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A KINETIC STUDY OF THE FORMATION OF THE SUPERCONDUCTING A15 PHASE IN THE Nb-Al-Si SYSTEM

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(M. S. thesis)

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and 1700°C for 15 seconds was the most suitable for the secondary heat treatment. The highest critical temperature found thus far was 18.78°K.

I. INTRODUCTION

Superconductivity is the name given to a remarkable combination of electric and magnetic properties which occurs in certain metals when they are cooled to extremely low temperatures. Kamerlingh Onnes succeeded in liquefying helium in 1908. He discovered that the electrical resistance of mercury fell sharply after it had been cooled by using liquefied helium. He also recognized that at 4°K mercury passed into a new state with electrical properties quite unlike common metals. This new state was called the 'superconducting state'.

Up to the present time, about half of the metallic elements and also a number of alloys have been found to become superconducting at low temperatures. The most popular superconducting material commercially available is niobium titanium, which has a critical temperature of 10°K. This alloy does not have good high field properties compared to other alloys, but it has a ductile nature, and therefore can be produced by conventional methods.

Most of the intermetallic compounds with higher superconducting properties are very brittle and are hard to fabricate. Many research projects have focused on these materials in order to make them available in the required forms. Several processes have been developed such as: the powder metallurgy approach by Bell Laboratory; the tape process by General Electric Co.; the "Bronze" technique and recently multi-filamentary wire by Lawrence Berkeley Laboratory's infiltration process.[1] Among these, the infiltration process shows much promise and many researchers believe that it will be used by major companies to fabricate superconductors in the near future. The "Bronze" process is also

attractive and has been effective in the fabrication of niobium tin (Nb_3Sn) and vanadium gallium (V_3Ga) composite superconductors. However, this process proved ineffective for aluminum-containing compounds which have higher critical fields and temperatures.

In contrast, the multifilamentary wire developed by Lawrence Berkeley Laboratory has proved to be effective not only for niobium tin (Nb_3Sn), but also for Nb_3Al, $Nb_3(Al,Ge)$, and, as now reported, for $Nb_3(Al,Si)$ compounds.

Previous research[3] with $Nb_3(Al,Si)$ has focused on infiltration temperature and time to obtain a composite free of intermetallic compounds. The presence of intermetallic compounds affects the ductility of the material and causes difficulties in the wire drawing stage.

The scope of this research is to use the kinetic approach to observe the behavior of the $Nb_3(Al,Si)$ system at elevated temperatures. From these observations, an optimized method to obtain the A15 phase will be sought to achieve a high critical temperature superconductor.

II. EXPERIMENTAL APPARATUS & PROCEDURES

1. Experimental Apparatus

a) Isostatic Press: This instrument was designed by Lawrence Berkeley Laboratory. A schematic diagram is shown in Fig. 1. It is comprised of a central cylinder which can be raised up and compressed to the desired pressure.

b) A-Bar furnance: A heating element is located in the central part of the vacuum shield. The bottom of the furnace is connected to a quartz tube containing a graphite crucible. Aluminum-Silicon of eutectic composition is contained in the crucible and a porous niobium sample is attached to a movable rod so the sample can be lowered to the crucible position easily. The lowest pressure it can achieve is in a range of 1 to 5 x 10^{-6} mm Hg. A complete diagram of the furnace is shown in Fig. 2.

c) Scanning Electron Microscope (SEM): This instrument is used to scan the microstructure of the material. It is connected to an Energy Dispersive Analysis of X-rays (EDAX). EDAX is an electron probe micro-analyzer which uses X-rays[2] to determine phase compositions.

d) Form rolling equipment: A motor is attached to two small grooved rolls. The distance between these rolls can be adjusted by a handle. This instrument is used to decrease the diameter of the material prior to the wire drawing stage. A schematic is shown in Fig. 3.

e) Wire drawing equipment: It consists of a motor which is connected to a clamp by several feet of cable. The clamp is attached

to the wire that was reduced to a desired dimension by drawing it through a carbide die as shown in Fig. 4.

2. Experimental Procedures

a) The following is a brief discussion on preparing an infiltrated sample.[3] It requires six steps to go from a powder to a final superconducting wire. These steps are: 1) isostatic compression of the niobium powder to achieve the desired porosity and green (i.e. unsintered) strength; 2) sintering the niobium rod to gain strength and ductility; 3) infiltrating the sintered porous body with Al-Si eutectic alloy to fill the pores with eutectic alloy; 4) providing a copper jacket around the infiltrated core for mechanical reduction; 5) mechanical reduction to obtain a multifilamentary wire with a desired diameter; 6) diffusion heat treatment to obtain $Nb_3(Al,Si)$ (A15) filaments. A schematic is shown in Fig. 5. The morphology of an infiltrated sample is shown in Fig. 11.

Nb powder having a size of -270 + 400 mesh was compacted in a rubber mold to a pressure of 30 ksi. The porosity of the 3/16 inch diameter green compact was determined to be 22%. The niobium rod was then sintered in the A-Bar furnace at 2200°C for 15 minutes. The sintering pressure was about 3×10^{-5} mm Hg. This pressure affects the ductility and the hardness of the material; therefore it should be kept as low as possible. After the rod was properly sintered, its temperature was decreased to about 600°C for a period of time, after which it was immersed in a 580°C Al-Si eutectic bath. After immersion, the chamber was backfilled with helium to atmosphere pressure as fast as possible with immersion of the porous body lasting exactly

30 seconds. The sample was then slowly cooled to prevent the formation of a fibrous structure in the Al-Si eutectic. This can be accomplished by either of the following two methods: 1) raise the small furnace up to the level corresponding to the position of the sample and slowly cool afterward (Fig. 6); 2) pull the sample to the level of the heating element in the A-Bar furnace and then cool slowly. The morphology of an infiltrated sample is shown in Fig. 11.

b) *A15 formation in infiltrated rod:* Infiltrated rods were cut into pieces about 0.1 to 0.2 inch long and wrapped with tantalum foil. These samples were contained in quartz tubes prior to heat treatments. Tantalum foil was used to prevent reactions occurring between the sample and quartz. These tubes were then backfilled with helium gas to 640 mm Hg. This pressure prevented Al from evaporating out of the sample and coating the inside surface of the tube at elevated temperatures. The tubes were then sealed at both ends.

