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ABSTRACT

A kinetic study has been made of the reactions occurring in the Nb-Al-Ge system at temperatures below 1000°C. This study has resulted in a two step heat treatment prior to the A15 formation reaction to be used to control the A15 formed. It was found that a Ge rich phase can be used to control the diffusion rate of the Al into the Nb. The interface between this barrier phase and the Nb matrix serves as the reaction site for the formation of the A15.

INTRODUCTION

As man's knowledge of matter has increased, his control over it
has increased proportionately. In the field of engineering man has
studied materials to gain an understanding of their complexities and
with such an understanding he has been able to improve their properties
through chemical alloying, thermal heat treatments and other means. The
formation of the non-equilibrium martensite phase in steels to increase
their strength is an example of this control. In the relatively new
field of superconductivity, research is being performed in the hopes that
eventually a more complete understanding of this phenomenon will be gained.
Superconducting properties are very dependent upon material parameters
such as chemical composition, grain size, impurities present, mechanical
deformation, and heat treatments as well as other parameters. At present
the majority of this research is being performed on the systems which have
the A15 type superconducting phase shown in Fig. 1. The high Tc's of the
A15 type phase accounts for this work (Nb_3Ga: 20.3°K; Nb_3(Al, Ga):
19.0°K, Nb_3Ge:23.2°K; and Nb_3Al: 18.9°K).[1-4]

The A15 system used in this study was the niobium-aluminum-germanium
ternary system. Recognized as a system with one of the highest upper
critical fields (410 kG at 4.2°K[5]), this ternary system has recently been
the subject of many research investigations, following its discovery by
Matthias, et al., in 1967.[6] As with the other A15 systems, much of this

research involves the development of a fabrication process suitable for use on a commercial scale.

Previous research on the Nb-Al-Ge system carried out at this laboratory[7,8] was concentrated on relatively high reaction temperatures used to form the A15 superconducting phase. This research showed a dependence of the critical transition temperature, T_c, upon the temperature used to form the A15 phase. T_c is the temperature at which a sample changes from the superconducting state to the normal resistive state when the sample is not in a magnetic field (H=0). The dependence of T_c on the reaction temperature was direct, the lower the reaction temperature the lower was the T_c. Previous research[7] showed that the critical current carrying capacity, J_c, also was dependent upon the temperature used to form the A15 phase. J_c is the current density at which a sample changes from the superconducting state to the normal resistive state at a given value of the applied magnetic field. J_c was found to increase as the reaction temperature used to form the A15 phase was decreased. This is due to the smaller A15 grains formed at the lower reaction temperatures. As the grain size decreases the volume fraction of the grain boundaries increases in the A15 phase. Grain boundaries are recognized as effective flux pinning sites, and thus account for the increase in J_c.

Other researchers[9] have shown that the maximum T_c in the binary A15 type Nb-Al system occurred with an aluminum content slightly greater

than that corresponding to the stoichiometric A15 compound. Figure 2

shows the results of that study. This fact coupled with the increase in

J_c was the impetus for the present research.

The goal of this research was to determine a kinetic approach

whereby the aluminum concentration of the A15 could be increased above

that of stoichiometry, at a low reaction temperature. With such an

approach, hopefully, the T_c would be high due to the high aluminum

concentration and the J_c would be high due to the small grains formed

at the low reaction temperature. Referring to the Nb-Al-Ge phase

diagram,[10] Fig. 3, this would correspond to entering the A15 region from

the aluminum rich side. At higher reaction temperatures it was found

that as the solubility of aluminum in niobium increases the tendency to

form the A2 solid solution increased, resulting in an A15 phase which

had a lower than stoichiometric aluminum concentration. The principal

A15 reaction temperature used for this work was 1000°C. This temperature

would allow the use of copper as a cladding material to aid in the wire

drawing process, without the necessity for its removal prior to the A15

formation heat treatment. Copper is also recognized for its ability

to stabilize superconductors due to its high thermal conductivity.

EXPERIMENTAL PROCEDURE

The samples used in this study were prepared using the powder metallurgy technique,[11] developed at the Lawrence Berkeley Laboratory, which is illustrated in Fig. 4. The research was performed on samples in the as-infiltrated condition. Niobium powder of 99.92% purity made by the hydride-dehydride process was purchased from Wah Chang. The -270 mesh as received powder was sieved using standard mesh screens to yield a powder of -270 +400 mesh size. The powder was then placed in a rubber tube with the ends sealed. Once in the rubber tubes the powder was cold isostatically compacted at a pressure of 30,000 psi for 1 minute and then removed from the rubber tubes. These green compacts, possessing low strength and ductility, were then placed in an Abar Model 90 vacuum furnace for sintering. The details of this furnace are illustrated schematically in Fig. 5. The samples were heated at 2250°C for 15 minutes in a vacuum on the order of 10^{-5} mm Hg. After sintering, the compacts were allowed to furnace cool under vacuum to approximately 650°C. The compacts, with a porosity of approximately 20%, were then lowered into a bath of molten Al-Ge alloy maintained at 650°C without exposing the bath or the compacts to the atmosphere. The composition of the bath was either the eutectic proportion (70% Al-30% Ge) or 80% Al-20% Ge.* Figure 6 shows these alloys on the phase diagram.[12]

* All percentages in this report are atomic.

The compacts were immersed in the bath for 30 seconds during which time the furnace was backfilled with helium to a pressure of 640 mm of Hg. This was done to insure complete infiltration. The fully dense samples produced by this procedure measured approximately 0.20 in. in diameter by 2.0 in. in length. Reaction samples .25 in. in length were then cut from these rods. Samples that were to be reacted longer than one hour were encapsulated in quartz tubes after evacuating and backfilling the tubes twice with helium to a pressure of 640 mm of Hg. Samples that were to be reacted less than one hour were placed in the Abar furnace and reacted in a helium atmosphere at a pressure of 640 mm of Hg after the furnace had been evacuated and backfilled twice with helium. After heat treatment the samples were cut in half. One half was mounted in Buehler epoxy and polished. Final polishing was done using one micron diamond paste. After polishing, the samples were etched for approximately 5 seconds using a solution of equal parts of HF, H_2SO_4, and H_2O, with 10 drops of H_2O_2 added to every 15 ml of the solution. This half of the sample was then analyzed using a scanning electron microscope equipped with an EDAX (Energy Dispersive Analysis of X rays) attachment. The EDAX attachment was used to analyze the composition of the phases present. The other half of the sample was used for critical transition temperature measurements. A standard inductive method was used with a Ge thermistor for temperature determination with an estimated uncertainty of 0.1°K. The reported values for T_c correspond to the points showing the highest rate of change of inductance in the transition region.

RESULTS AND DISCUSSIONS

As stated earlier in the report the goal of this research was to develop a kinetic approach to increase the aluminum concentration in the A15 phase of the Nb-Al-Ge system. The kinetic approach developed involves a two step heat treatment prior to the A15 formation heat treatment. For purposes of clarity these two heat treatments and their effects on the morphology of the sample will be treated separately.

