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EXPERIMENTAL INVESTIGATION OF DENSIFICATION
OF POWDERED A 15 PHASE IN THE SYSTEM Nb-Al-Ge

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ABSTRACT

An investigation of the densification of precompounded powder of the
A 15 phase $Nb_3(Al,Ge)$ was made. The influence of various parameters such
as additives, temperature, pressure and time in sintering of this material
was studied. Since cold pressing followed by sintering did not produce
sufficient density, the hot pressing technique was used. By hot pressing
at $1450°C$ for $\frac{1}{2}$ hour under 6 KSI pressure, about 95% densification was
achieved.

The results of these experiments provide information that could lead
to the development of a viable process for producing superconductors
based on this compound.

I. INTRODUCTION

The phenomenon of superconductivity was discovered by Kammerlingh Onnes in 1911[1]. In 1933 Mendelssohn[2] reported results obtained with a superconducting solenoid made of a lead-bismuth alloy, but the maximum current density was found to be quite low.

For more than twenty years afterwards the use of superconductors for the construction of magnets received little attention.

In 1954, Hardy & Hulm[3] reported a transition temperature (T_c) of 17.1°K in the A 15 structure of V_3Si.

Subsequent research lead to the discovery by Matthias et. al.[4] of the A 15 compound Nb_3Sn which has a critical temperature of 18.05°K. Superconductors based on this compound are now commercially available.

The A 15 compound $Nb_3(Al,Ge)$ has a critical temperature of 20.7°K[5-7] and a critical field[8] (H_{c2}) of 410 kG. These are the highest values for any stable superconductor known so far. A transition temperature above 20.5°K is above the boiling point of hydrogen-an economic advantage. Since the discovery of this system, interest in the alloys of Nb-Al-Ge system increased tremendously. In spite of the considerable number of investigations, no commercially successful method of manufacturing this material is available.

If the $Nb_3(Al,Ge)$ compound is to be used commercially, it must be available as long lengths of tape or wire capable of carrying a higher current density in a stronger magnetic field and at higher temperature than any contemporary alternative. Although work on producing $Nb_3(Al,Ge)$ by sputtering is now yielding promising material in terms of current carrying capacity,[9] this approach would appear to be limited by the low

rate of deposition and, consequently, production. Alternative methods of production therefore merit attention. The feasibility of the powder metallurgy process has recently been reported by Löhberg et. al.[10] who fabricated tape of $Nb_3Al_{0.75}Ge_{0.25}$ by swaging rolling and heat treatment. Measurements of critical current density (J_c) in steady transverse magnetic fie... is up to 150 kOe at temperatures up to $16°K$ show values of the order of 10^4 A/cm^2 at $13°K$ and 120 kOe, and 10^3 A/cm^2 at $16°K$ and 95 kOe. But this method cannot be utilized technically due to the great difficulty in producing ribbons or wires of long lengths. The extreme brittleness and considerable porosity are believed to be the main problems.

Knowledge of densification and plasticity behavior of this material would be useful in developing a technique for producing long lengths of wires of $Nb_3(Al,Ge)$ material.

II. OBJECTIVE

A full understanding of the plastic deformation of the A 15 compound $Nb_3(Al,Ge)$ can be achieved only through a very detailed study requiring considerable time, effort and special test facilities. For this reason, it was necessary to limit the scope of this research; this report examines only the densification behavior of the A 15 phase $Nb_3(Al,Ge)$.

The basic objective of this research program is to determine whether powder of the $Nb_3(Al,Ge)$ compound can be fully densified when subjected to heat and pressure, and, if so, what are the optimum conditions.

III. COMMENTS ON THE Nb-Al-Ge SYSTEM

Figure 1 shows a phase diagram[12] of Nb-Al-Ge system at 1840 ± 20°C. The A 15 phase occurs in three two-phase fields with A 2, σ, and $Nb_5(Ge,Al)_3$ as the second phase. In the three phase field, A 15, σ phase and $Nb_5(Ge,Al)_3$ coexist. After annealing at 1840°C, alloys in the interval $Nb_{75}Al_{20.5}Ge_{4.5} - Nb_{75.3}Al_{19.5}Ge_{5.1}$ have a highest critical temperature of 19.3 K [12]. By subsequent heating at 800°C, the alloys $Nb_{75.8}Al_{18.2}Ge_{6.0} - Nb_{76.0}Al_{17.7}Ge_{6.3}$ reach a highest value of 19·9° K. Specimens in this interval also show maximal critical temperatures after heating at other temperatures <1000°C. The highest value of T_c equal to 20.1°K was reached after heating at 750°C, which in accord with Refs. 13 and 14 is the most favorable aging temperature. According to Matthias, et al.[5] the transition temperature near the stoichiometric composition $Nb_{12}Al_3Ge$ reanged from 19.9 to 20.3°K. Transition temperature values exceeding 20.3°K were all found in samples in which niobium solid solution coexisted with the A 15 phase.[12]

The effect of an ordering anneal at 725°C is to increase T_c, but to decrease, at least at 4.2°K, the current carrying capacity. The annealing according to Löhberg[10] et al. apparently reduces the number of the pinning centers.