The sample was heated at an elevated temperature of 650°C for 1 hour (Fig. 7) or 600°C for 11 hours (Fig. 8). Either process was found to be suitable for the first heat treatment. These treatments produced approximately the same composition. A Scanning Electron Microscope (SEM) and Energy Dispersive Analysis of X-rays (EDAX) were used to determine the compositional relationship (quantitative analysis) in the various phases present. The composition in Figs. 7, 8 and 9 are in weight per cent.

For the second heat treatment, the sample was heated at 1700°C for 15 seconds to obtain $Nb_3(Al,Si)$ (A15) (Fig. 9). The critical temperature (T_c) was measured by a standard inductive method using

a Ge thermistor for the temperature determination with an estimated uncertainty of 0.1°K. The reported values correspond to the points showing the highest rate of change of the inductance in the transition (superconducting to normal) region.

c) A15 formation in the wire: After the porous body was completely infiltrated with Al-Si eutectic, it was clad with a tantalum tube (0.25 in O.D., 0.025 in. wall thickness) and a copper tube (0.5 in. O.D. and 1/16 in. wall thickness). The tantalum tube served as a barrier to prevent diffusion from the outer covering toward the infiltrated core during the second heat treatment. The copper tube helped to smooth the wire during the wire drawing stage. After the infiltrated core had been clad, it was reduced through the following three procedures: swaging,[4] form rolling and wire drawing. At the end of the form rolling and during the wire drawing stage, copper tended to crack during mechanical reduction. This was due to the large degree of reduction of the thicker jacket which caused strain hardening and residual stress. Therefore, it was annealed at 300°C for 5 minutes whenever cracks started to occur. A schematic of the wire drawing technique is shown in Fig. 15.

For the primary heat treatment, a 2 in. long wire was etched with 70% nitric acid solution. This solution reacted with copper. As a result, the copper jacket disappeared on the outside of the wire. Finally, it was heated at 600°C for 1 hour or 650°C for 10 minutes in a quartz tube backfilled with He gas to 640 mm Hg. After the primary heat treatment, the wire was heated at 1700°C for 15 sec. to obtain the A15 superconducting phase.

III. RESULTS AND DISCUSSION

The aluminum silicon eutectic has a melting point of 577°C. After the niobium rod has been infiltrated with Al-Si eutectic, it is not good practice to heat the infiltrated sample above 1000°C to obtain the A15 phase. The reason is that at this high temperature the eutectic composition will melt and vaporize, both of which are not desired phenomena.

There is an alternative way to obtain the A15 phase by using two separate heat treatments:

a) Primary heat treatment: After the sample had been infiltrated with Al-Si eutectic, it was reacted at temperatures close to the melting point of the eutectic composition. The reason is that aluminum is a highly reactive material. Above 700°C, it will completely react with niobium to form an intermetallic compound. This happens in a matter of minutes.

Heating at 600°C for 11 hours or 650°C for 1 hour was suitable to form a barrier of intermetallic compound around the pores. The barriers inhibited Al-Si from leaving the pores in the infiltrated sample. The morphology of samples following this primary heat treatment is illustrated in Figs. 7 and 8. The barrier is composed of approximately 52 w/o Nb, 42 w/o Al and 6 w/o Si.

Referring to Fig. 12, this composition corresponds to the region of $NbAl_3$ in the Nb-Al phase diagram. This phase is very stable at 600°C. Experiments have proved its composition remained unchanged even after 25 hours at 600°C. The Al-Si alloy inside the pores is no longer of eutectic composition. It has changed to an aluminum

rich phase surrounded by barriers of Al-Nb compound. The thickness of the barrier versus time at constant temperature is shown in Fig. 10.

The reaction for wires is similar to that for infiltrated rods. The only difference is the diffusion path which is now much shorter. This is due to the small diameter of the wire compared to the much larger size of the infiltrated sample. 600°C for 1 hour is found suitable for the primary heat-treatment.

b) *Secondary heat treatment: After the sample was reacted in the* primary heat treatment, it was heated at a high temperature to obtain the A15 phase. A15 formation temperatures above 1000°C were emphasized for this study. Experiments have shown that T_c is related to the heat treatment temperature. The result obtained from 1700°C for 15 seconds is found to be the most suitable for producing A15 superconducting material.

Figure 9 shows the morphology of a sample following the secondary heat treatment. Two things have happened during this stage. 1) Al diffused and reacted with Nb to form a compound of 82 w/o Nb, 8 w/o Al, and 10 w/o Si. Converting weight per cent into mole fraction, this composition corresponds to the $Nb_3(Al-Si)$ (A15 phase). This phase is very stable at 750°C. Experiments have proved its composition remains unchanged after 96 hours of annealing. This area corresponds to the dark region surrounding the voids. 2) Al diffused further and reacted with Nb to form a compound of 66 w/o Nb, 5 w/o Al, 29 w/o Si. Converting weight per cent into mole fraction, this composition corresponds to $Nb_5(Al,Si)_3$. It also corresponds to the "light color" region in Fig. 9. During the secondary heat treatment, there was

a change in crystal structure as Al-Si combined with niobium. This gave rise to many voids in the sample.

A15 formation at temperatures less than 1000°C was also investigated. However, reactions at these temperatures resulted in the A15 layer becoming too thin for composition determination by X-ray analysis.

Figure 14 shows the change of T_c with time as samples are reacted at 850°C. The time dependence is very small.

The procedure for the secondary heat treatment of the infiltrated rod was used also for the wire. 1700°C for 15 seconds is suitable for the forming of very fine A15 filaments.

Table 1 shows the critical temperatures observed for infiltrated rods and wires as a function of reaction temperature, time and of a post reaction anneal* at 750°C for 96 hours. The highest value observed was 18.8°K for a wire reacted at 1700°C for 15 seconds and annealed for 96 hours at 750°C.

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*see Appendix A.

IV. CONCLUSION

For the Nb-Al-Si system, the kinetic study has helped to obtain the A15 superconducting phase by using two separate heat treatments. Samples were heated at 600°C for 11 hours or 650°C for 1 hour to develop a barrier around the pores for the primary heat treatment. During the secondary heat treatment, the A15 phase was obtained by heating samples at 1700°C for 15 seconds. This A15 superconducting phase gave a critical temperature of 18.24°K.

The same procedure was used for wire, 600°C for 1 hour in the primary heat treatment and 1700°C for 15 seconds for the secondary heat treatment. Very fine A15 filaments were obtained and gave a T_c of 18.78°K.