Primary Heat Treatment

Following infiltration with the eutectic alloy or the 80% Al-20% Ge alloy the sample has the morphology shown in Fig. 7. The pores have been filled with the alloy and no reaction between the niobium and the aluminum or the germanium can be detected. After infiltration the sample is heated for one hour at 600°C. The morphology of the sample following this primary heat treatment is illustrated in Fig. 8. As shown in Fig. 8, two things have occurred during this heat treatment. First the germanium has changed from the eutectic lamellar structure to a single phase (Phase 1, Fig. 8) consisting entirely of germanium. At the same time this was occurring the aluminum has reacted with the niobium to form a phase which is 18.9% Nb-79.1% Al-2% Ge, (Phase 2, Fig. 8). Referring to the Al-Nb phase diagram[13] (Fig. 9) this phase corresponds to the intermetallic compound $NbAl_3$ rich

in Al. As shown by Fig. 10 this phase is very stable at 600°C with its composition remaining unchanged even after 8 hours at 600°C. One hour at 600°C is needed to insure that all of the aluminum has reacted with the niobium. Note the position of the aluminum in relation to the germanium -- the aluminum-niobium phase is surrounding the unreacted germanium (Fig. 8).

Secondary Heat Treatment

With the aluminum fully reacted with the niobium following the primary heat treatment the sample is ready for the secondary heat treatment which consists of 5 minutes at 750°C. The morphology of the sample following this heat treatment is shown in Fig. 11. As shown in Fig. 8 and 11, two things have happened during this short heat treatment. First, the germanium has reacted with the niobium to form a phase which is 25.6% Nb-24.7% Al-49.7% Ge. Second, the position of the aluminum relative to the germanium has changed. Referring to the line scans in Fig. 8 and 11, the aluminum-niobium phase, (Phase 1, Fig. 11), is now surrounded by the germanium rich phase, (Phase 2, Fig. 11). At this point the aluminum is constrained from moving about by two things. First, the aluminum has reacted with niobium and is tied up in Phase 1 of Fig. 11. Second, the aluminum is surrounded by the germanium rich phase with only a slight bit of it being in that phase. This germanium rich phase acts as a barrier to contain the aluminum. With the aluminum reacted and contained in this manner the sample is ready for the A15 formation heat treatment.

A15 Formation

Again the principal A15 formation reaction temperature for this
work was 1000°C. this temperature is below the melting point of
copper (1080°C) and will allow its use as a cladding material during the
wire drawing phase of fabrication without the necessity for its
removal prior to the A15 formation heat treatment.

Figure 12 shows the change in T_c with time as the sample
is held at 1000°C. For reaction times of less than 24 hours for these
samples the change in inductance with temperature was so gradual that
accurate T_c measurements could not be made. As illustrated by the
figure, under these conditions there occurred a maximum in the T_c after
48 hours at 1000°C. The morphology of a sample reacted for 48 hours at
1000°C with a T_c of 11.6°K is shown in Fig. 13. Note the composition of
the A15 phase, (Phase 3, Fig. 13), 62.6% Nb-32.7% Al-4.7% Ge. The
aluminum concentration is substantially above that of stoichiometric A15
which along with possible residual strain account for the low T_c. Galev
and Rabin'kin have reported the effects of hydrostatic pressure and
residual strain on the Nb-Al-Ge system.[14] Also note the change in the
composition of the barrier germanium rich phase (Phase 2, Figs. 11 and
13). The aluminum concentration has decreased from 24.7% to 14.9%.
It appears that some, if not all, of the aluminum in the A15 phase has come
from the barrier phase.

Previous research[6] at this laboratory has produced, without using

this kinetic approach, A15 which is on the aluminum lean side of

stoichiometry. Using the kinetic approach the A15 is now on the

aluminum rich side. For a sample reacted 4 hours at 1000°C after the

primary and secondary heat treatments, the change in inductance with

temperature was more pronounced than that for a sample reacted 4 hours

at 1000°C without the primary and secondary heat treatments. Presumably

this indicates that the germanium rich barrier phase enhances the

homogeneity of the A15 formed.

A15 formation temperatures less than 1000°C were also investigated.

However in the samples reacted at these lower temperatures the A15 layer

formed was too thin for x-ray analysis for composition. Figure 14

illustrates the change in T_c with time as samples are reacted

at 850°C. Although the onset of superconductivity remained at or near 12°K

for these samples, the homogeneity of the samples showed improvement up

to 72 hours at 850°C, after which the T_c and the homogeneity of the A15

deteriorated. The maximum T_c under these conditions at 850°C occurred

at 72 hours and was equal to 11.4°K. Consistent with earlier research,

the T_c was found to decrease with A15 formation temperature. Table 1

illustrates this point for reaction temperatures investigated which were

above 1000°C.

Anneals

Improvements in T_c's on the order of 1-2°K have been reported
following long heat treatments at low temperatures (~750°C) following
A15 formation. These "ordering anneals" have had the most effect on
samples reacted at high temperatures (>1200°C). The influence of
these anneals on samples reacted at 1000°C was investigated. Several
samples were prepared using the primary and secondary heat treatments
followed by 48 hours at 1000°C. After encapsulation in quartz tubes these
samples were annealed for various times at 750°C. Subsequent T_c
measurements showed no increase in the T_c, even after annealing for 168
hours at 750°C. It is concluded from this that the amount of disorder
occurring in the A15 formed at 1000°C in these samples was small.

Effect of Mechanical Reduction

It should be remembered that up until this point no mechanical
reduction has been performed on the samples used in this study, either prior
to or following any of the heat treatments. To gain some insight into the
effect of mechanical reduction on the formation of the A15 phase, a
series of samples were prepared in the following manner. Following the
secondary heat treatment a rod approximately 1.5 in. long by 0.34 in. in
diameter was placed in a copper tube and form rolled until the diameter
of the rod was 0.225 in. This was a reduction ratio of 66%. After
rolling, the copper was removed and the rod cut into reaction samples
0.25 in. in length. These samples were then heat treated in the same
manner as previous samples.

For all of the rolled samples the T_c was found to be lower than that of similarly reacted unrolled samples. This reduction in the T_c may be due to the change in A15 composition as well as residual strain[15] that may be present in the samples. For a sample given the primary and secondary heat treatments, rolled, and then reacted 48 hours at 1000°C, the superconducting phase had the following composition 54.2% Nb-43.9% Al-1.9% Ge. This represents an increase in the aluminum concentration of 11.2% and a decrease in the germanium concentration of 2.8% over that of a similarly reacted unrolled sample. Two possible mechanisms for this change in composition may be occurring either separately or concurrently. First, it is possible that rolling has impaired the ability of the germanium rich barrier phase to control the aluminum content in the A15 phase. Second, rolling may have imparted crystallographic defects to the niobium matrix which allows it to form an A15 phase richer in aluminum. In either case, this represents a definite means for control over the aluminum content of the A15 phase.

CONCLUSIONS AND RECOMMENDATIONS

In conclusion it can be said that the aluminum content of the A15 phase of the niobium-aluminum-germanium system may be increased to the aluminum rich side of the A15 region through the use of a kinetic approach. This kinetic approach involves the use of a two step heat treatment prior to that used for the formation of the A15 phase. The primary heat treatment consisted of heating the sample for one hour at 600°C. The secondary heat treatment of 5 minutes at 750°C creates a barrier phase around the niobium-aluminum phase formed in the primary heat treatment. Should the continuity of this barrier phase be disrupted, as by mechanical reduction, the aluminum content of the A15 will be substantially above that of stoichiometry with a resulting detrimental effect on the superconducting parameter T_c.

With the two step heat treatment sequence completed the material is ready for the A15 to be formed. At a reaction temperature of 1000°C, there was found to be a maximum in the T_c which was reached after heating the sample for 48 hours. This maximum in the T_c was 11.6°K. The critical transition temperature occurs over a narrower and higher temperature range when the kinetic approach is used indicating an improvement in the stoichiometry and the homogeneity of the A15 formed at 1000°C.