IV. EXPERIMENTAL PROCEDURES

A. Preparation of Precompounded Powder

Niobium, Aluminum and Germanium powders (see Table 1) were weighed
out to a nominal composition of 75 at.% Nb, 18.75 at.% Al, 6.25 at.% Ge.
They were thoroughly blended in a glass container with Al_2O_3 pellets for
3 hours. The powder was then pressed at 40 ksi in the form of small
rectangular compacts. These compacts were arc melted using a non-consumable
tungston electrode in water-cooled copper crucibles in an argon atmosphere.
Allowances were made when formulating alloys to compensate for a small
weight loss, attributable mainly to the evaporation of aluminum that
occurred on melting. A standard melting procedure was adopted to control
the weight loss and the compacts were inverted and remelted four times to
ensure complete fusion and improved homogeneity.

The arc melted buttons were homogenized at $1840°C$ for 2 hours in an
ABAR furnace in argon atmosphere.

Mechanically polished sections for metallographic examination were
etched in a solution containing equal volumes of sulphuric acid, hydro-
fluoric acid and water, to which a few drops of hydrogen peroxide were
added. Phase identification was facilitated by anodizing for 5 minutes
in a 10 wt. % aqueous solution of citric acid at 25 V. The anodizing tech-
nique employed caused each phase present to have a characteristic color
when viewed in the optical microscope. The colors of the four possible
phases that could appear are:[14] niobium-solid solution (blue-green), A 15
phase (gray-purple), and two minor solute rich phases (pink & orange).

A micrograph of the structure after anodizing is shown in Figure 2. The
sample consisted of more than 95% homogeneous A 15 phase, and less than

5% of solute rich phases which were present mainly at the grain boundaries.

The arc melted buttons were crushed into small pieces and then ball milled in a planetary grinder with Al_2O_3 pellets.

The powder was analyzed by x-ray diffraction. X-ray diffraction analysis confirmed the metallographic findings.

The powder was then screened through a 400 mesh sieve. This -400 mesh powder was used in all subsequent experiments.

B. Compaction Procedure

A rubber mold, 1/4" diam. and 1" long was used to contain the powder. The rubber mold was filled in three layers of powder with two separating rubber discs. Thus three cold pressed tablets were obtained from a single rubber mold. The rubber mold was submersed in an oil chamber and hydrostatic pressure of 60 KSI was applied for 2 minutes. The sample thickness after compaction was usually in the range of 2/16" — 3/16".

C. Sintering Procedure

Sintering was done in an ABAR vacuum furnace. The heating element was a split tungston cylinder 1" in diameter and 2 1/2" long. The temperature, up to $1700°C$, was measured using a Pt — Pt. 10% Rh thermocouple. A vacuum of 2×10^{-5} mms of Hg or better was employed before back filling with helium. The sample was contained in an Al_2O_3 crucible and sintered for 1/2 hour (unless otherwise stated). The temperature of the ABAR furnace was raised slowly to the required temperature. It usually took half an hour to reach the desired steady state temperature. The sample was held at this temperature for one hour and then allowed to cool in the

helium atmosphere by turning off the heat supply to the ABAR furnace. The temperature fell very rapidly ($\approx 130°$ C/sec) initially and then slowly below $300°$ C.

D. Hot Pressing Procedure

Figure 3 shows the hot press used. The powder was contained and hot pressed in a split graphite die $1/8" \times 3/8"$ and $1"$ long with a ram type plunger. Pressure was applied on the plunger by a hydraulically driven ram while radiant heat was supplied by a tantalum filament around the graphite die. The temperature of the sample was measured by using a Pt — Pt. 10% Rh thermocouple inserted radially into the graphite die. There was a $1/8"$ graphite wall between the sample and the tip of the thermocouple. The tip of the thermocouple was enclosed in a small Al_2O_3 tube to avoid contact between the thermocouple tip and the grahpite die, thereby preventing contamination of the thermocouple.

There was a radial temperature gradient in the graphite die. A second thermocouple in the actual location of the sample was used to calibrate the measuring thermocouple. The plot of actual temperature of the sample against the measured temperature is shown in Fig. 4.

Hot pressing was always done under a vacuum (5×10^{-5} mms of Hg) as indicated by an ionization gauge at the main outlet tube. The maximum pressure that could be applied was limited to 7,000 psi due to the low strength of the graphite die. Attempts in doubling this pressure by using a special graphite material failed.

A pressure of 6,000 psi was applied and then the sample was slowly heated. There was a lag in sample temperature on heating because of the time needed to conduct heat through the graphite die. The temperature was

raised slowly and the sample temperature was allowed to stabilize at the temperature. The entire heating procedure took about one hour. The sample was held at this steady state temperature for 1/2 hour. After hot pressing for 1/2 hour, the sample was allowed to cool in vacuum by turning off the heat supply to the hot press. The temperature fell rapidly (130° C/sec) initially and then slowly below 300° C.

E. Density Measurements

Accurate density measurements are crucial in densification experiments. Since the samples were not of well-defined geometrical shape, the water displacement principle was used in determining the volume of the samples. A sample was weighed in air and its weight noted. It was then vacuum impregnated with epoxy. The vacuum impregnation with epoxy was repeated until two consecutive weights of the epoxy impregnated sample were equal. This weight was recorded. The sample was then weighed in water and its weight was recorded. To be sure of effective epoxy impregnation in the sample, its weight in air before and after submersing in water should have been equal. This confirmed that at least the surface of the sample was fully coated with epoxy. The density of th mple was calculated from the formula: —

$$\text{Density} = \frac{\text{wt. of sample in air}}{\text{wt. of epoxy impregnated} \atop \text{sample in air}} - \frac{}{\text{wt. of epoxy impregnated} \atop \text{sample in water}}$$

The density of an arc melted Nb-Al-Ge button after homogenizing was found to be 7.722 gms/cc. This value was used as the theoretical density.