Post heat treatment annealing at 750°C for 96 hours was effective for improving the T_c of the samples reacted at high temperatures.

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4. Christopher Rutan, M.S. thesis (to be published), 1978.

5. Kent E. Douglas, A Low Temperature Kinetic Study of the Formation of the Superconducting A15 Phase in the Nb-Al-Ge System, M.S. thesis, LBL-7629, March 1978.

Table 1. Critical temperature of samples reacted at different temperatures.

Reaction temperature (^{o}C)	Reaction time	Sample condition	Annealed for 96 hrs. at 750^{o}C	Critical temperature (^{o}K)
850	3 hrs.	I.R*	NO	9.59
850	4 hrs.	I.R	NO	9.66
850	5 hrs.	I.R	NO	9.70
850	6 hrs.	I.R	NO	9.74
850	7 hrs.	I.R	NO	9.80
850	8 hrs.	I.R	NO	9.86
850	9 hrs.	I.R	NO	9.59
850	10 hrs.	I.R	NO	9.78
1000	1/2 hr.	I.R	NO	10.00
1100	1/2 hr.	I.R	NO	11.70
1200	1/2 hr.	I.R	NO	13.00
1400	5 min.	I.R	NO	15.10
1600	3 min.	I.R	NO	16.50
1800	1 min.	I.R	NO	16.80
1700	15 sec.	I.R	YES	18.24
1600	3 sec.	WIRE	YES	17.10
1600	5 sec	WIRE	YES	17.10
1700	3 sec.	WIRE	YES	18.24
1700	5 sec.	WIRE	YES	18.24
1700	10 sec.	WIRE	YES	18.24
1700	15 sec.	WIRE	YES	18.78

*I.R: Infiltrated rod.

APPENDIX A: ANNEALING

During the secondary heat treatment (15 seconds at 1700°C), the arrangement of the Nb-Al-Si atoms is not highly ordered. This is due to reacting the samples at high temperatures. Rearrangement of these atoms can be achieved by annealing at a low temperature. Many samples were annealed at 750°C for 96 hrs. and the critical temperature was found to increase by 1°K. For samples reacted at temperatures below 1000°C, the annealing procedure was not necessary because disordering is small at low temperatures.

FIGURE CAPTIONS

Fig. 1. Isostatic Compressor Equipment.

Fig. 2. Schematic diagram of the A-Bar 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-Si alloy, and 14) resistance heater.

Fig. 3. Form rolling apparatus.

Fig. 4. Apparatus for wire-drawing.

Fig. 5. Infiltration process.

Fig. 6. A control method for slow cooling of the infiltrated sample.

Fig. 7. Primary heat treatment for a sample at 650°C for 1 hour (all values are in weight per cent).

Fig. 8. Primary heat treatment for a sample at 600°C for 11 hours (all values are in weight per cent).

Fig. 9. Secondary heat treatment at 1700°C for 15 seconds (all values are in weight per cent).

Fig. 10. Thickness of the barrier vs. time.

Fig. 11. Morphology of an infiltrated sample, showing sections of aluminum-silicon eutectic surrounded by a niobium matrix.

Fig. 12. Nb-Al phase diagram.

Fig. 13. Nb-Al-Si phase diagram at 1840°C.

Fig. 14. Critical temperature vs. time at 850°C.

Fig. 15. Wire drawing procedure.

Fig. 16. Morphology of a sample after it had been form-rolled and annealed.

Fig. 17. A general picture of a 0.038" O.D. wire (including outside jackets).

