconducting A-15 phase formed at the lower temperatures is much smaller than that formed at the higher temperatures. Consequently, despite the increased critical current density, the overall current-carrying capacity of the superconductor is reduced at the lower temperatures. The reduction in critical current density at the higher temperatures is most probably due to the lack of pinning centers for flux lines at those temperatures.

Further understanding of the kinetics of the superconducting phase of the Nb-Al-Ge system at high temperatures was therefore considered necessary. The growth of the A-15 phase and its grains with time and temperature was thus studied and the results are presented in a later section. Another important aspect of the study was the interaction between the various phases present.

II. EXPERIMENTAL STUDIES

The specimen used for this study were produced by the infiltration technique because the porous nature of the dip-

ping rod enables several reacting regions randomly dispersed in the sample to be studied at the same time, giving a statistical meaning to the measured parameters.

Porous niobium rods about 2 1/2 in. in length and 1/8 in. in diameter were prepared by isostatically pressing niobium powder (– 270 + 400 mesh) of 99.9% purity at a pressure of 30 000 psi. This pressure has been found to give adequate porosity and green strength for subsequent infiltration.² Each rod was then suspended in the center of the heating element of an Abar furnace, Fig. 1, and sintered at a temperature of 2200 °C for 15 min under a vacuum of less than 10^{-5} mm Hg.

The aluminum-germanium eutectic was prepared by arc-melting an aluminum (99.999% pure) and germanium (99.999% pure) mixture of the eutectic composition (i.e., 53 parts by weight Ge, to 47 parts by weight Al) under an argon atmosphere in a copper-chill mold. The buttons so prepared were cooled, overturned, and remelted to ensure proper mixing of the components. They were then cleaned by polishing off the outer layers and melted together in a quartz tube in the Abar furnace under a helium atmosphere. This was repeated several times with the eutectic being placed upside down each time to ensure that all lighter and heavier impurities had been cleaned off.

Before sintering the Nb rod, the cleaned eutectic was first placed below the Abar furnace (Fig. 1). As the sintered rod cooled down, the eutectic was heated to 600 °C (its melting temperature is 424 °C). With the eutectic melted and at 600 °C and the rod also at about 600 °C, the latter was lowered until it was completely immersed in the molten eutectic. The furnace was then backfilled with helium to a pressure just below atmospheric, forcing the eutectic to enter and completely fill the pores. The rod was kept immersed in the melt for 5 min to ensure adequate infiltration before being pulled up and allowed to cool to room temperature. A cross section of an infiltrated specimen is shown in Fig. 2. Each infiltrated rod was then cut into pieces of about 3/16-in. length, the ends ground, and reacted.

For the reaction, the furnace was first evacuated to a pressure less than 10^{-5} mm Hg, backfilled with helium to prevent excessive evaporation of aluminum during reaction at high temperatures, and then heated to temperature while the specimen was shielded from the heat. Under steady state