Theoretical densities of samples containing alloying additives were calcu-
lated using the law of mixtures. The relative density measurements reported
were the ratio of the measured density to the theoretical density.

V. DENSIFICATION EXPERIMENTS

A. Sintering Experiments

Experiments to study densification by sintering compacts of powdered $Nb_3(Al,Ge)$ were carried out. The influence of parameters such as temperature, additives, pressure and time were investigated.

1. Influence of Temperature:

The precompounded powder was compacted and then sintered at 950, 1150, 1350, 1550, 1660°C. Density measurements are shown in Fig. 12. The micrographs (Fig. 5A, 6A, 7A, 8A, 9) and the density measurements clearly indicate that by compacting and sintering even up to temperatures of 1660°C, considerable porosity ($\approx$ 35-40%) remains.

2. Influence of Additives:

Copper and silver, on account of their low melting points and also good conductivity and ductility were selected as additives for liquid phase sintering. Powder blends of the A 15 compound with 10 wt. % of either copper or silver were compacted and then sintered at 950, 1150, 1350 and 1550°C. Density measurements (Fig. 12) and corresponding micrographs (Figs. 5B, 6B, 7B, 8B) show that silver has a very small effect on densification. The addition of copper, however, showed considerable improvement in densification as seen in Fig. 12. Microstructures (Fig. 5 , 6C, 7C, 8C) are in conformity with density measurements.

Since copper had a significant effect on densification, the influence of concentration was investigated. Blends containing 5%, 10%, and 20% by weight of copper powder were compacted and then sintered at 950°, 1150°

and 1350°C. The relative densities are shown in Fig. 12.

Attempts were made to coat the A 15 powder particles with copper instead of blending. An aqueous solution of copper chloride containing 10 wt. % of Cu was mixed with A 15 powder in a glass container. The slurry was heated with continuous stirring. The water was slowly evaporated resulting in a $CuCl_2$ coating on the A 15 powder particles. The copper chloride coating was reduced to copper by heating in a hydrogen furnace at 300°C for 2 hours. X-ray analysis indicated that during the above process of coating, the A 15 phase was completely destroyed. For lack of any other easily accessible coating method, these experiments were not further pursued. In another experiment 90 wt. % of Cu was alloyed with 10 wt % of Si to form a Cu-Si alloy having a melting point $\approx$ 820°C. A blend containing 10 wt. % of the Cu-Si alloy was compacted and then sintered at 750, 950°C, 1150° and 1350°C. Since the Cu-Si alloy had a lower melting point than copper ($\approx$1080°C) densification by the introduction of liquid phase sintering was expected at lower temperatures. But surprisingly no densification could be achieved. Apparently the Cu-Si alloy was spontaneously oxidized at room temperature.

3. Influence of Pressure:

The A 15 compound alone and with 10 wt. % Cu powder was hydrostatically compacted at 30, 40, 60, 80 and 100 ksi and then sintered at 1150°C for one hour in a helium atmosphere. Fig. 13(a) shows the measured densities. A small increase in density with pressure was observed.

4. Influence of Time.

The same two materials were compacted and sintered at $1150°C$ for 1, 3, 5, 20, 30, 40 and 60 hours. The density measurements obtained are shown in Fig. 13 (b). Longer sintering times did not change the densities of the samples.

B. Hot Pressing Experiments:

A 15 powder was hot pressed at temperatures of $1100°$, $1200°$, $1300°$, $1325°$, $1370°$, $1400°$, $1450°$ and $1500°C$. From density measurements (Fig. 14) it is evident that no densification is produced below $1350°C$. But between 1350 and $1400°C$, substantial densification ($\approx90\%$) is obtained. At higher temperatures, densification improves further to about 95% of theoretical at temperatures of $1450°C$ and above.

Attempts in hot pressing A 15 + 10 wt. % Cu powder resulted in non-uniform densities, probably due to squeezing out of the melted copper on the die surface.

VI. DISCUSSION AND CONCLUSION

Strikingly different densification behavior was apparent from the
sintering experiments. No attempt will be made to describe the kinetics
or analyze the mechanism of sintering as various kinds of driving forces
and transport mechanisms come into play. This would require separate and
very detailed studies. But from the photomicrographs of the sintered samples
of the A 15 phase, it appears that up to temperatures as high as 1550°C,
the driving forces for sintering are not strong enough to cause any
sintering in $Nb_3(Al,Ge)$ powder. Only at about 1660°C does the first stage
of sintering begin, slightly improving the connectivity. The degree of
precompaction or longer sintering periods had little effect.

Copper was introduced as an additive in the sintering of the A15 com-
pound to provide liquid phase flow which would improve the connectivity
and density by filling up the pores between A 15 particles. From the micro-
structures, it may be seen that around 1150°C sintering begins, and im-
proves slightly with increasing temperatures. Full density could not be
achieved and 20-25% porosity remained in the sintered samples.

Silver as an additive did not improve sintering to any noticeable
degree. X-ray analysis of sintered samples with copper and silver additives,
indicates that the A 15 phase is maintained but free silver or copper was
not observed.