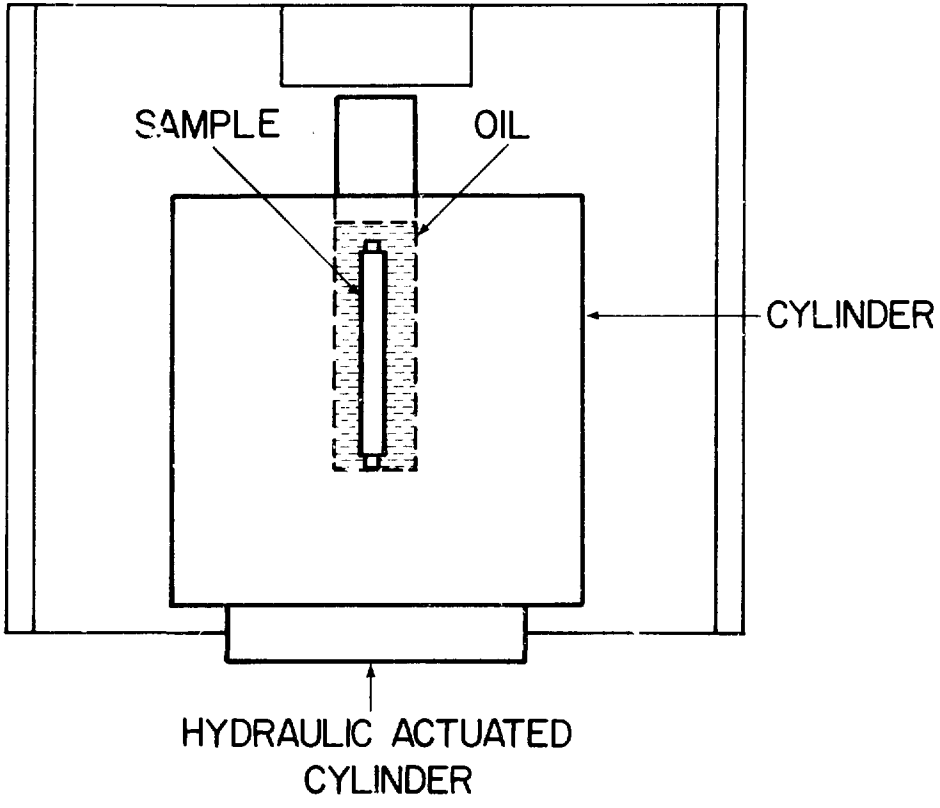

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Figure 1

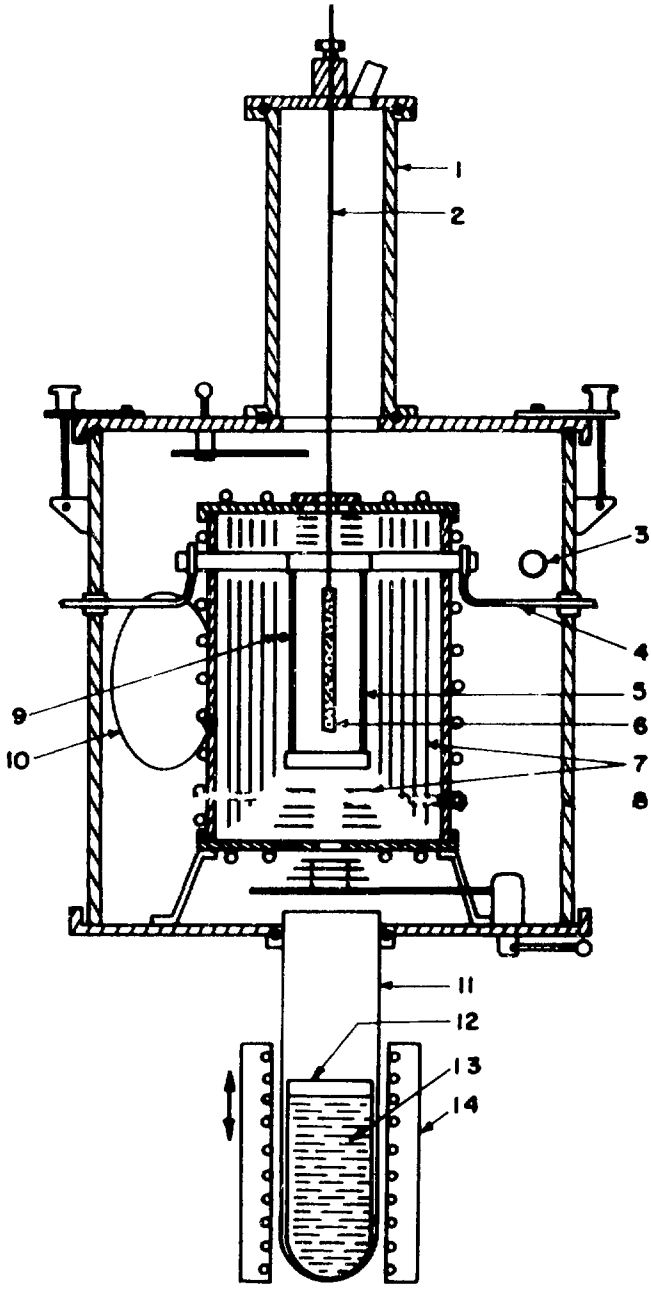

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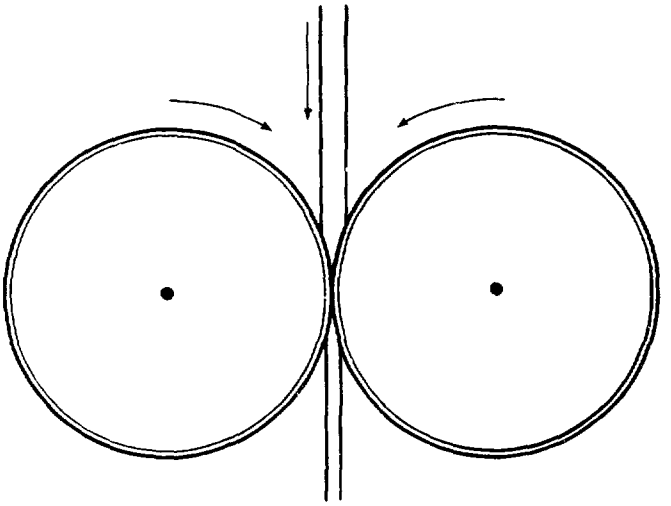
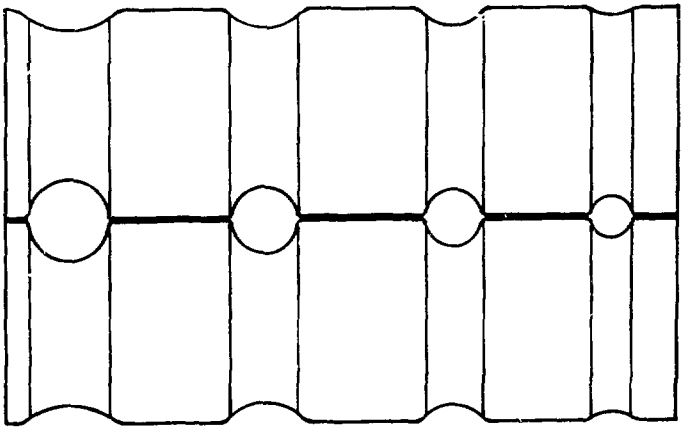
Figure 2



Side View



Top View

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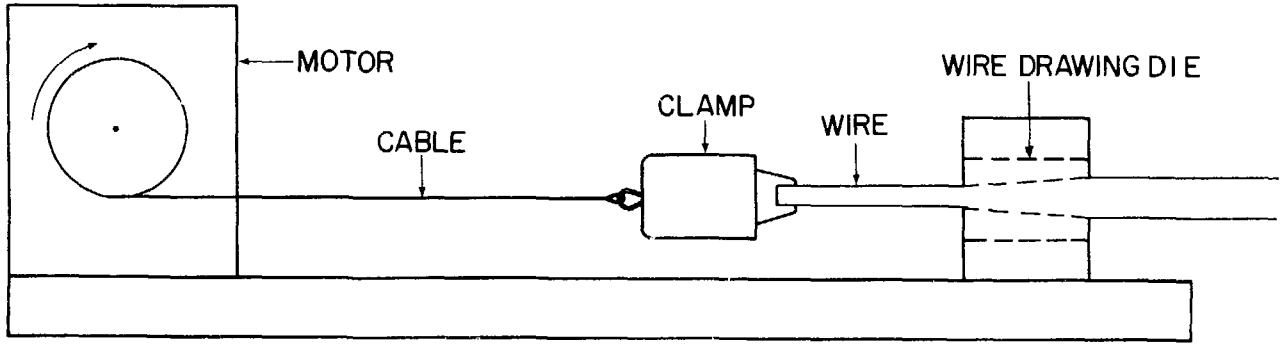
Figure 3