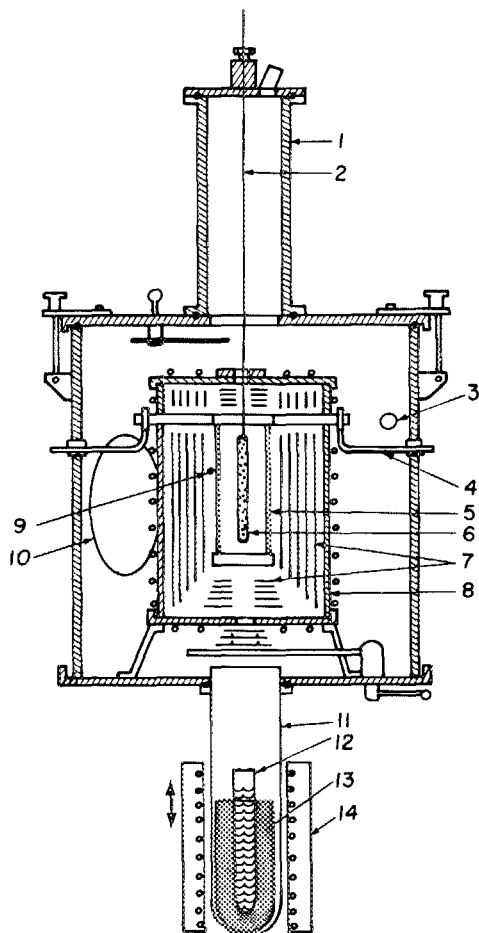


FIG. 1. Abar furnace. 1. Extension tube, 2. tantalum rod, 3. back filling port, 4. electrical leads, 5. tungsten mesh heating element, 6. Nb specimen, 7. radiation shields, 8. water-cooled wall, 9. W-5% Re vs W-26% Re thermocouple point, 10. vacuum connection, 11. quartz tube, 12. smaller quartz tube containing Al-Ge eutectic, 13. graphite crucible, 14. electric heater.

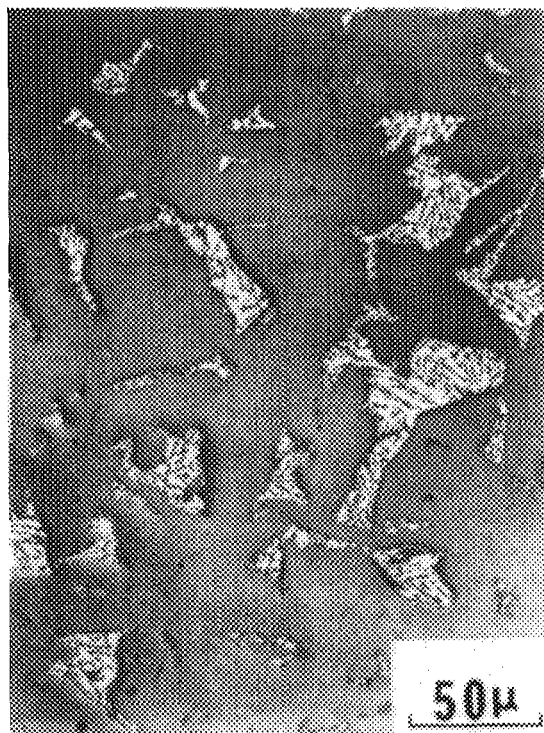


FIG. 2. Sintered Nb compact infiltrated with Al-Ge eutectic.

conditions, the sample was lowered to the heating zone for the required time and then raised back and again shielded from the heat while it cooled.

A. Sample analysis

Reacted samples were mounted in Kold Mount resin, ground, polished, and then etched in a solution of sulphuric acid, hydrofluoric acid, and water, mixed in equal proportions and to which a few drops of hydrogen peroxide had been added. Etched samples were anodized in a Pickleshimer solution at 27 V for 6 min to facilitate phase identification. Under these conditions, the various phases were identified by the following colors: Nb solid solution (A-2 phase)—light gray; A-15 phase—light blue; Al-rich (σ) phase—blue; Ge-rich phase—deep blue.

Photomicrographs of the anodized sample were taken at several positions over the cross section at 1000 \times magnification. Measurements of the A-15 phase thickness were made using vernier calipers of resolution 0.05 mm, taken directly from the photomicrographs. Several readings were taken for a given condition of time and temperature and then averaged.

A number of methods are available for measuring grain sizes.^{3,4} On close study of these methods and the specimen under study, it was decided that none of them would be suitable for the current analysis. Consequently, a new method was developed for this analysis. Even though it is not a standard method, it still gives a measure of the grain size variation with time and temperature. Each grain size was measured in two directions normal to each other with vernier calipers and the readings averaged to give the size of that particular grain. Several grains were measured from each sample as well as other samples at the same time and temperature conditions and averaged. The A-15 phase thickness and grain size average values obtained are listed in Table I.

The temperature range investigated was selected on the basis of a previous investigation which had shown that critical temperatures obtained for reaction temperatures below 1300 °C were not significant compared to those for higher temperatures¹ and that they actually increase with increasing temperature. 1840 °C was the highest temperature selected since the highest temperature to which the system can be subjected without partial melting is 1870 °C.

TABLE I. A-15 phase readings (overall average values).