Hence, it may be concluded that the conventional pressing and sintering
technique is ineffective for densification of A 15 powder.

Porosity was substantially eliminated by hot pressing around 1400°C.
It is possible that hot working could be employed in the temperature range
1350-1400°C. However, heating above 1000°C degrades the superconducting
properties and would cause serious problems in hot working on a production

scale. In our experiments we were limited by a 6,000 psi pressure in hot pressing due to the graphite dies used. It is very possible that with high hydrostatic pressure, the temperature for plastic flow could be reduced below 1000°C. It is reported by Martynov[15] et. al. that considerable room temperature plastic flow has been observed in samples of V_3Ga and V_3Si in response to upset testing in high pressure in the 300 KSI range.

VII. AREAS OF FUTURE STUDY

In this work we have made some preliminary determinations of the influence of heat and pressure on the densification of $Nb_3(Al,Ge)$ powder. There are many areas open to further investigation and optimization.

Lowrie[16] has reported by very careful tensile experiments on a diverse group of brittle intermetallic compounds a value of 0.65 of the absolute melting point for the onset of ductility. This is considerably lower than the value of 0.88 reported by Tamman and Dahl.[11] Exceptions have been noted by others. In the present work, a value of 0.76 was indicated.

A detailed study regarding the combined influence of high temperature and high pressure on the plasticity of the A 15 compounds should be attempted. This work might be facilitated by the information available on advances made in refractory material processing.[17]

ACKNOWLEDGMENTS

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Table I. Source materials used.

Material	Source	Nominal Purity	Form
Nb	Wah Chang Albany	99.9	Powder(-400)
Al	Contronics Corp.	99.9	Powder(-325)
Ge	Orion Chemical Co.	99.9999%	Powder(-400)
Cu	Asco	99.99	30-37 μ
Ag	Englehard Industry	99.95	Powder(-400)

FIGURE CAPTIONS

Fig. 1. The Nb-Al-Ge phase diagram at 1840°C.

Fig. 2. Anodized arc melted button of A 15 Nb_3(Al,Ge)

Fig. 3. Hot Press.

Fig. 4. Plot of temperature calibration in hot press.

Fig. 5. Photomicrograph of samples after sintering at 950°C

     (a) A 15

     (b) A 15 + 10 wt. % Ag

     (c) A 15 + 10 wt. % Cu

Fig. 6. Photomicrograph of samples after sintering at 1150°C

     (a) A 15

     (b) A 15 + 10 wt. % Ag

     (c) A 15 + 10 wt. % Cu

Fig. 7. Photomicrograph of samples after sintering at 1350°C

     (a) A 15

     (b) A 15 + 10 wt. % Ag

     (c) A 15 + 10 wt. % Cu

Fig. 8. Photomicrograph of samples after sintering at 1550°C

     (a) A 15

     (b) A 15 + 10 wt. % Ag

     (c) A 15 + 10 wt. % Cu

Fig. 9. Photomicrograph of sintered A 15 powder at 1660°C

Fig.10. Photomicrograph of hot pressed A 15 samples at

     (a) 1100°C

     (b) 1300°C

Fig.11. Photomicrograph of hot pressed A 15 powder at

(a) 1400°C

(b) 1450°C

Fig. 12. Plot of relative density of A 15, A 15 + Ag and A 15 + Cu vs. temperature.

Fig.13. Plot of relative density of A 15 and A 15 + 10 wt. % Cu vs

(a) Pressure

(b) Time

Fig.14. Plot of relative density of hot pressed samples of A 15 vs temperature.

XBL 761-6346

Figure 1

100×   XBB 761-308

Figure 2

Figure 3

Figure 4

XBL 761-6345

(c)

(b)