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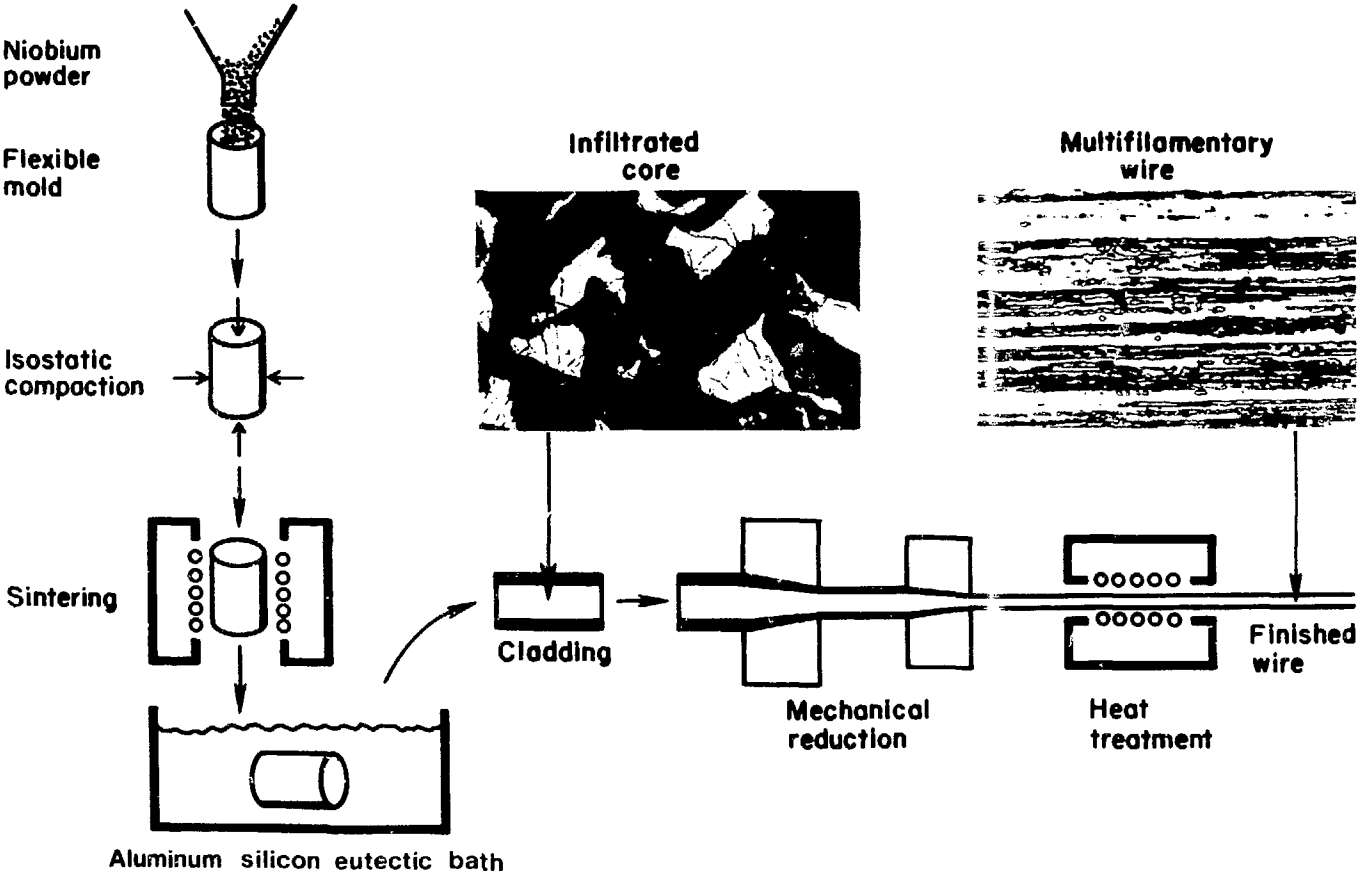

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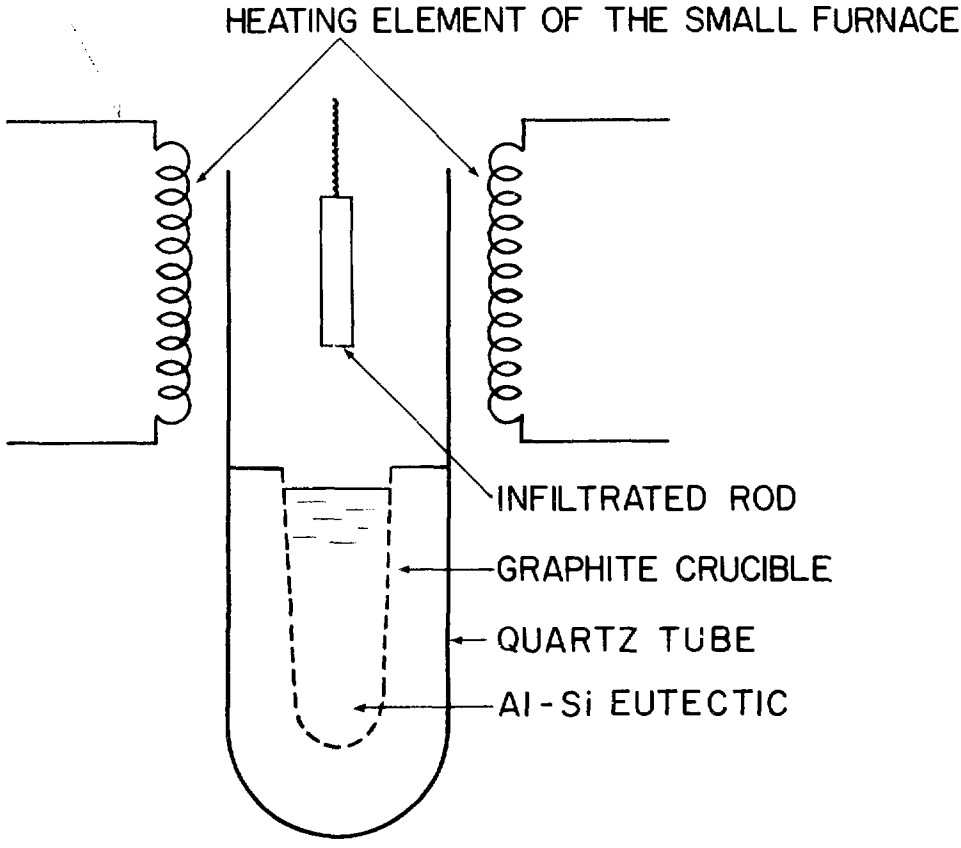
Figure 5