Time (sec)	Phase thickness (microns)				Grain size (microns)		
	1300 °C	1500 °C	1700 °C	1840 °C	1500 °C	1700 °C	1840 °C
10			1.62	1.87			
20			1.92	2.51		3.10	7.45
60		1.90	2.63	3.59		5.51	11.18
180						6.64	16.26
300		3.73	5.38	8.35	4.87	8.79	28.48
600		4.68			6.09		
900	3.02	5.16	6.79		6.63	12.66	41.00
1200		5.95			7.73		
1800	4.27	6.35			8.73	16.06	
3600	5.20						
7200	7.68						

Phase identification was done on etched but unanodized specimen using a scanning electron microscope equipped with an EDAX (energy dispersive analysis of x rays).

III. RESULTS AND DISCUSSION

A. Growth of the A-15 phase

The growth of the superconducting A-15 phase is shown in Fig. 3 on a log-log graph where the phase thickness is plotted against the reaction time. The straight-line nature of the log graphs indicates a rapid increase in the A-15 phase thickness during the early stages of a reaction, the rate reducing substantially at long reaction times, even though the phase continues to grow. The growth rates observed could be explained by the fact that the A-15 phase is sandwiched between phases rich in Nb on one side and rich in Al and Ge on the other side, Figs. 4(a) and 4(b), so that as growth proceeds, the diffusion path increases, and the rate of growth therefore decreases.

Different reactions are involved at various stages of the growth process. At short times or lower temperatures when the A-15 phase is sandwiched between the A-2 phase (niobium solid solution) and the sigma (σ), Al-rich phase, Fig. 4(a), the growth process may involve a phase decomposition on the σ -phase side and interfacial reaction on the solid solution side. The transformation process is one of reconstructive growth involving the breaking of the bonds of the σ -phase and its rearrangement to form the A-15 phase. This is the interfacial reaction. Processes involving interfacial reactions are often interpreted by diffusion data alone due to the basic diffusion mechanism involved. However since this is a ternary system, analysis on a purely diffusion basis using Fick's laws would require a very complex treatment demanding the use of four diffusion coefficients all of which vary with composition.

On the other hand, from Fig. 3, the growth process can be described by a power law of the form:

$$d = at^n,$$

where d = A-15 phase thickness, a = rate constant, t = reaction time, and n = reaction (growth) index. The points were fitted with straight lines using the linear least squares analysis with a correlation of ± 0.96 (Table II) which shows a good straight line relationship between the

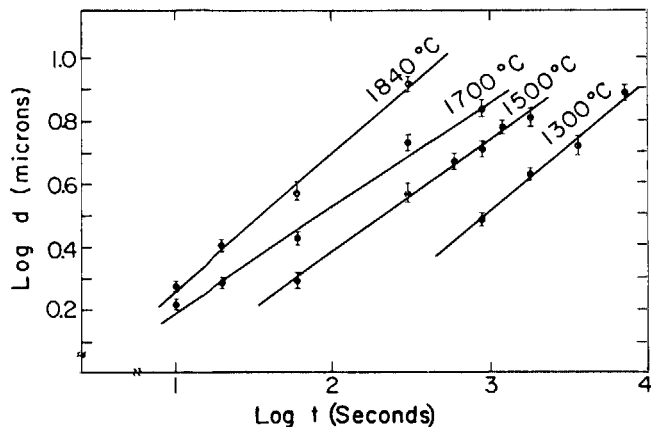
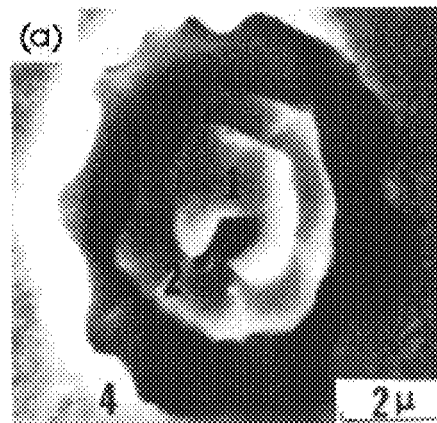
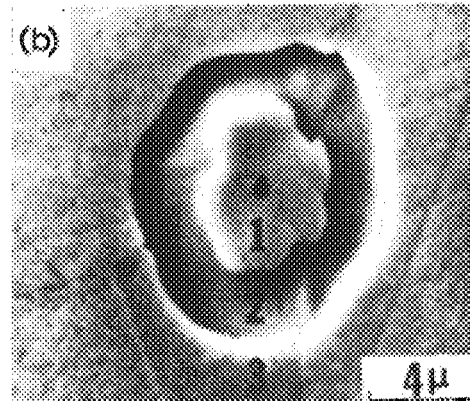