(a)
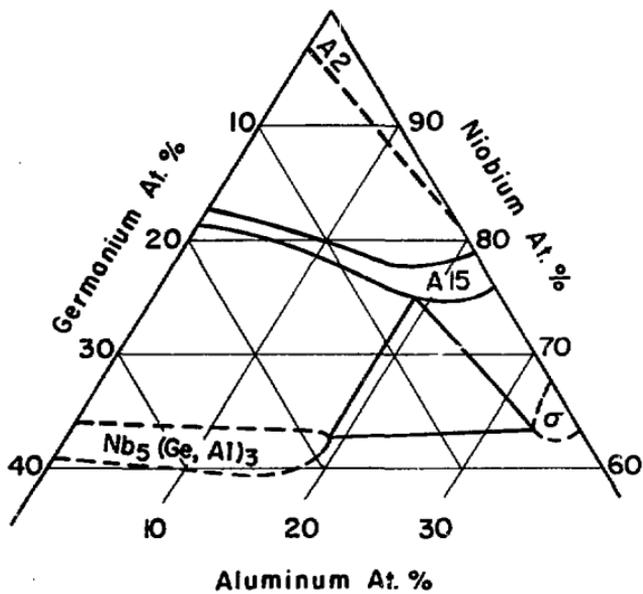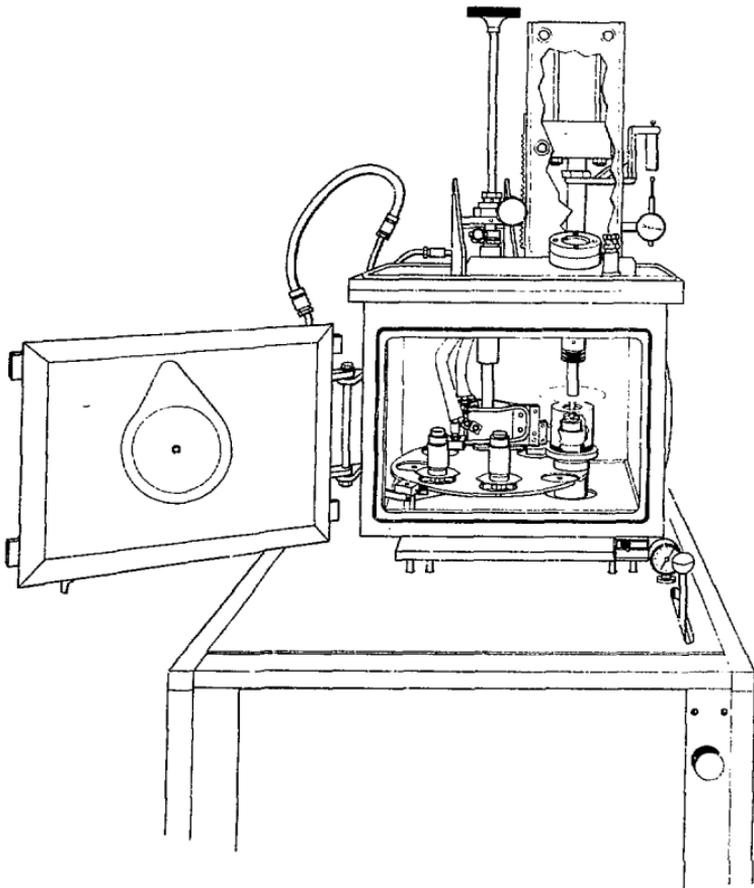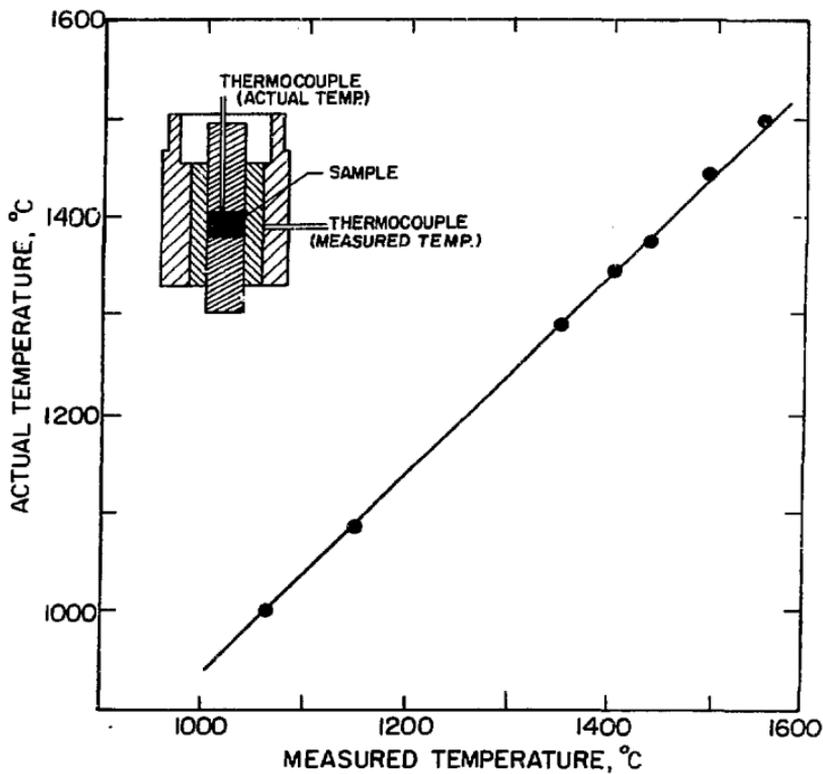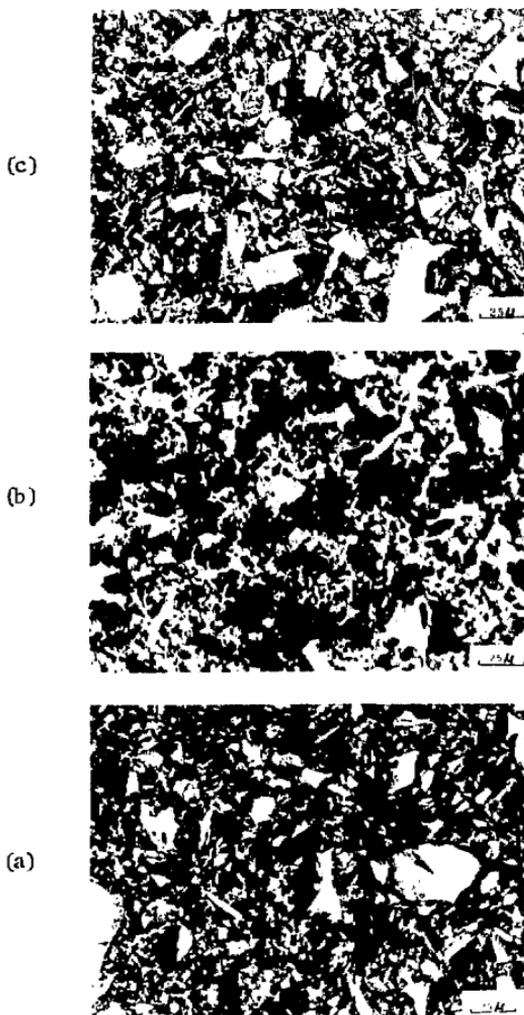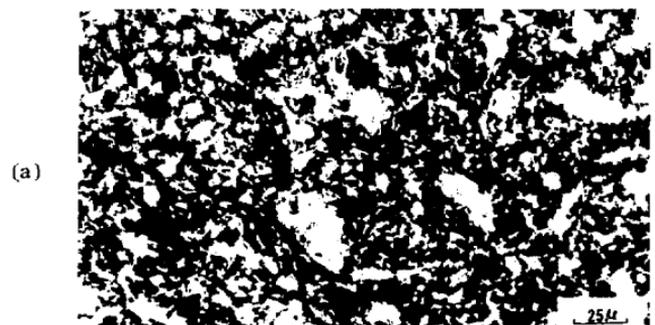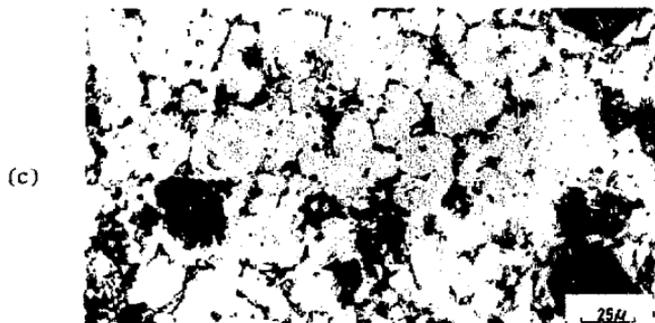
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Figure 5

