LBL-10007
CONF-790815--33

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular
Research Division



Presented at the International Cryogenic Materials
Conference, Madison, WI, August 21-24, 1979

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August 1979

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

# RESEARCH ON THE MONOLITHIC PROCESS OF MAKING A-15 SUPERCONDUCTING MATERIALS

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## INTRODUCTION

The A-15 superconducting materials are intrinsically brittle and special processing techniques must be used to form them into wires or tapes. A number of manufacturing techniques have been suggested for laboratory use or commerical application. These include "bronze" process[1,2], "in situ" process[3-6], infiltration method[7], chemical vapor deposition[8], powder metallurgical (P/M) process[9,10], and others[11,12]. While considerable success has been obtained with these various manufacturing methods, they have the common drawback of being metallurgically elaborate and difficult to accomplish in practice.

The metallurgically simplest method of wire manufacture involves casting an ingot of the desired composition and extruding or drawing the cast material into a wire. Virtually all conducting wires, including ductile Nb-Ti superconducting wires, are manufactured in this way. It is possible that variations on conventional wire making practice may also be used for manufacture of A-15 superconducting wires or tapes[13-15].

A monolithic processing technique which should succeed in producing superconducting wires containing $A_3B$ phases is described in reference 14 about the V-Ga system. From V-Ga phase diagram[16,17](Fig. 1), one can design a process in which V/Ga ingots with compositions V-10∿20 at. % Ga are made homogeneous by annealing at temperatures above the ordering temperature (∿1300°C). The ingot is subsequently cooled at a rate sufficient to suppress the formation of the $V_3Ga$ ordered phase and a supersaturated solid solution of Ga in V is obtained. The solution is relatively ductile and amenable to processing through wire drawing or tape rolling. The superconducting phase is then introduced by precipitation with heat treatment

at a temperature below the ordering temperature. A process of this type is most straightforward in the V-Ga system, whose phase diagram contains a solid solution region above the ordered $V_3Ga$ compound, but modifications of it could easily be designed for other systems of the $A_3B$ type[18].

While the monolithic process has been used with some success, its practical implementation faces substaintial difficulty. The three most obvious problems are the following:

1. Quench-cracking. In order to achieve a homogeneous solid solution at room temperature, the ingot must be cooled sufficiently rapidly to suppress the formation of the A-15 phase. However, the rapid cooling of alloys frequently results in a phenomenon known as quench-cracking, in which the alloy spontaneously fractures due to thermal stresses on cooling.

2. Low Temperature Brittleness. After the sample has been successfully quenched to form a homogeneous solid solution at low temperature, it still does not follow that the sample can be successfully formed into a wire or tape. The matrix phases of interest, V or Nb, are bcc-structure refractory metals which typically have high ductile-to-brittle transition temperatures, with the result that their solid solutions are extremely brittle at low temperature.

3. Non- stoichiometry, as indicated by the breadth of the stability field of the $V_3Ga$ in the V-Ga phase diagram. It is well-known that the superconducting properties of the A-15 compounds deteriorate as the compounds deviate from the true $A_3B$ composition. It may, therefore, prove difficult to achieve good superconducting transition temperatures if the alloy is intentionally made lean in solute so as to facilitate melting and wire and tape fabrication.

In this paper we describe how these problems are overcome, at least in the laboratory sense, to achieve V/Ga wires and tapes having very promising superconducting transition temperatures.

## EXPERIMENTAL PROCEDURE AND RESULTS

The alloys investigated here were prepared by arc melting pure starting components under an argon atmosphere. The starting materials were V, 99.9% and Ga, 99.999% pure. During melting, the samples were inverted on the copper hearth and remelted at least four times to achieve complete alloying between the V and Ga. There is, of course, a loss of Ga during melting through varporization. The composition of the starting mixture of V and Ga is chosen so as to achieve a desired Ga content after melting and homogenization. The nominal composition of the final product is then calculated on the assumption that the observed sample weight loss was due to the vaporization of Ga.