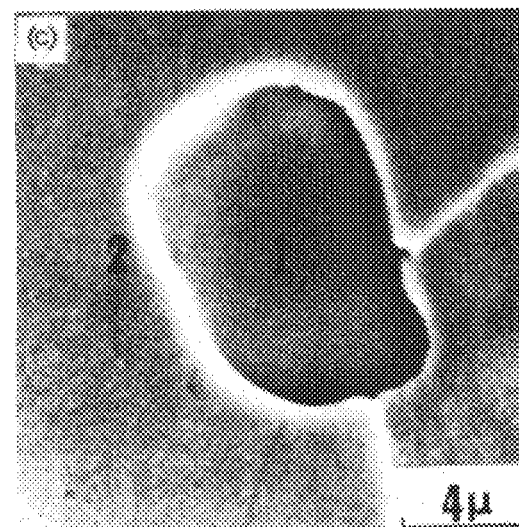
FIG. 3. Variation of the A-15 phase thickness with time.



1	2	3	4
Ge-rich Phase	Al-rich Phase	A-15 Phase	A-2 Phase
Nb: 39.8%	Nb: 50.2%	Nb: 70.0%	Nb: 95.1%
Al: 32.3%	Al: 43.0%	Al: 26.8%	Al: 4.5%
Ge: 27.9%	Ge: 6.8%	Ge: 3.2%	Ge: 0.4%



1	2	3
Ge-rich Phase	A-15 Phase	A-2 Phase
Nb: 41.6%	Nb: 61.6%	Nb: 86.2%
Al: 31.1%	Al: 25.2%	Al: 10.8%
Ge: 27.3%	Ge: 13.2%	Ge: 3.0%



1	2
A-15 Phase	A-2 Phase
Nb: 63.6%	Nb: 86.7%
Al: 23.0%	Al: 10.7%
Ge: 13.4%	Ge: 2.6%

FIG. 4. Scanning electron micrograph showing microstructural changes with reaction. (a) Specimen reacted at 1700 °C for 5 sec; (b) specimen reacted at 1700 °C for 1 min; (c) specimen reacted at 1700 °C for 15 min.

TABLE II. Slopes and correlation for Figs. 3 and 5(a).

Temperature	Phase thickness		Grain size	
	Slope (n)	Correlation (r^2)	Slope (n)	Correlation (r^2)
1300 °C	0.42	0.96		
1500 °C	0.36	0.99	0.33	-0.99
1700 °C	0.34	-0.99	0.35	0.99
1840 °C	0.44	-0.99	0.46	-0.97

points. The growth indices obtained from the slopes of the lines vary between 0.34 and 0.44. This indicates a growth rate less than that predicted by the simplified form of Fick's second law which gives a growth index of 0.5. This reduction in growth rate must be due to the involvement of other processes as discussed above.

The growth index obtained compares with the value of 0.35 obtained by Suenaga and his co-workers^{5,6} in their study of the Nb₃Sn system. The basic difference in these two studies other than the materials is the treatment temperature which was much lower for the Nb₃Sn (700 °C) and thus re-

sulted in long reaction times (hours). However, it appears that the growth mechanisms for the A-15 phase are similar in the two cases, since in Suenaga's work, the A-15 phase (Nb₃Sn) is also sandwiched between phases rich in Nb on one side and Sn on the other side. Another reason given by Suenaga *et al.* to explain the deviation from the parabolic growth law is the effect of the increasing grain size, which tends to suppress the intermetallic layer growth.

B. Grain growth

The variation of grain growth with time for different temperatures is shown in Fig. 5(a). The straight lines obtained for the log-log plot depict a power growth law of the form:

$$G = Kt^n,$$

where G = average grain size, K = rate constant, t = reaction time, and n = growth law index.

The degree of fit of the straight lines as measured by the correlation coefficient was of the order of ± 0.97 (Table II). The growth law indices lie between 0.33 and 0.46, increasing with increasing temperature, which explains the thermally activated nature of the process.