XBB 7512-8342

Figure 6

(c)

(b)

(a)
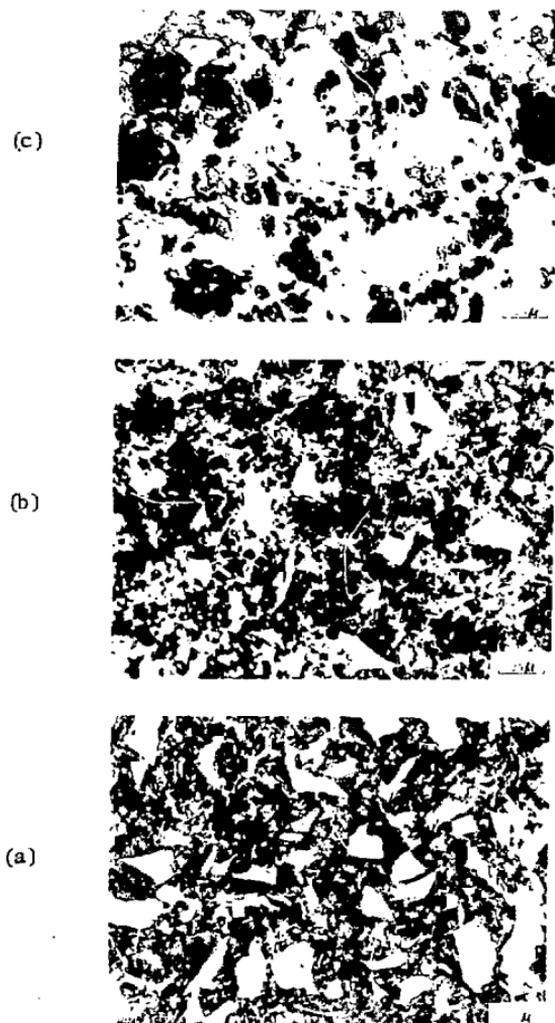
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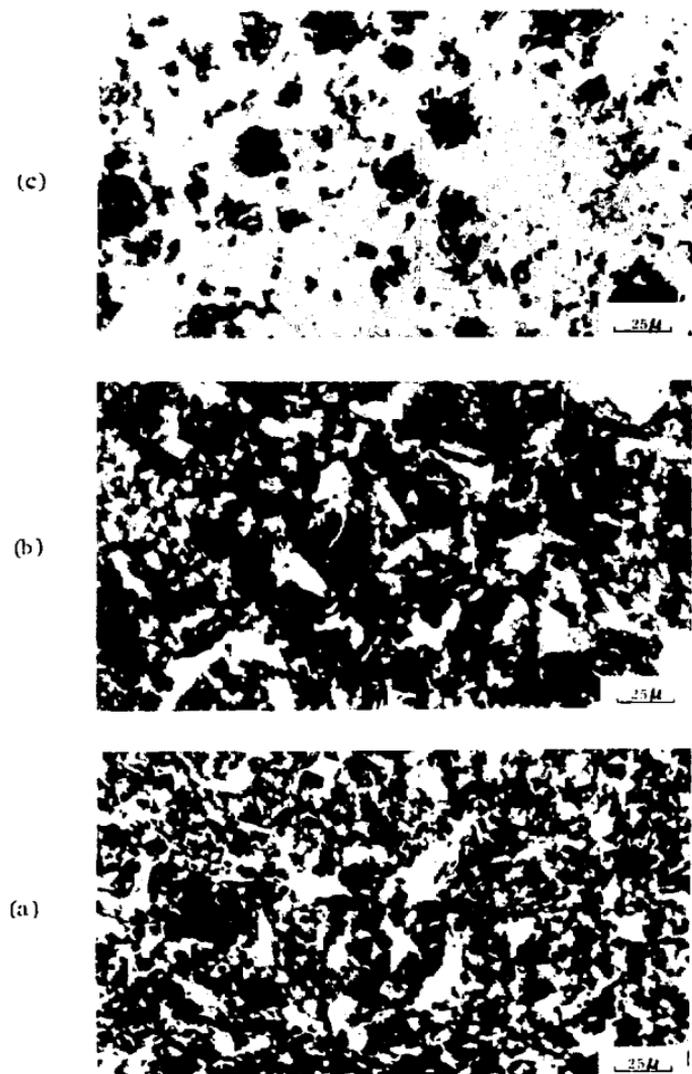