Post heat treatment anneals at 750°C were ineffective for improving the T_c of the samples reacted at 1000°C.

From the results of this study, the following points are recommended for further research. A higher degree of control over the aluminum content in the A15 phase may be possible with changes in the barrier phase created during the secondary heat treatment. One possible means of changing this barrier would call for the germanium concentration of the bath used during the infiltration process to be increased. This would place more germanium in the pores for reaction, thus allowing a thicker barrier phase to be created. A thicker barrier may result in a reduction in the aluminum available to form the A15.

Future research should also investigate the effect of mechanical reduction prior to the primary heat treatment on the A15 stoichiometry. Wire drawing the sample prior to any reaction heat treatments would be easier due to the lack of the intermetallic phases created during the reaction heat treatments.

ACKNOWLEDGMENT

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Table 1

Reaction temperature (°C)	Time (sec)	T_c (°K)
1300	60	13.6
	900	14.1
1200	540	14.7
	900	12.8
1100	180	13.2
	540	12.7
1000	24 hr	11.2
	48 hr	11.6
850	24 hr	11.3
	72 hr	11.4

XBL 784—530

FIGURE CAPTIONS

1. Structure of the A15 phase.

2. Critical temperature vs. composition for Nb_3Al from R.E. Seimens
    and D.J. Griffiths.

3. Nb-Al-Ge phase diagram at 1840°C from A. Müller.

4. Schematic diagram for the infiltration process for producing
    multifilamentary superconducting wire.

5. Schematic diagram of the Abar furnace: (1) extension tube;
    (2) tantalum rod; (3) back filling port; (4) electrical leads;
    (5) heating element; (6) niobium specimen; (7) radiation shields;
    (8) water cooled wall; (9) W-5% Re vs. W-26% Re thermocouple
    junction; (10) vacuum connection; (11) quartz tube;
    (12) graphite crucible; (13) liquid Al-Ge alloy, and (14)
    resistance heater.

6. Al-Ge eutectic phase diagram.

7. Optical micrographs of as-infiltrated samples: (a) infiltrated with
    eutectic Al-Ge and (b) infiltrated with 80% Al-20% Ge.

8. SEM micrographs of a sample reacted 1 hour at 600°C, (a) high
    magnification, (b) Ge line scan of (a), (c) Al line scan of (a),
    (d) low magnification.
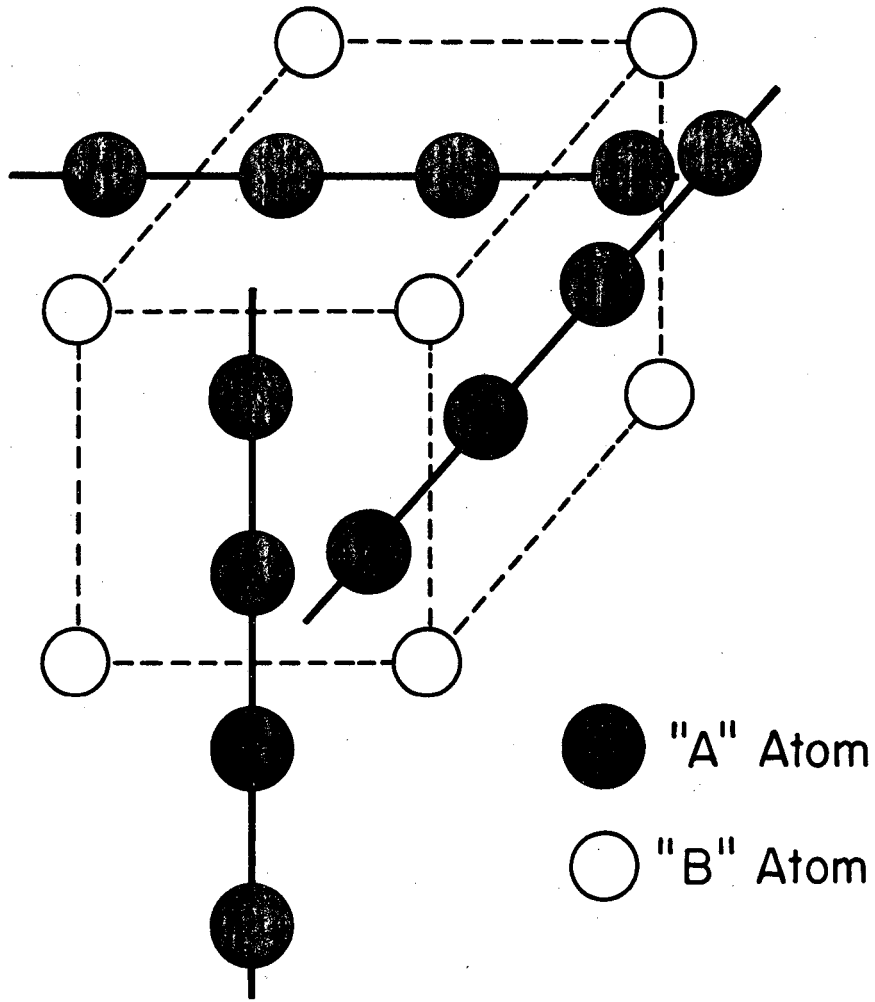
A15 structure
formula type A₃B