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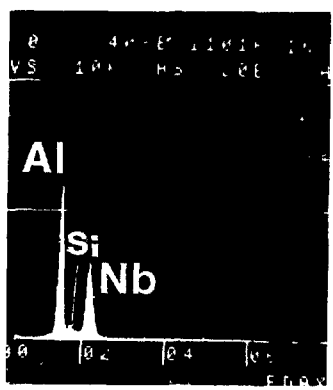
650°C FOR 1 hr

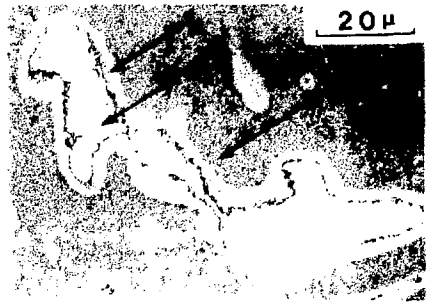
Phase 1	Nb	49%
	Al	47%
	Si	4%
Phase 2	Nb	0%
	Al	98%
	Si	2%
Phase 3	Nb	100%
	Al	0%
	Si	0%



EDAX analysis for phase 1

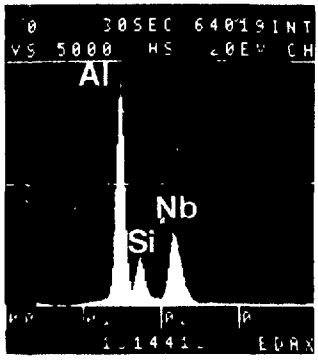
XBB 780-14859

FIGURE 7



600°c FOR 11 hrs

PHASE 1	Nb	52%
	Al	42%
	Si	6%
PHASE 2	Nb	0%
	Al	98%
	Si	2%



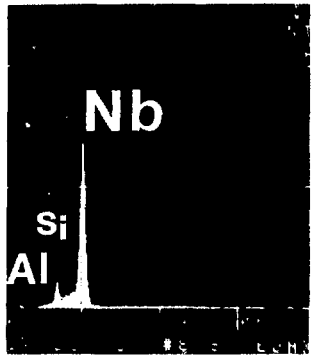
EDAX analysis for phase 1

PHASE 3	Nb	100%
	Al	0%
	Si	0%

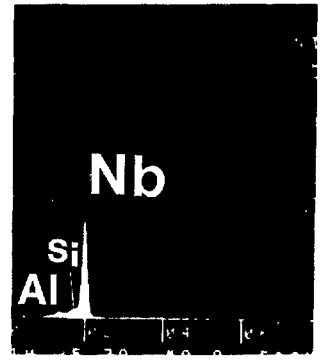
Figure 8

XBB 780-14860

Phase 1	Nb	82%
	Al	8%
	Si	10%
Phase 2	Nb	66%
	Al	5%
	Si	29%



EDAX analysis for phase 1



EDAX analysis for phase 2

FIGURE 9

XBB 780-14861

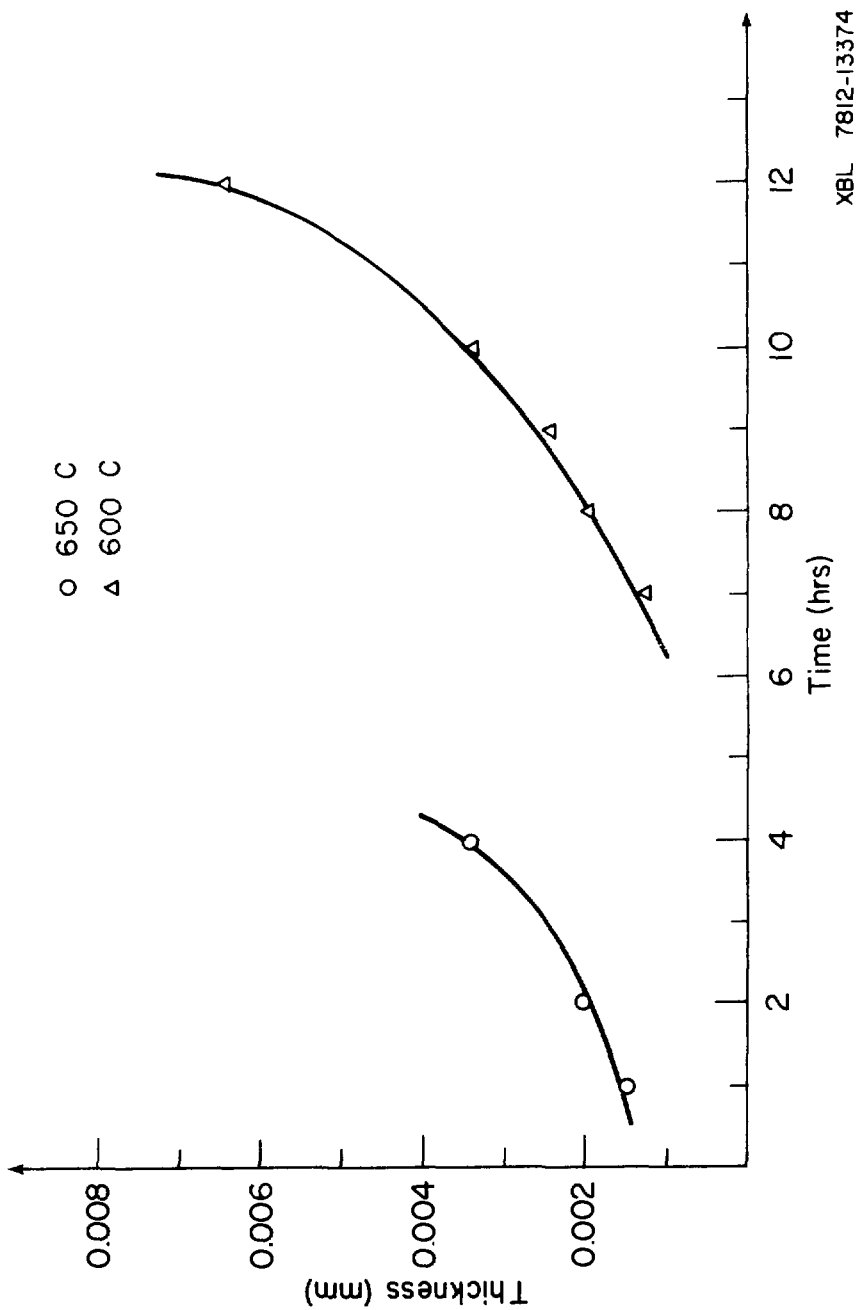

o 650 C
Δ 600 C
Thickness (mm)
0.002
0.004
0.006
0.008
2
4
6
8
10
12
Time (hrs)
XBL 7812-13374