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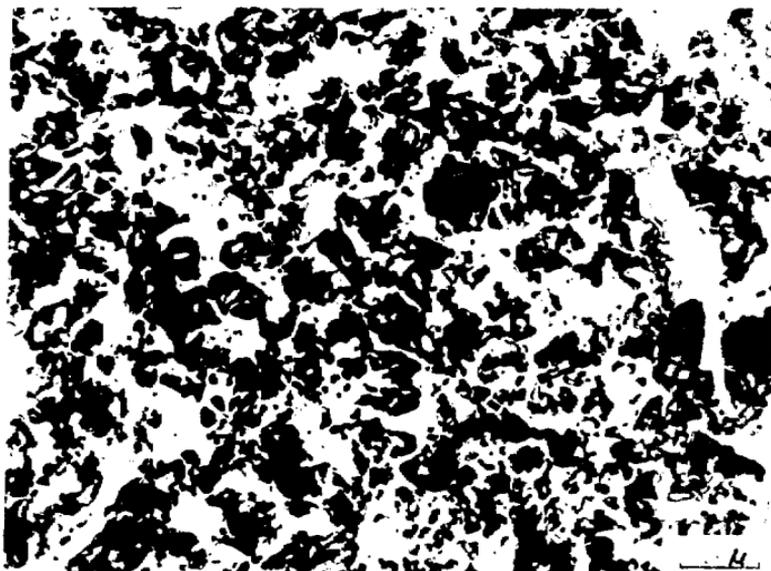
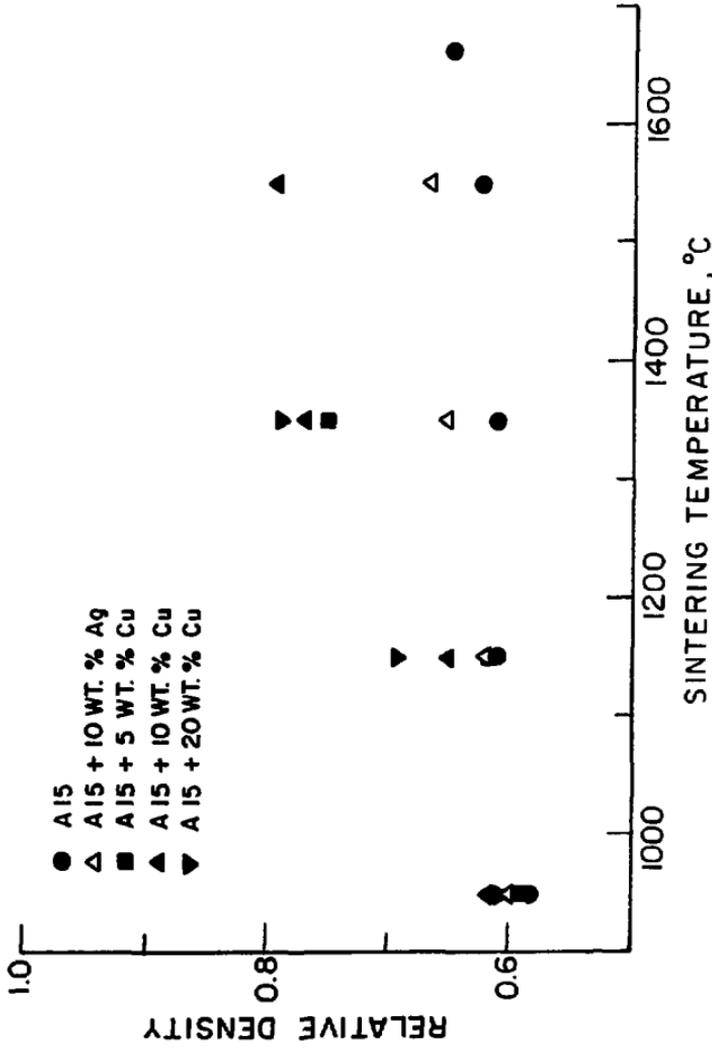XBB 761-561

Figure 9

(b)
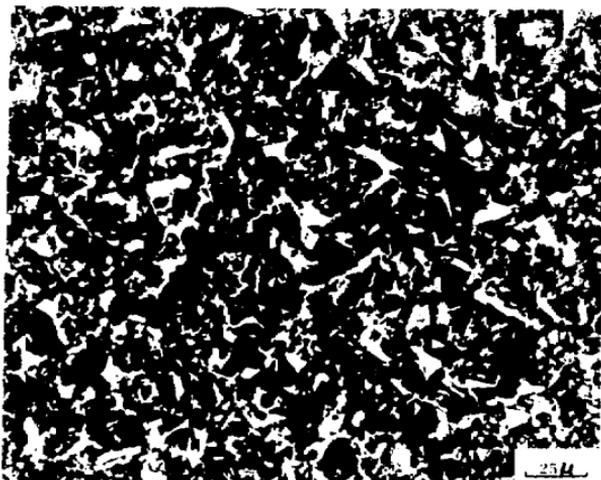
(a)