Figure 1

XBL 784—526

Figure 2

Aluminum At. %

XBL 761-6346

Figure 3

THE INFILTRATION PROCESS FOR PRODUCING MULTIFILAMENTARY SUPERCONDUCTING WIRE

Figure 4

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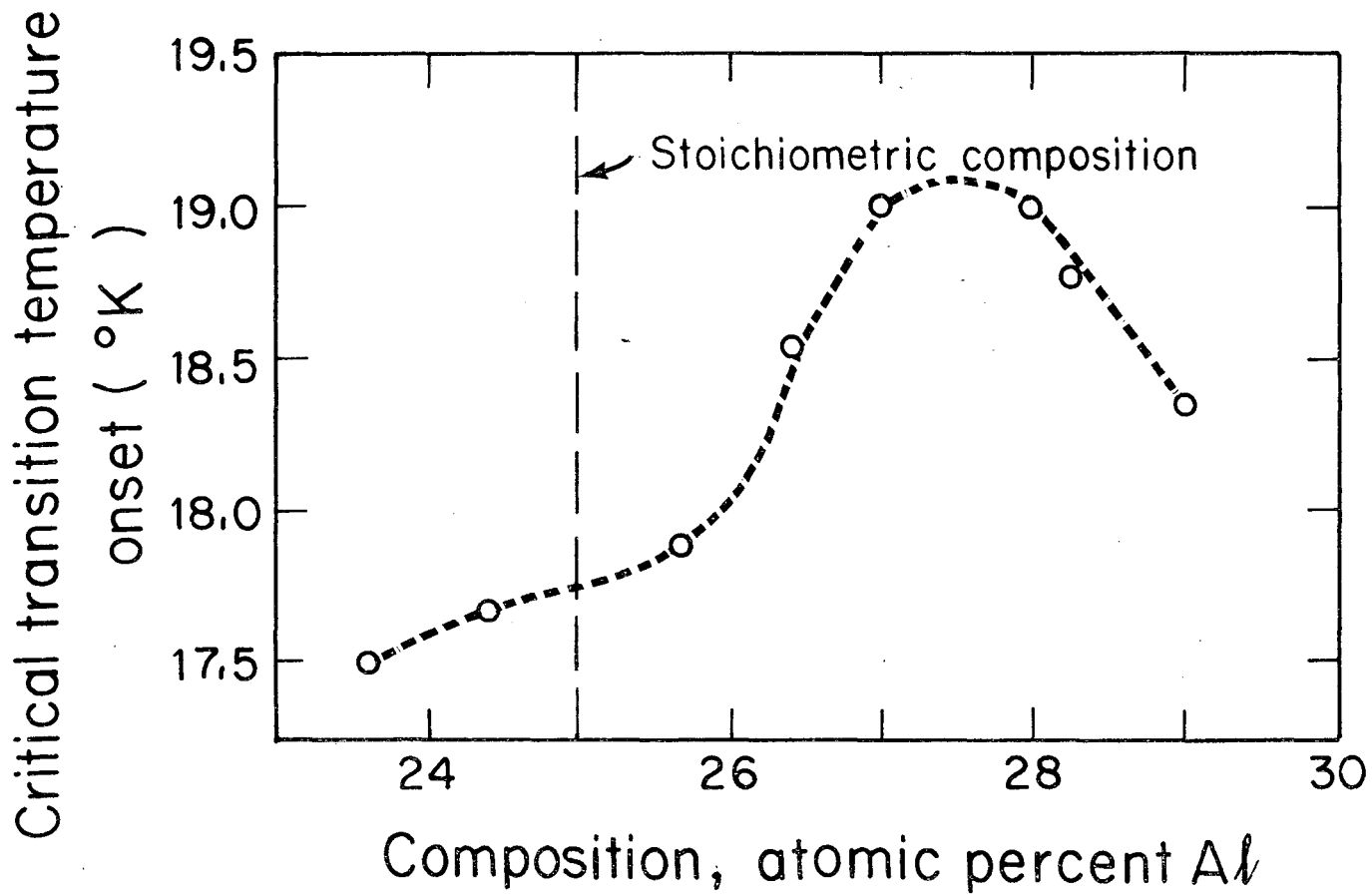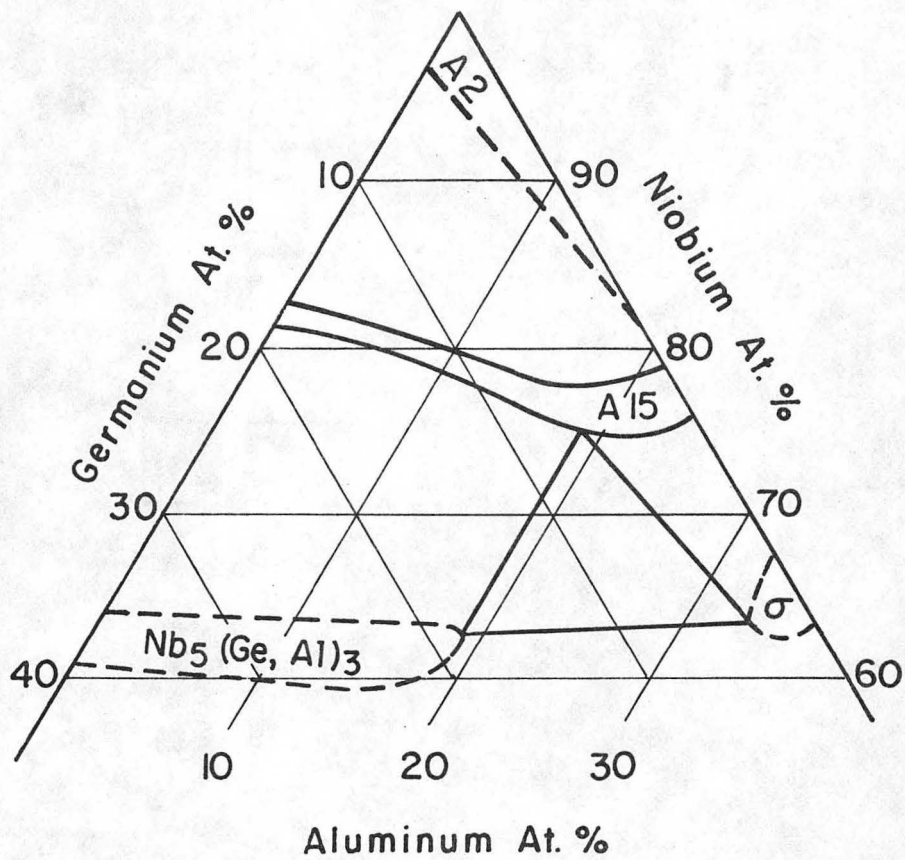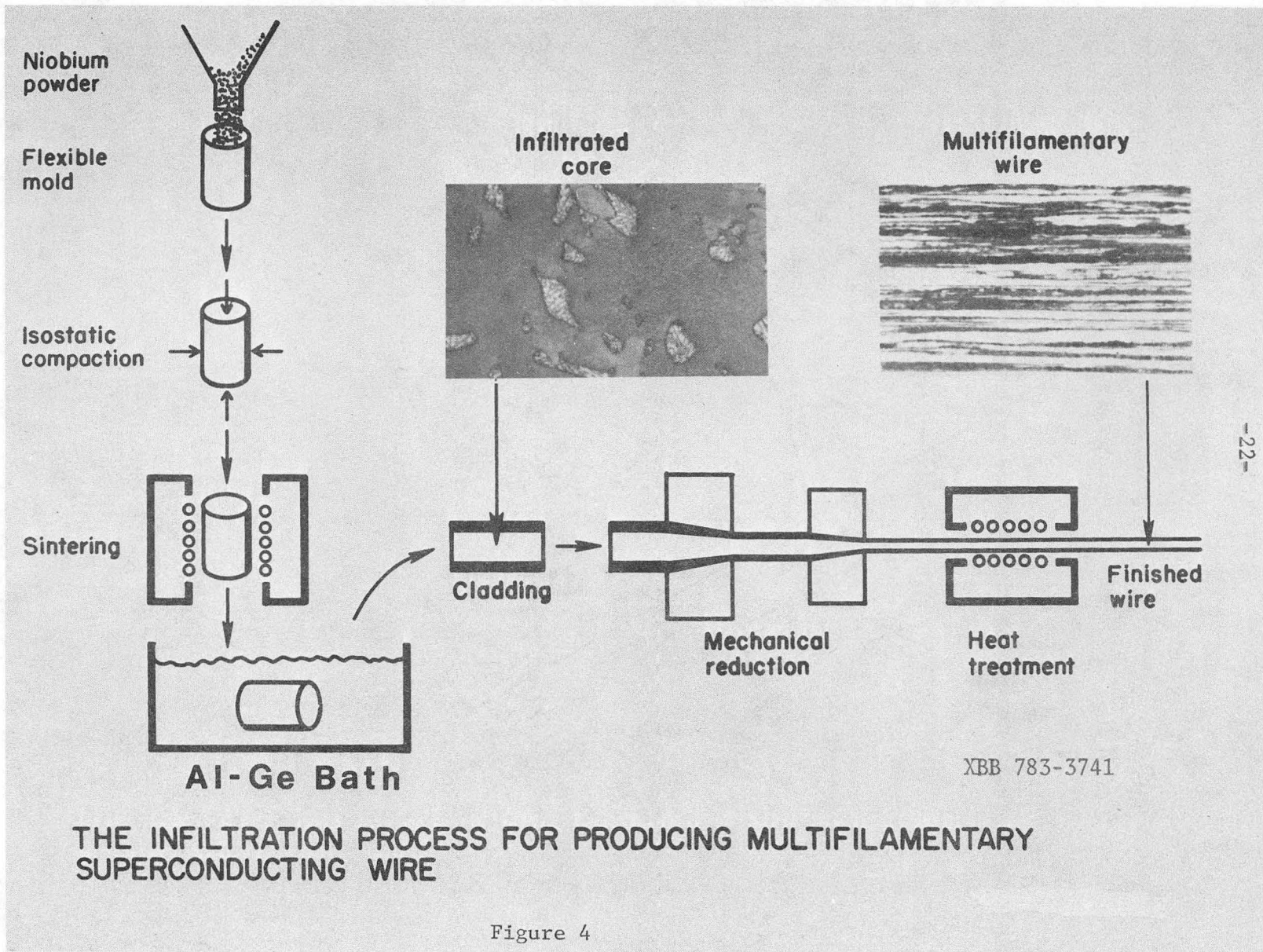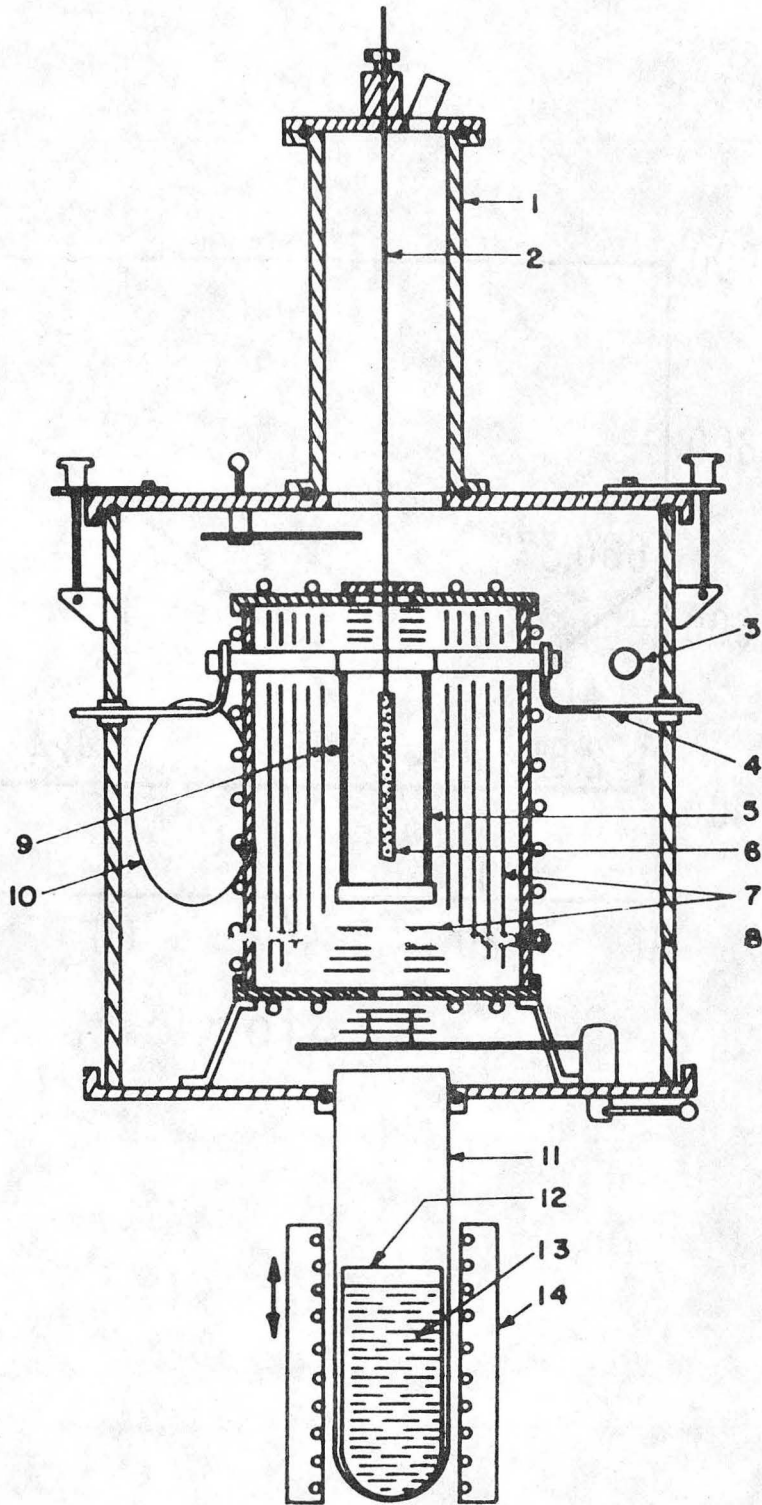
XBL 7210-7043

