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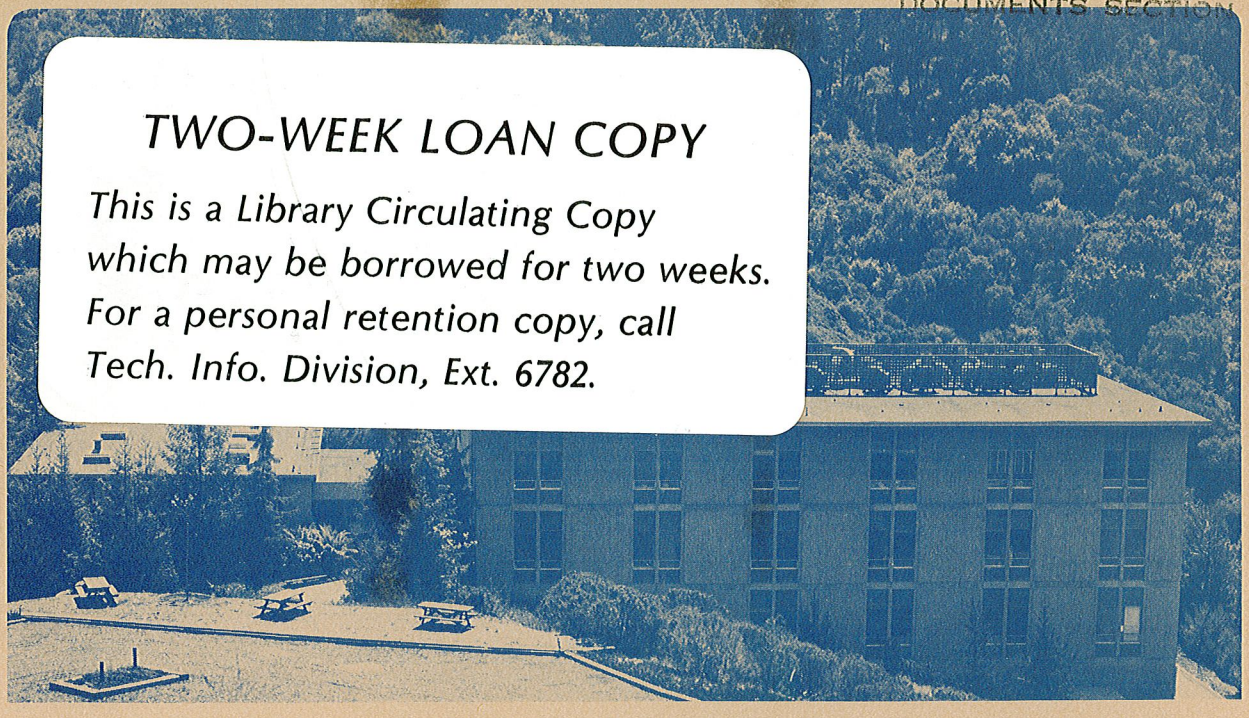

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MICROSTRUCTURE AND PROPERTIES OF A15 SUPERCONDUCTORS FORMED BY DIRECT PRECIPITATION

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Abstract

Superconducting materials were made by quenching supersaturated solutions of V-Ga and Nb-Al, deforming the quenched specimens, and then precipitating the A15 phase by aging at intermediate temperature. The critical current characteristics of the product materials depend both on the inherent properties of the A15 phase, which presumably reflect its composition, and on the details of the precipitation process, which determine the grain size, continuity, and volume fraction of the A15. These features of the precipitation process differ qualitatively between V-Ga and Nb-Al. They are described and used to interpret the critical current characteristics.

Introduction

Multifilamentary superconducting wires which utilize the Nb_3Sn and V_3Ga A15 compounds to achieve high current-carrying capabilities in high magnetic fields have been successfully manufactured by the so-called "bronze" process[1,2]. However, for thermodynamic reasons the bronze process is inapplicable to some of the most promising of the A15 superconducting compounds, including Nb_3Al[3], $Nb_3(Al,Si)$, and Nb_3Ge[4]. If these compounds are to be successfully used in wound superconducting devices, alternative manufacturing techniques must be developed.

An alternative approach which has been under investigation in our laboratory is the "direct precipitation process"[5,6], which has the metallurgical advantage of being the simplest possible way of manufacturing an A15 superconducting wire. In this process the elements which form the A_3B A15 compound are arc melted in proportion which permits the formation of an A-rich homogeneous solution at elevated temperature. The homogenized solution is quenched to low temperature at a rate sufficiently rapid to prevent the formation of the A15 phase, and then rolled or drawn at low temperature into a tape or wire. After deformation the material is aged at intermediate temperature to precipitate the A15 phase.