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Figure 10

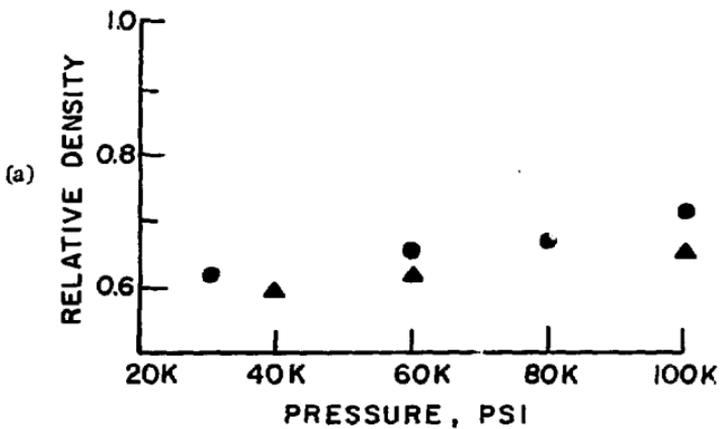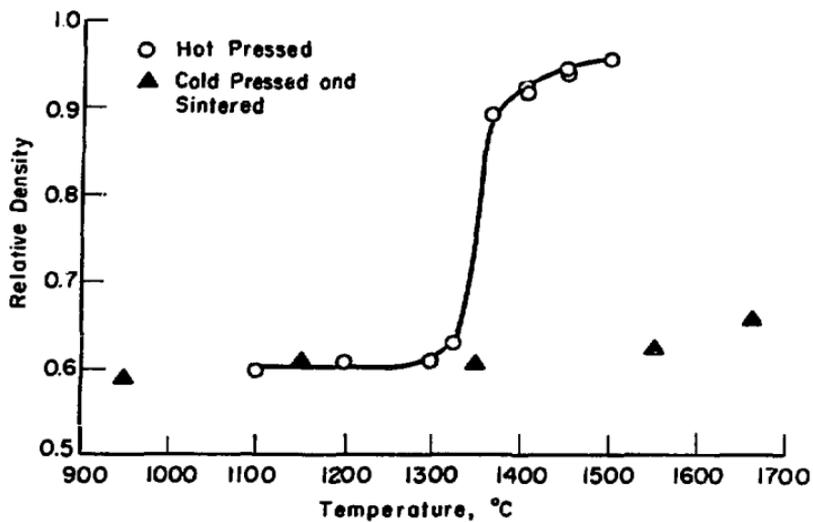(b)

25μ

(a)

25μ
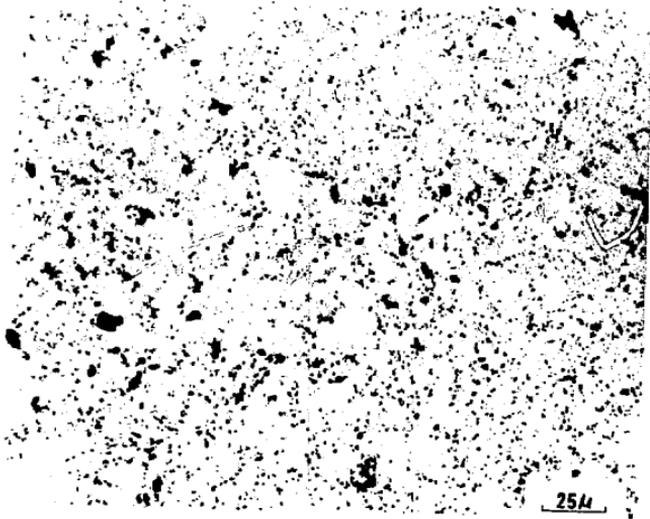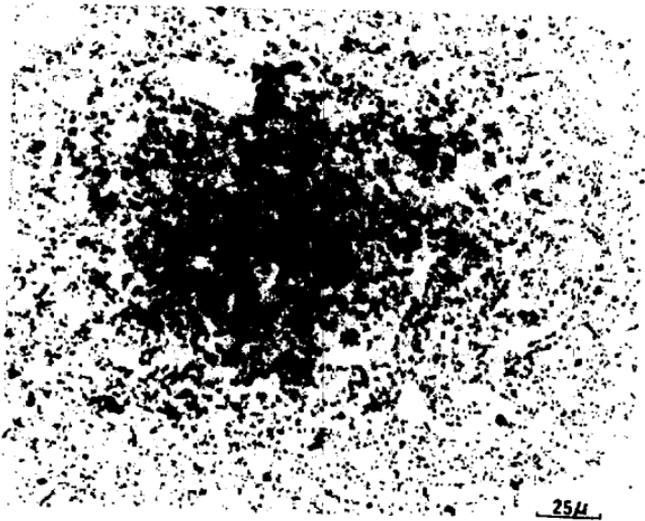
XBB 7512-8841

Figure 11

Figure 12

XBL 7511-9412

XBL7511-9413

Figure 13

Figure 14