Figure 5

XBL778-1802

Figure 6

10 μm

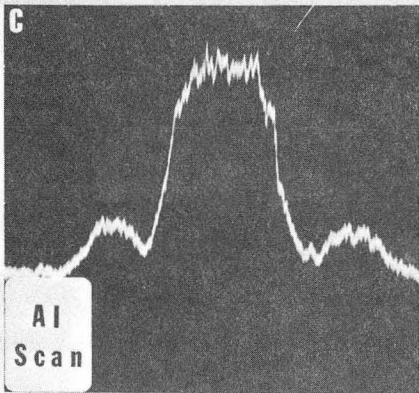XBB 783-3742

Figure 7

1 Hour at 600°C

Phase 1	Nb	0.	A%
	Al	0.	
	Ge	100.	
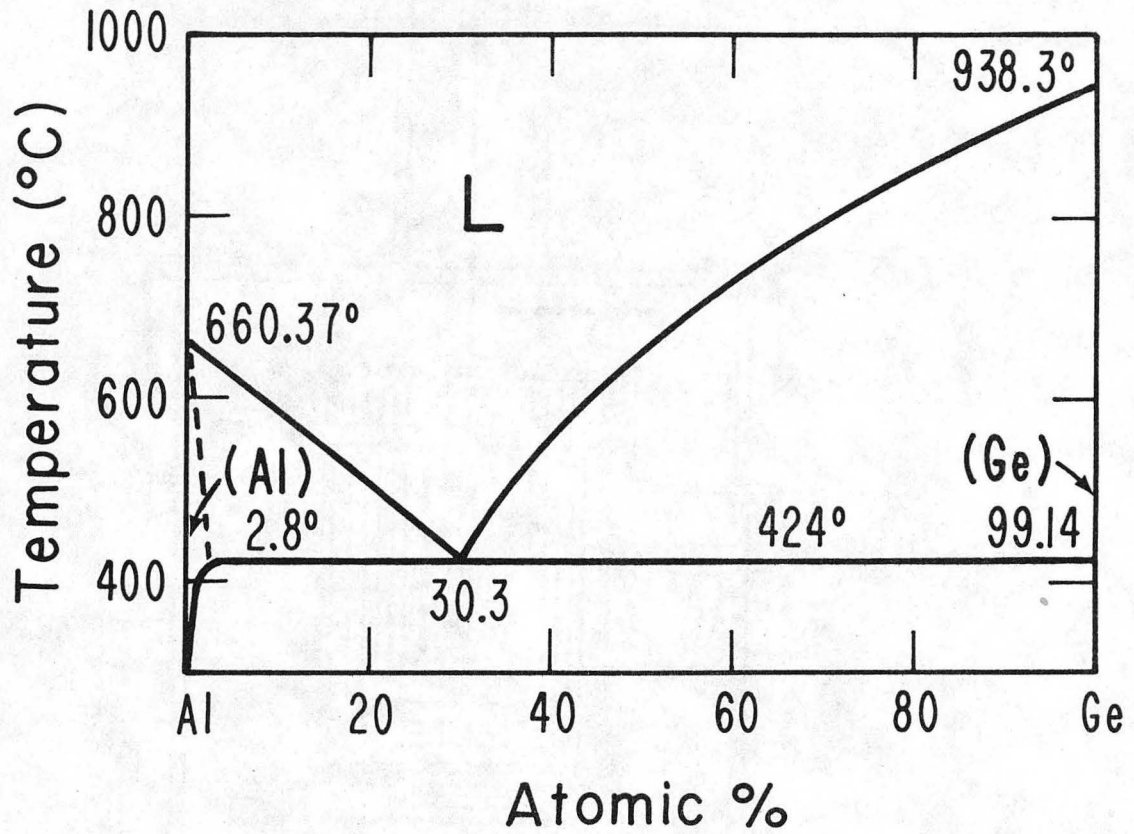
Phase 2	Nb	18.7
	Al	78.9
	Ge	2.4
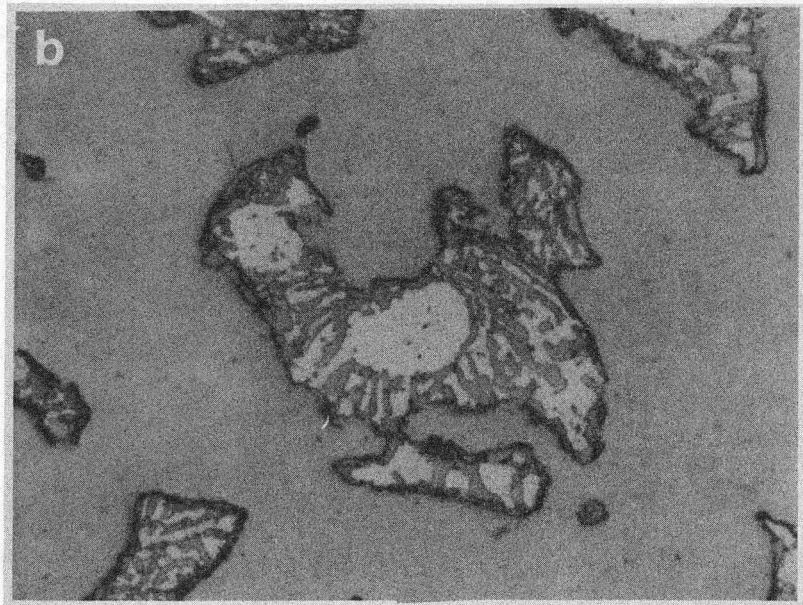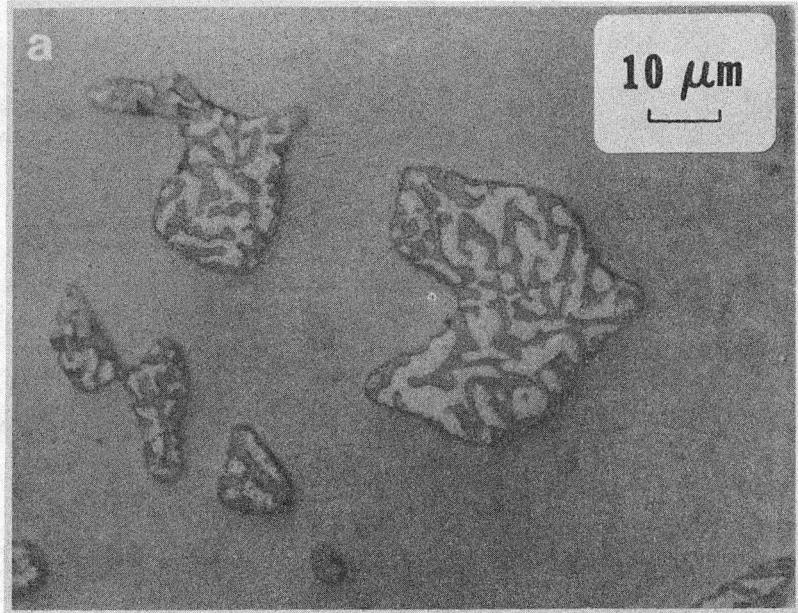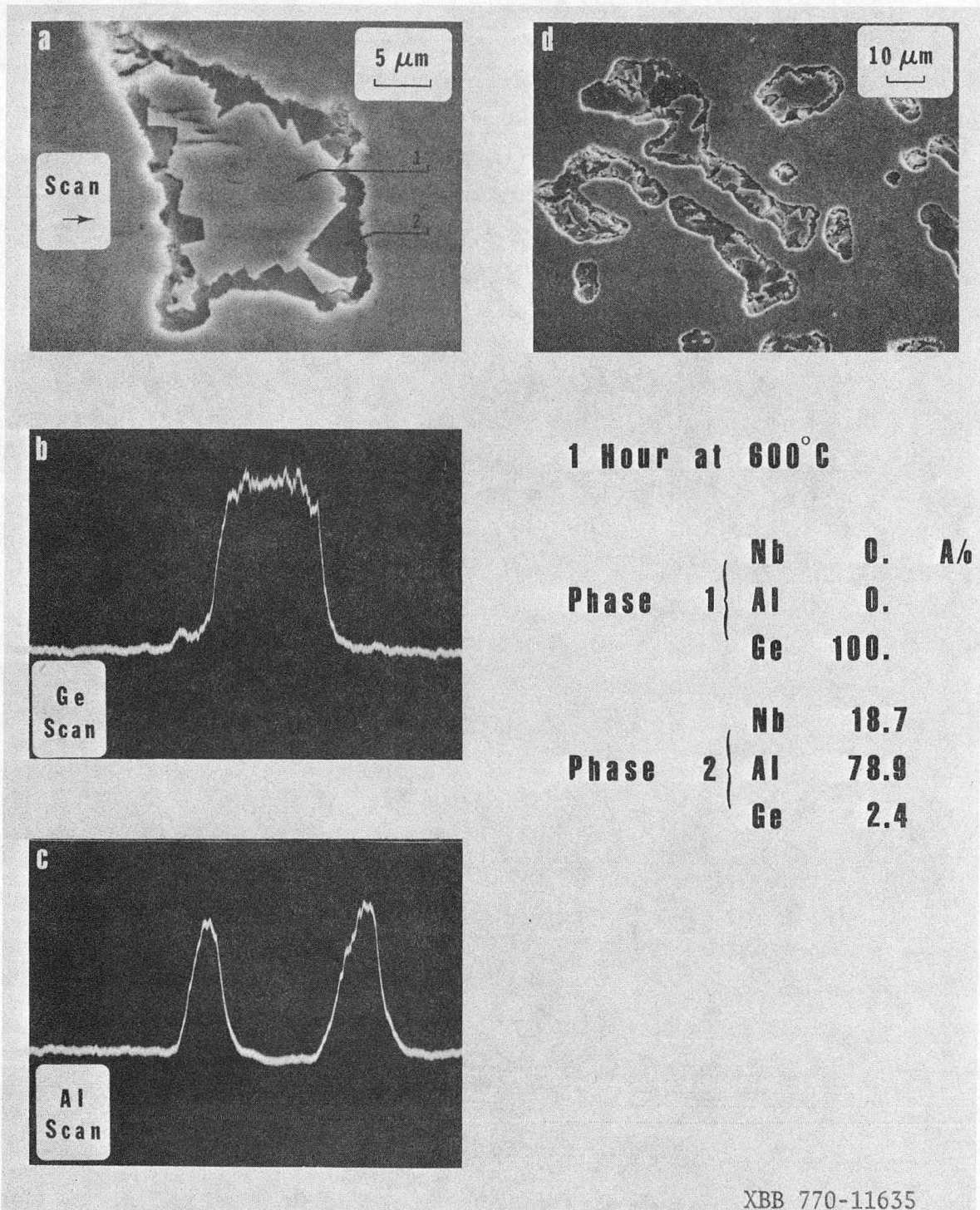
XBB 770-11635