For high purity metals and dilute alloys, an index of $n = 0.5$ for grain growth was proposed by Simpson and his co-workers.⁷ However, the results of the present studies have shown that this does not necessarily apply to alloys with the component elements in substantial concentrations. In this case, grain boundary motion may involve more complex phenomena than ordinary solute-boundary interaction and values of n less than 0.5 which vary with the system under consideration and the reaction conditions are possible. The results of this study agree with those of Suenaga and his co-workers,⁵ who obtained an experimental grain growth exponent of 0.35 ± 0.02 and a calculated value of 0.41 ± 0.06 .

An important phenomenon observed from the graphs is the change in grain size from 1500 to 1700 °C, a 200 °C temperature difference, and from 1700 to 1840 °C, a difference of 140 °C. The change is found to be much greater for the latter than the former, an effect which is more clearly seen from the isochronal curves in Fig. 5(b). This is due to an abnormal grain growth, manifesting itself in a steep rise in the isochronal curves at about 1720 to 1740 °C.

C. Phase changes

Four different phases are known to exist in the Nb-Al-Ge system at the temperatures investigated, viz.,

- (1) Ge-rich phase Nb₅(Ge,Al)₃,
- (2) Al-rich phase Nb₂(Al,Ge),
- (3) A-15 phase Nb₃(Al_{0.8}Ge_{0.2}),
- (4) A-2 phase (Nb solid solution).

All four phases generally exist in the early stages of a reaction irrespective of the temperature and are disposed as shown in Fig. 4(a). The Ge-rich phase forms the innermost layer, surrounded immediately by the Al-rich sigma phase, then the superconducting A-15 phase. All three phases are embedded in the niobium solid solution.

As the reaction proceeds at a given temperature, the Al-

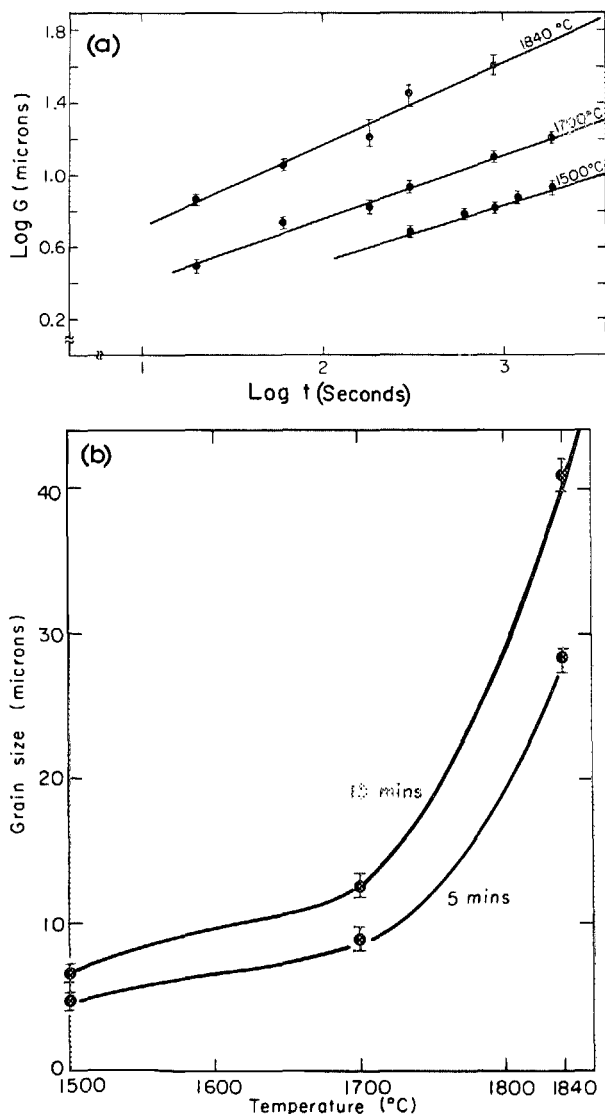


FIG. 5. Grain growth in the A-15 phase. (a) log-log plot of average grain size vs time; (b) average grain size-temperature plot (isochronal plots).

rich phase gradually transforms to the A-15 phase, Fig. 4(b). At still longer reaction times the Ge-rich phase is also transformed leaving only the A-15 phase in a matrix of niobium solid solution. It was found that on reacting at 1840 °C for 15 min, the A-15 phase occupies a greater volume of the specimen than does the niobium solid solution. The two-phase system is shown in Fig. 4(c).