The samples investigated in this work had nominal compositions in atom percent, V-14~19 at. % Ga. The ingots were homogenized at a temperature of 1350°C for 24 hours to achieve a homogeneous starting material. During homogenization the samples were wrapped in tantalum foils and encapsulated in quartz tubing. There is a slight further loss of Ga during the homogenization treatment, and this loss is accounted for in computing the final composition.

Following homogenization the samples were either quenched in water or quickly air cooled at room temperature. No quench-cracking was observed during quenching of the samples. Moreover, both optical microscopy and x-ray diffraction indicated that the precipitation of the A-15 phase was suppressed during the quench. The suppression of precipitation was further confirmed by superconducting transition temperature measurements,

using the inductive method with a calibrated germanium resistance thermometer, which showed no critical transition temperature ($T_c$) above 5°K. The homogenization plus fast cooling treatment hence seemed successful in avoiding both quench-cracking and precipitation of the A-15 phase.

In the homogenized and quenched condition the V/Ga samples were brittle, and fractured catastrophically on deformation at room temperature. A scanning electron fractographic analysis of broken sample surfaces (Fig. 2) revealed that the fracture mode was almost entirely quasi-cleavage, indicating that the brittleness of these samples is due to the normal low temperature brittleness of the bcc matrix structure. The ductile-to-brittle transition temperature of bcc alloys is known to increase with grain size. Optical microscopy revealed that during the homogenization treatment substantial grain growth had occurred, giving a typical sample grain size larger than 1 mm.

To avoid low temperature brittleness, the samples were deformed at 700∿800°C. The total reduction in thickness accomplished during the warm rolling was ∿75%.

Examination of the specimens after warm reduction by 75% at 700-800°C revealed that there is a slight precipitation of the A-15 phase during mechanical deformation. A measurement of the supreconducting transition temperature of the specimens after warm deformation at 800°C gave $T_c$ ∿9-10°K, and $T_c$ ∿5°K at 700°C.

Following warm deformation the samples were aged to precipitate the A-15 phase. The aging treatments were conducted over a range of temperatures from 600°C to 1000°C and for a number of aging times. The superconducting transition temperatures of the procut were then measured as a function of aging temperature and time.

The onset superconducting transition temperature is plotted as a function of aging temperature and time for the V-18.5 at. % Ga samples in Fig. 3, for the V-17.5 at. % Ga samples in Fig. 4, and for the V-14 at. % Ga samples in Fig. 5. The maximum $T_c$ measured was ~14.8°K, a value which compares favorably to the 15.4°K which is believed to be the maximum attainable critical temperature for the stoichiometric $V_3Ga$ composition[19]. For aging temperatures of 800°C or below there is an apparent maximum in the curve of critical temperature versus aging time. With aging temperatures of 800°C to 1000°C the critical temperature decreases to a value of 10°K or below when the aging time is made long.

## DISCUSSION

Reference to the equilibrium phase diagram shown in Fig. 1 reveals that for the sample compositions used here (14-19 at. % Ga) and for aging temperatures in the range 600°C to 1000°C the specimens fall within a two-phase region. At equilibrium these samples would therefore be expected to contain an A-15 phase, of composition determined by the edge of the two-phase region at the particular aging temperature. At 1000°C the predicted composition of the A-15 phase is ~20 at. % Ga, which, according to the work of Das et al.[17], has $T_c$ <10°K. Because the equilibrium concentration of the A-15 phase becomes progressively leaner in Ga as the aging temperature is decreased, successively lower transition temperatures would be expected from equilibrium considerations. However, under the non-equilibrium conditions, established during initial aging in the present work, the reverse happens. While aging at 1000°C eventually leads to a $T_c$ near 8°K, and aging at 800°C also eventually yields a rather low $T_c$, the maximum value of $T_c$ increases when lower aging temperatures are used.

The observation of higher $T_c$ is almost certainly associated with the small size of the initial precipitate particles and with the high degree of supersaturation under which they form. Preliminary transmission electron microscopic analysis of the specimens aged at lower temperatures to near maximum $T_c$ does show diffraction evidence for A-15 precipitates within the V/Ga matrix. However, the precipitates are extremely fine and have not yet been clearly resolved.