Figure 8

XBL7110-7429

Figure 9

Figure 10

XBL 784—527

1 Hour at 600°C
5 Min at 750°C

		Nb	18.7	A%
Phase	1	Al	78.9	
		Ge	2.4	
		Nb	25.6	
Phase	2	Al	24.7	
		Ge	49.7	
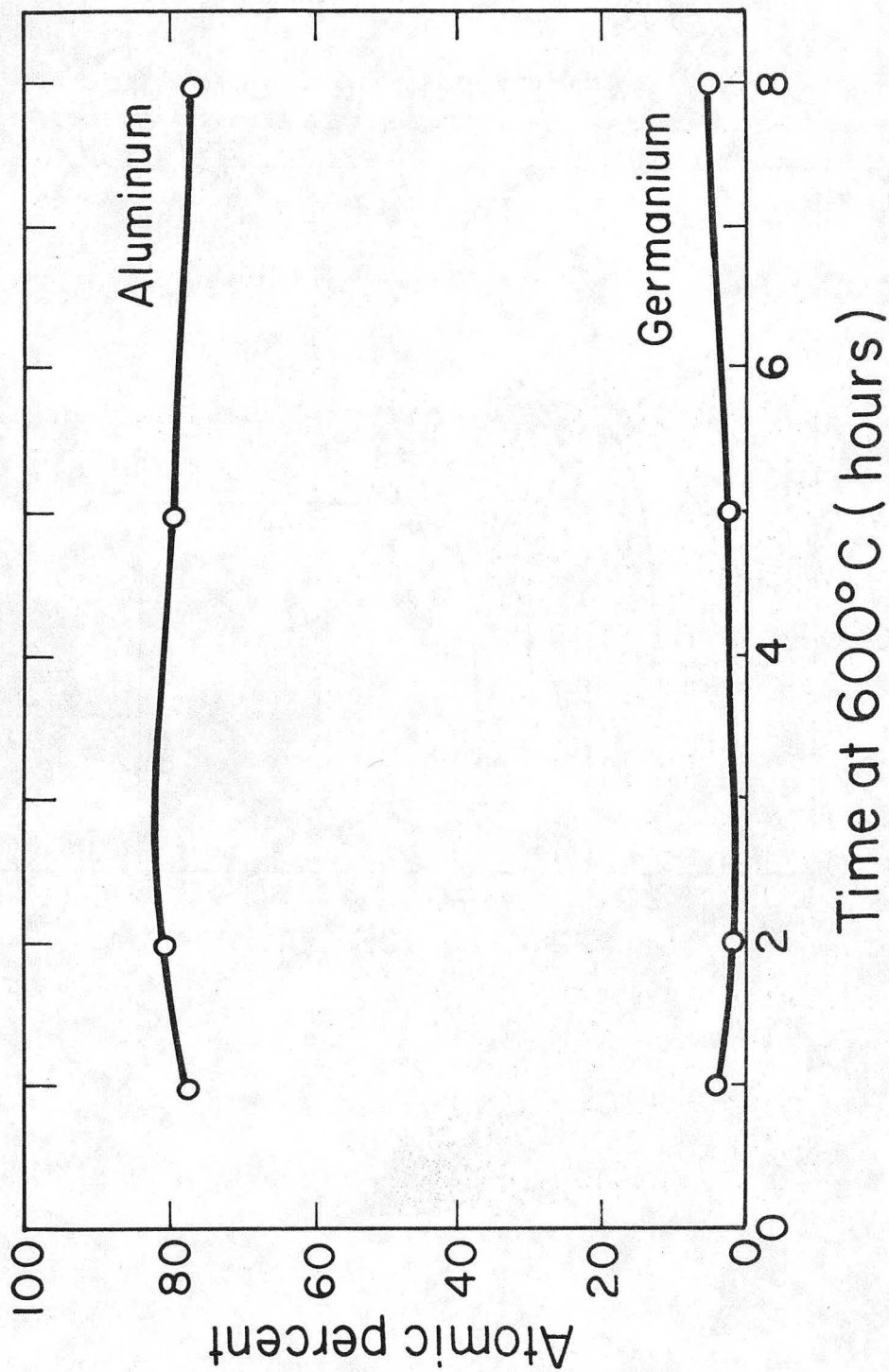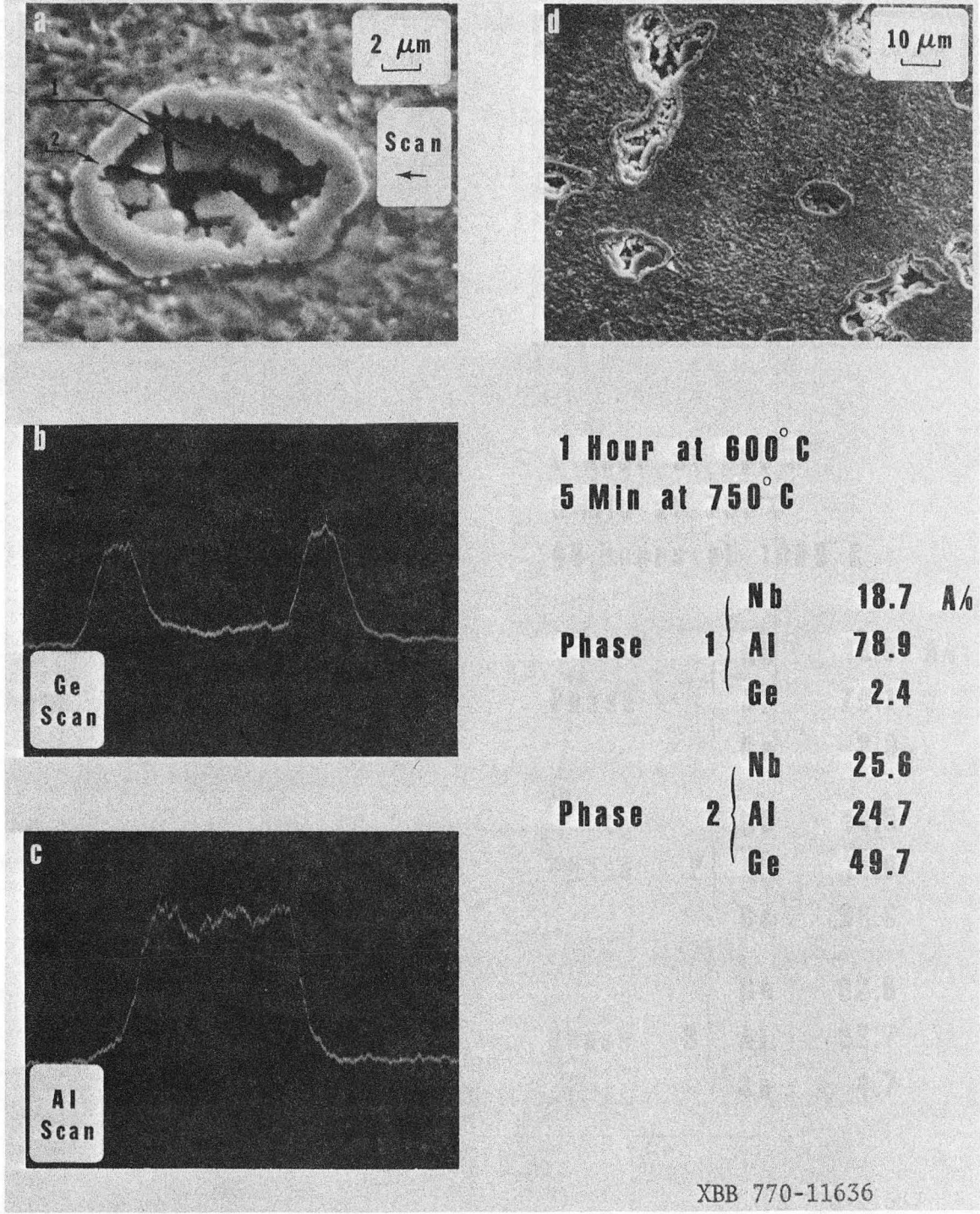
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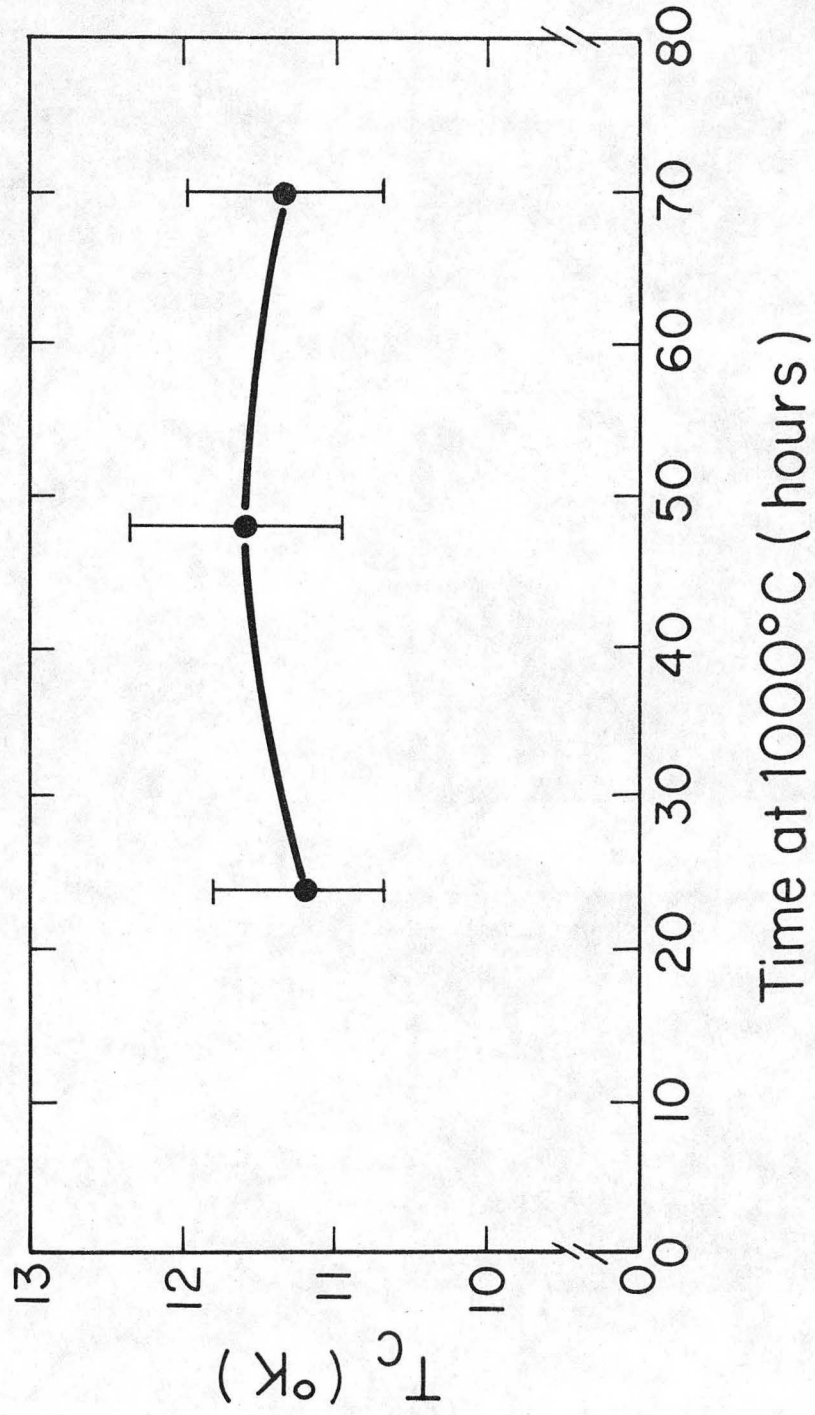
Figure 11