Since the transformation process depends on several variables, the time required for the disappearance of the Ge-rich and Al-rich phases is not specific and for a given temperature may cover a time range. However these time ranges are generally smaller for the higher temperatures than for the lower ones. In addition, the transformations start much sooner at the higher temperatures. For example, no σ -phase was found in a specimen reacted at 1700 °C for 5 min and no Ge-rich phase at all after reacting at 1700 °C for 30 min, but all four phases continued to exist after an hour's reaction at 1300 °C. Quantitative EDAX analyses of the various compositions, Fig. 4, show slight deviations from stoichiometry. This deviation, in the case of the superconducting phase, could explain why the critical temperatures obtained by Pickus *et al.*,¹ were not as good as some of the reported values. The A-15 compositions given in Table III shows a trend towards stoichiometric composition as the reaction temperature is increased for a given time.

It must be noted from Table I and Figs. 4(a) and 4(b) that

TABLE III. Changes in A-15 composition (At. %) with time and temperature of reaction (determined by EDAX).

Readings taken at 1700 °C for 5 sec		
Element	Analysis No. 1	Analysis No. 2
Nb	61.7	70.0
Al	34.5	26.8
Ge	3.8	3.2
Readings taken at 1700 °C for 1 min		
Element	Analysis No. 1	Analysis No. 2
Nb	61.6	59.2
Al	25.2	31.9
Ge	13.2	8.9
Readings taken at 1700 °C for 15 min		
Element	Analysis No. 1	Analysis No. 2
Nb	63.6	62.2
Al	23.0	24.2
Ge	13.4	13.6
Readings taken at 1500 °C for 15 min		
Element	Analysis No. 1	Analysis No. 2
Nb	63.4	64.9
Al	26.1	23.8
Ge	10.5	11.3
Readings taken at 1840 °C for 15 min		
Element	Analysis No. 1	Analysis No. 2
Nb	64.8	64.0
Al	26.7	27.3
Ge	8.5	8.7

at short reaction times, the average thickness (size) of the various phases is usually less than 4 μm . However, the area sampled during EDAX analysis generally occupies a diameter of about 2 to 5 μm . Consequently, it is possible that in obtaining some of the phase compositions, the area under analysis by the EDAX could have overlapped the surrounding phases and resulted in a composition reading that was not precisely representative of the particular phase. The error so introduced would be greater for smaller phases or shorter times. This explains the substantial variation in readings obtained from the same sample, especially at shorter reaction times (Table III). Thus, results obtained at higher temperatures and for longer reaction times are more reliable than those obtained at lower temperatures and shorter reaction times.

IV. CONCLUSIONS

A study of the Nb-Al-Ge system has shown the existence of four phases at the beginning of a reaction, the innermost two layers, the Ge-rich and the Al-rich phases, transforming gradually to the A-15 phase as the reaction proceeds. EDAX analysis of the phase compositions (Table III), show that specimens reacted for short times and at higher temperatures have compositions closer to stoichiometry than those reacted for longer times. In other words, high reaction temperatures and short reaction times would produce the best T_c values in the presence of excess niobium, and this agrees with the work of Pickus and his co-workers,¹ whose measured T_c values were higher for shorter reaction times.

The A-15 phase thickness was observed to increase with time, for a given reaction temperature. This means an increase in the current carrying capacity, assuming a constant critical current. In addition, the average grain size was found to increase with time and temperature, the change becoming drastic above 1700 °C as a result of abnormal grain growth. This again agrees with the results of Pickus and his co-workers¹ who obtained low critical current density values at temperatures above 1600 °C. The flux lines then lack pinning centers as a result of the coarse grains. The results of this investigation indicate that the potential of the system can be fully realized by compromising on both the reaction time and temperature. However, if a means could be found for pinning the flux lines at high temperatures, then substantial current-carrying capacities could be obtained after short reaction times at high temperatures, in addition to the better critical temperatures.

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