The small A-15 particles which initially precipitate from the supersaturated parent matrix will be expected to differ from the equilibrium A-15 phase in two aspects; composition and state of internal strain.

It is to be expected that particles at relatively low temperature will retain some strain for rather long aging time. The internal strain is known to influence the critical transition temperature in ways which remain poorly understood[20-22]. According to references 20 and 23, however, the effect is small.

There are thermodynamic reasons to anticipate that the sever supersaturation present at the time the particles form may cause them to have a more nearly stoichiometric composition than the equilibrium phase diagram would suggest. The thermodynamic argument follows directly from Gibbs[24] who pointed out that the energetic barrier to the formation of a small particle of a new phase within a supersaturated matrix is minimized when the new phase forms in a state such that the chemical potential of each component remains constant. If both the parent and product phases are incompressible then the relevant chemical potential is the relative chemical potential, which is equal to the slope of the free energy versus the composition curve of the parent solution measured at its mean composition, as illustrated in Fig. 6. The most favorable composition of small

precipitate phase is that composition at which its free energy vs. composition curve, at the same temperature, has an equal slope. The predicted result, illustrated in Fig. 6, is that small precipitate particles formed under significant supersaturation will tend to be richer in solute than indicated by the equilibrium phase diagram. If the free energy vs. composition curve of the precipitated phase has a strong minimum near its stoichiometric composition, in the sense that the curvature of the free energy curve is very high, then the precipitate will have a thermodynamic tendency to form initially in an almost stoichiometric composition. This thermodynamically preferred solute enrichment of the initial precipitate particles currently seems to offer the most plausible explanation for their very high transition temperatures.

In order to draw the supersaturated solid solution into a wire or tape, however, it did prove necessary to use warm working treatments at 700~800°C. Attempts to deform the samples at room temperature encountered severe brittleness problems. This result was not surprising since the V/Ga matrix is a body-centered cubic phase which is known and expected to undergo classic ductile-brittle transition behavior as the deformation temperature is lowered. The ductile to brittle transition temperature in body-centered cubic metals is known to be a strong function of the alloy grain size. Due to the extensive homogenization of the samples, the grain size of the alloy in the as-quenched state is large, approximately 1 mm. The ductile-brittle transition temperature is therefore high and warm working procedures are necessary if the alloy is not to crack during deformation. Lower working temperatures could presumably be used if the alloy is treated so as to refine its initial grain size, either by making chemical additions to inhibit grain growth during the homogenization step,

or by deforming and recrystallizing the alloy prior to the principal working operation. Research along these lines is currently in progress.

## CONCLUSIONS

The principal conclusion of the present research is that it is possible to produce high $T_c$ wires or tapes from the V-Ga system by a monolithic process in which an ingot is cast as a supersaturated solution of V and Ga, homogenized at elevated temperature, quenched to preserve the supersaturation, formed into a wire or tape, and finally heat treated at a relatively low temperature to precipitate the superconducting phase. To achieve exceptionally high critical temperatures, the precipitation reaction must be carried out at temperatures below approximately 750°C. The measured critical temperature then becomes a function of the aging time, and reaches a maximum value as high as 14.8°K in alloys containing 17-19 at. % Ga. The reason for the exceptionally high critical temperature when the precipitation is carried out a lower aging temperatures is not established, but may be plausibly interpreted as due to a thermodynamic tendency for small precipitates formed from highly supersaturated solid solutions to be rich in solute content.

## ACKNOWLEDGEMENTS

This work was supported by the Diviision of Materials Sciences, Office of Basic Energy Sciences and by the Division of Magnetic Fusion Energy, U. S. Department of Energy under Contract No. W-7405-Eng-48.

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## FIGURE CAPTIONS

Figure 1. The relevant portion of the V-Ga equilibrium phase diagram as reported by van Vucht et al.[16] (dot-dash lines) and modified by Das et al.[17] (solid lines).