Figure 12
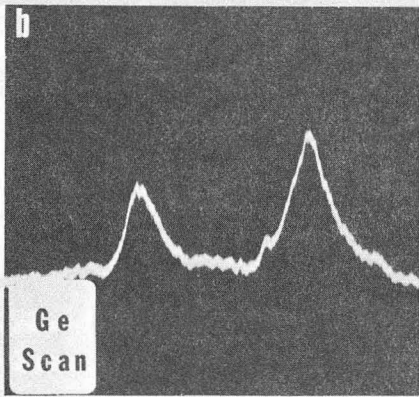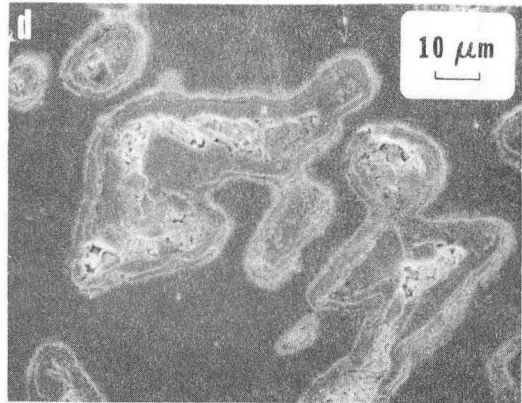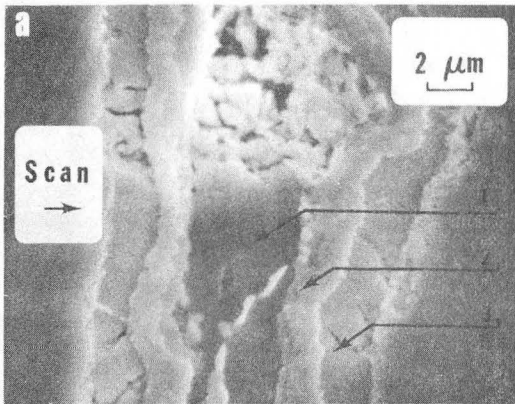
XBL784-528

1 Hour at 600°C
5 Min at 750°C
48 Hours at 1000°C

Phase	1	Nb	18.9 A%
		Al	79.1
		Ge	2.0
Phase	2	Nb	46.5
		Al	14.9
		Ge	38.6
Phase	3	Nb	62.6
		Al	32.7
		Ge	4.7

XBB 770-11637

Figure 13

Figure 14

XBL 784-529