Figure 10

XBB 780-14862

Figure 11

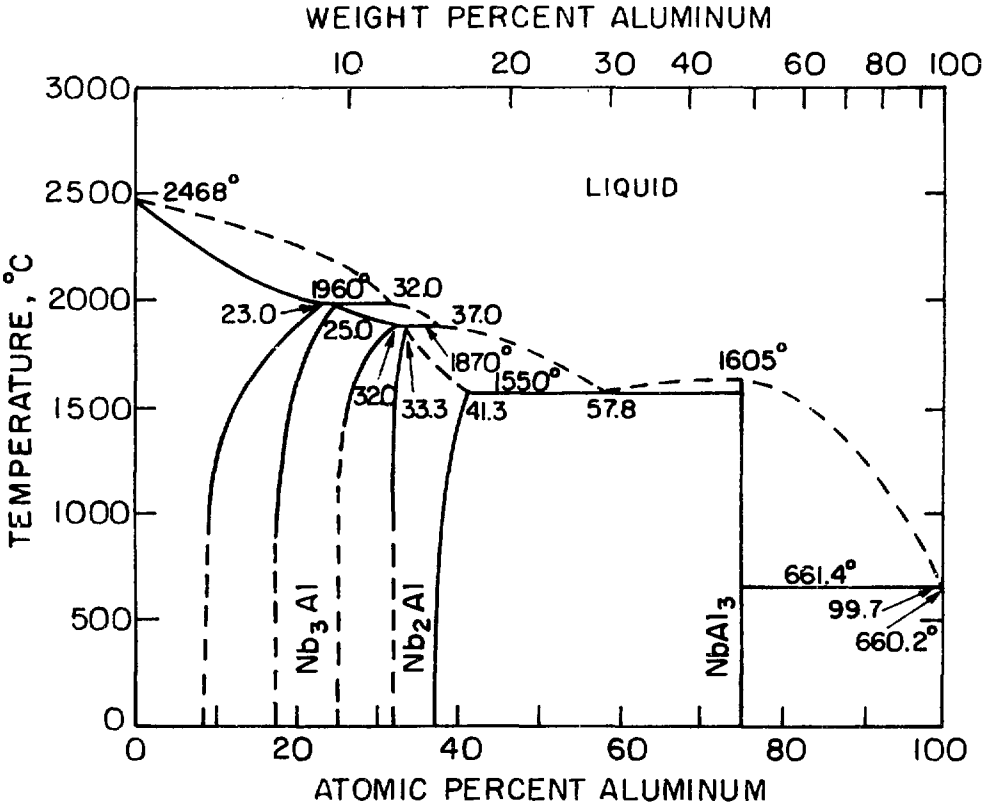


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Figure 12

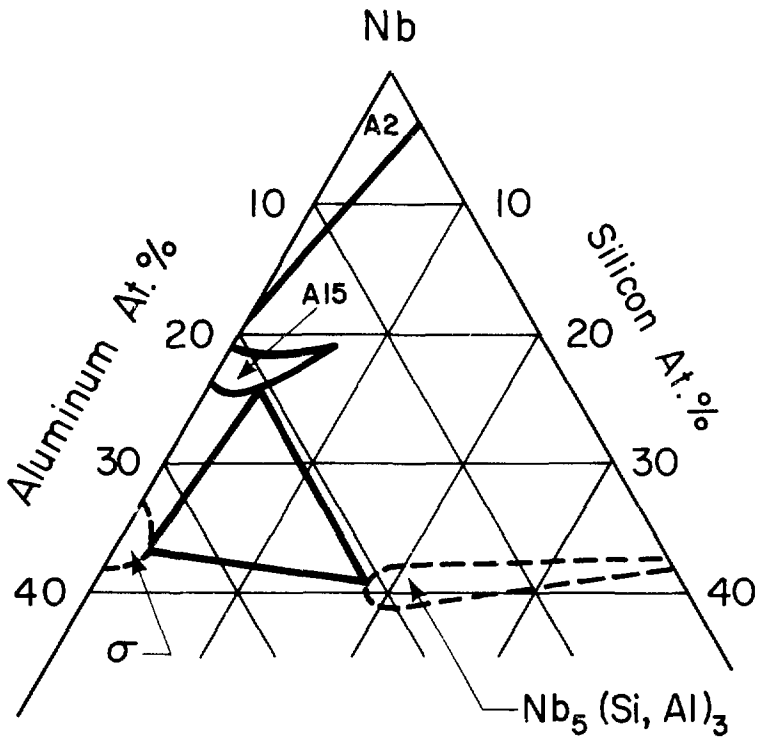

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Figure 13

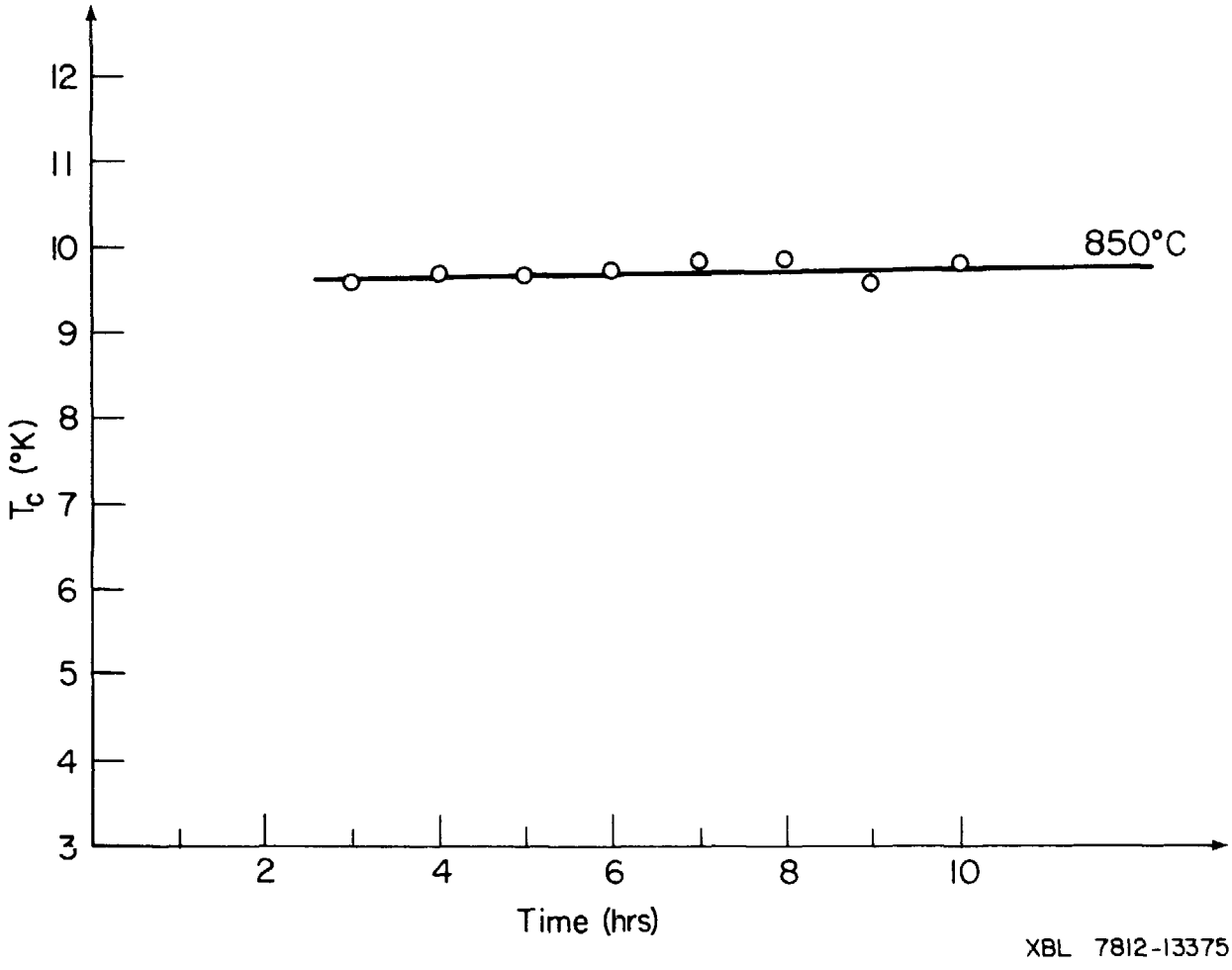


Figure 14

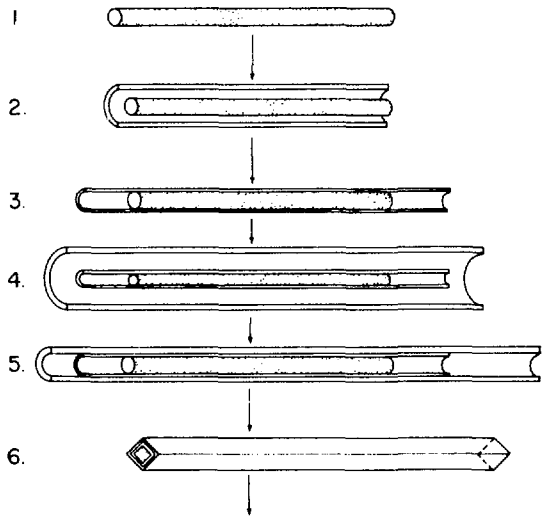
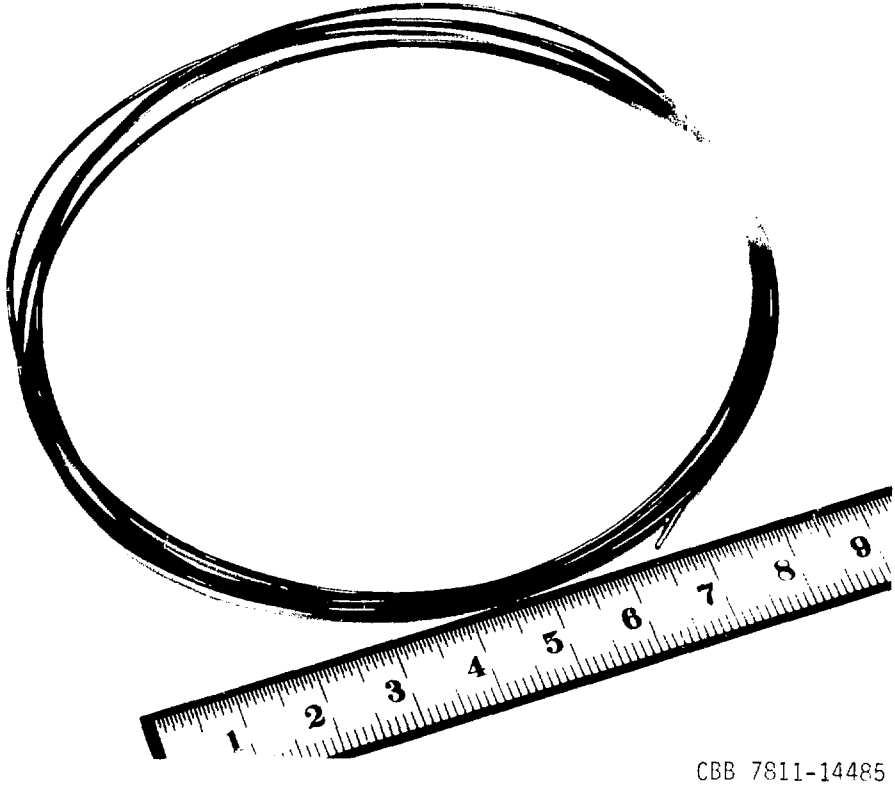

1
2.
3.
4.
5.
6.
7. HEATED AT 400°C FOR 1/2 HOUR FOR STRAIN RELIEF (Figure 16).
8.
INFILTRATED CORE
TANTALUM TUBE 0.25" O.D, 0.025" THICK
SWAGE TO TIGHT FIT
COPPER 0.5" O.D, 1/16" THICK
SWAGE TO TIGHT FIT
FORM ROLLING TO SMALLEST SIZE (approx. 0.1" O.D)
WIRE DRAWN TO DESIRED DIAMETER (Figure17)
(NOTE: ANNEAL AT 300°C FOR 5 MINUTES EVERY TEN DIES FOR STRESS RELIEF)
XBL 7812-13379

Figure 15

Figure 16



CBB 7811-14485

Figure 17