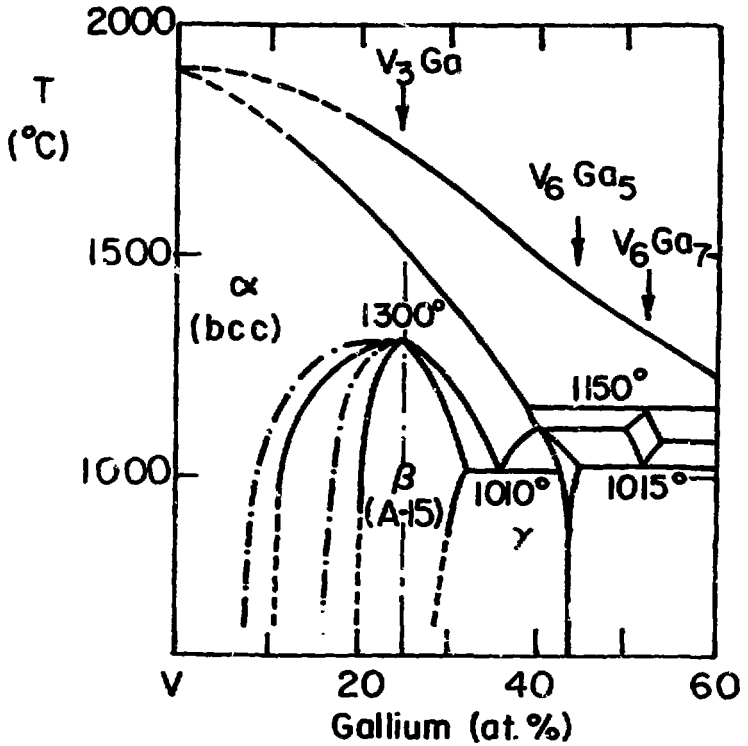
Figure 2. Scanning electron fractograph of a V-17.5% Ga sample broken after homogenization and quenching. The fracture occurs primarily through transgranular cleavage.

Figure 3. The critical transition temperature of deformed 18.5% Ga samples as a function of aging time for various aging temperatures.

Figure 4. The critical transition temperatures of deformed 17.5% Ga samples as a function of aging time for various aging temperatures.

Figure 5. The critical transition temperatures of deformed 14 at.% Ga samples as a function of aging time for various aging temperatures.

Figure 6. Schematic illustration of Gibbs free energy vs. composition at given temperature. $C_1$ and $C_2$ are the equilibrium compositions of the hypothetical $\alpha$ and A-15 phases at this temperature. $C_1^*$ is the composition of the supersaturated solid solution and $C_2^*$ is the preferred composition of the initial A-15 precipitation.

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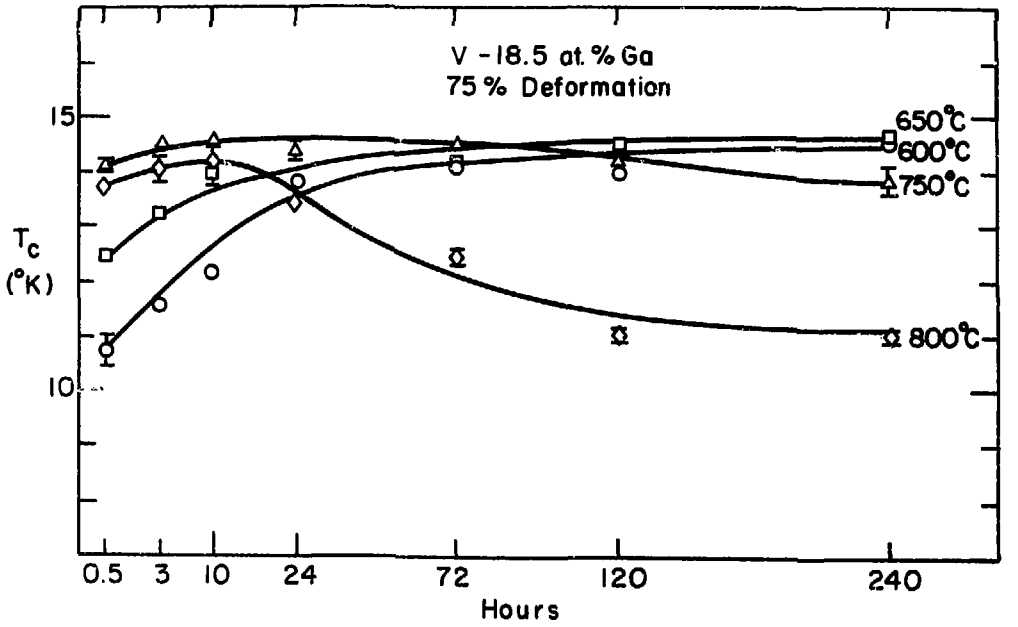


Figure 3. The critical transition temperature of deformed 18.5% Ga samples as a function of aging time for various aging temperatures.

XBL798-6765

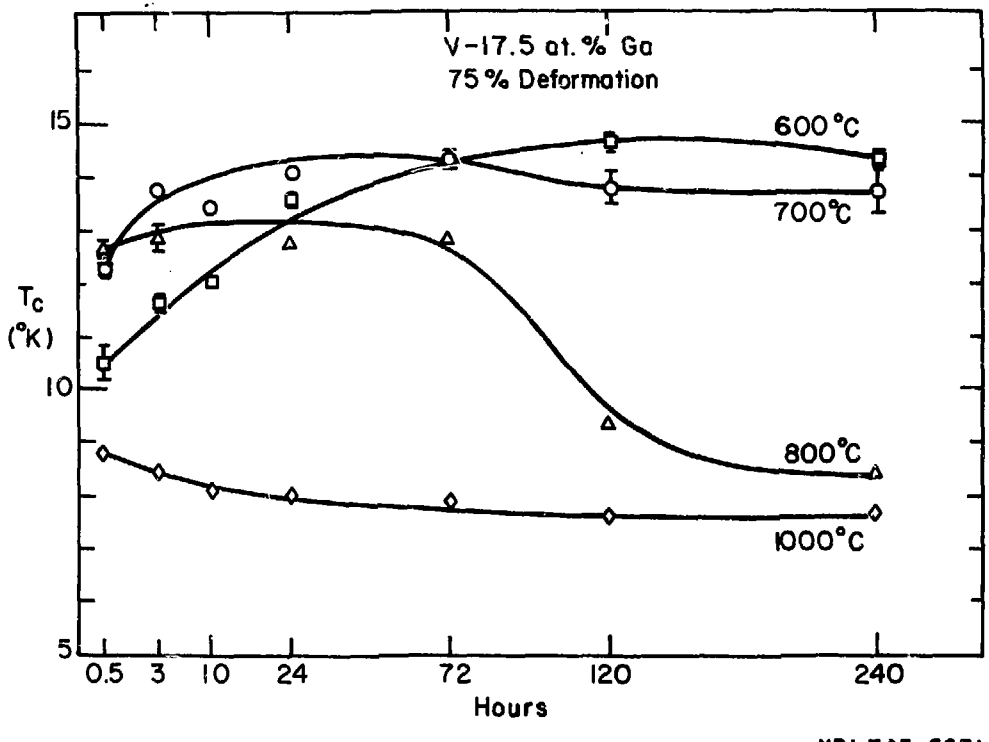


Figure 4. The critical transition temperatures of deformed 17.5% Ga samples as a function of aging time for various aging temperatures.

XBL793-5871

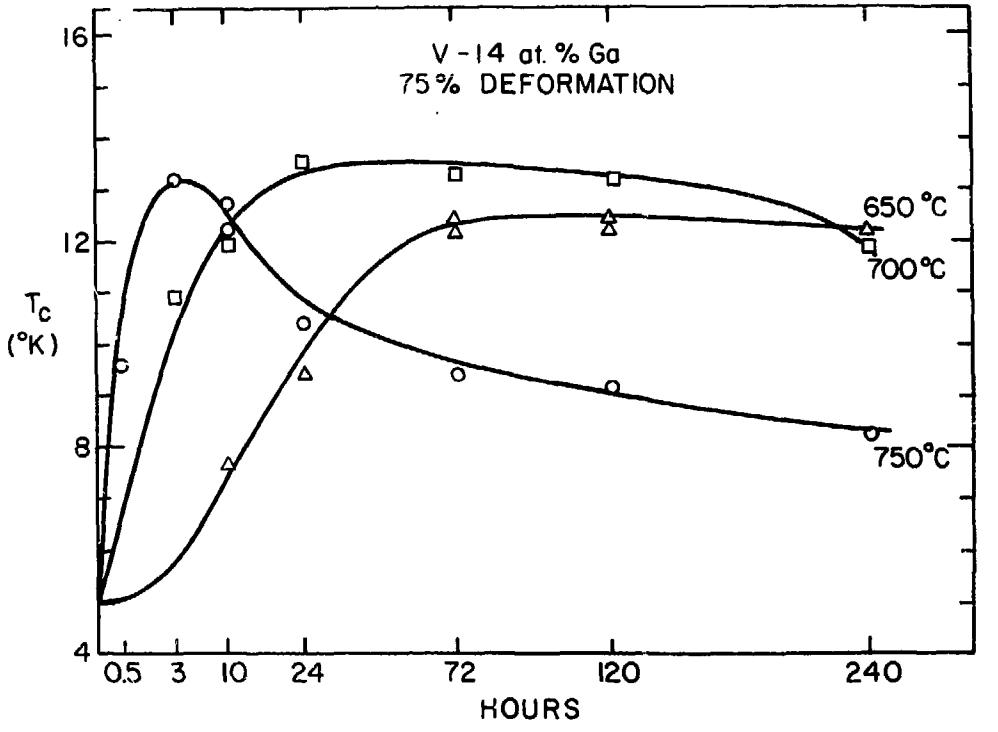


Figure 5. The critical transition temperatures of deformed 14 at. % Ga samples as a function of aging time for various aging temperatures.

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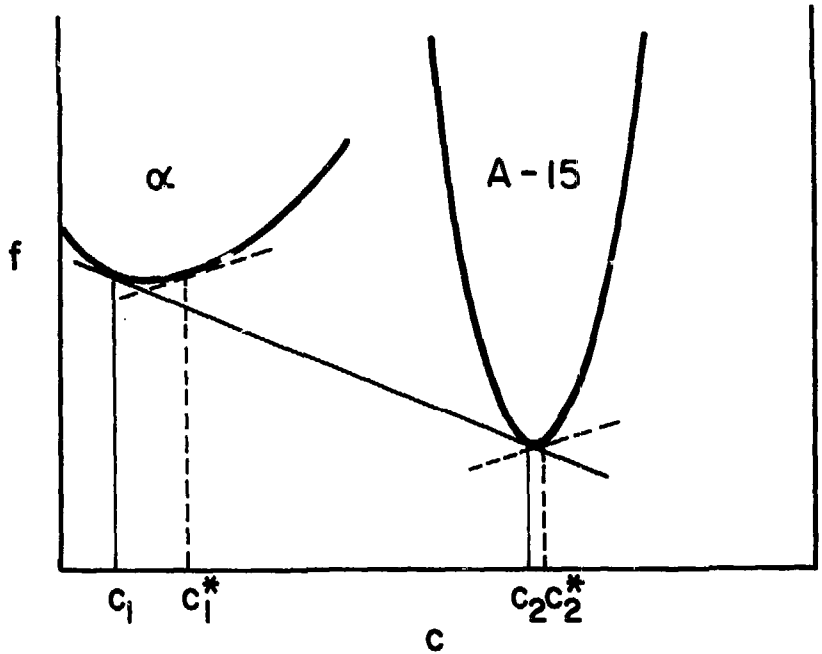


XBL793-5877

Figure 6. Schematic illustration of Gibbs free energy vs. composition at given temperature. $C_1$ and $C_2$ are the equilibrium compositions of the hypothetical α and A-15 phases at this temperature. $C_1^*$ is the composition of the supersaturated solid solution and $C_2^*$ is the preferred composition of the initial A-15 precipitation.