In our work the direct precipitation process was first applied to the V-Ga system, whose simple phase diagram in the A15 composition range makes it a natural candidate. The studies were subsequently extended to include the Nb-Al system, which is of direct engineering interest. The experimental details and initial properties obtained have been published elsewhere[5,6]. A15 superconductors were successfully manufactured from both the V-Ga and Nb-Al systems. Their critical current characteristics were good but not competitive with those obtainable in the better multifilamentary wires. Microstructural investigations were hence undertaken to characterize the precipitation process and to provide guidelines for property improvement. The present paper reports some of the results and implications of these microstructural studies.

Characteristics of the Direct Precipitation Process

The direct precipitation process yields a superconducting material in which discrete crystallites of the A15 phase are distributed through a matrix of residual solution. The critical current characteristic of the material at 4.2K is expected to be a function of at least four parameters: the stoichiometry of the A15 phase, the grain size of the A15 precipitates, the continuity of the precipitate network, and the aggregate volume fraction of A15. The first parameter is related to the composition of the A15 phase; the latter three concern its microstructural characteristics.

A. Composition

The composition of the A15 phase should determine

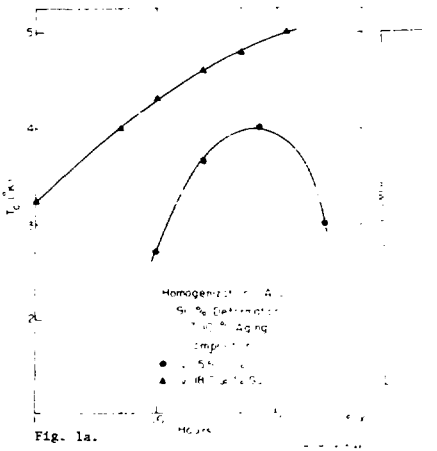

Fig. 1a.

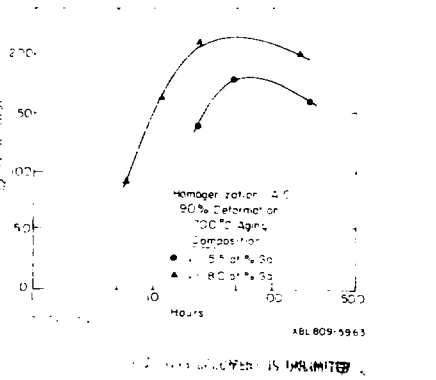

Fig. 1. (a) Critical temperature versus aging time for V-Ga. (b) Critical field versus aging time for V-Ga.

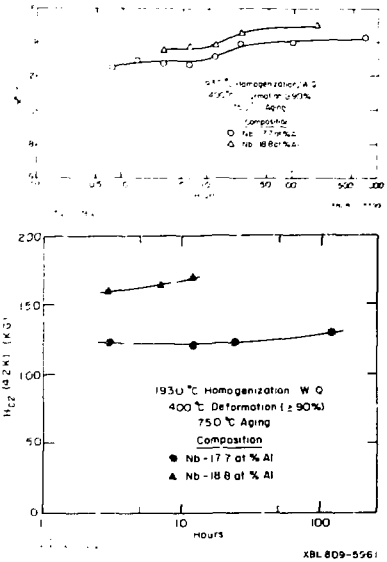

Fig. 2. (a) Critical temperature versus aging time for Nb-Al. (b) Critical field versus aging time for Nb-Al.

inherent superconducting properties such as its critical temperature (T_c) and upper critical field (H_{c2}). Hence these properties have been used as a rough measure of composition. A more exact determination is available through scanning transmission electron microscopy (STEM); the relevant studies are now in progress.

Examples of the critical temperature and upper critical field of precipitated V-Ga are given in Fig. 1. Those of precipitated Nb-Al are shown in Fig. 2. The critical temperatures were determined by an inductive method with a calibrated germanium resistance thermometer. The critical fields were estimated by extrapolating the critical current characteristic as suggested by Kramer[7]. Assuming that the precipitated crystallites have a range of compositions, the former technique will tend to measure the properties of the most nearly stoichiometric (highest T_c) particles, while the latter will reflect a composition closer to the mean. Hence, it is not surprising that the property curves have slightly different shapes. Preliminary results do suggest, however, that the T_c measurement gives a reasonable indication of composition when the particles are well-developed. Careful STEM analysis of the Al5 phase in V-18 at% Ga after 24 hrs aging at 700°C gives a Ga content slightly above 23 at.%. The measured T_c, 14.6K, is in good agreement with that previously determined[8] for V_3Ga having this Ga content.

In V-Ga aged at 700°C both the critical temperature and critical field increases with the Ga content of the starting alloy. They tend to reach a maximum, then decrease after long aging times, a behavior pattern which suggests an eventual decrease in the Ga content of the Al5 phase. The maximum T_c of V-18Ga, 15K, corresponds to a nearly stoichiometric Al5 phase; the maximum critical field also suggests a Ga content near 25 at.%. The critical temperature and the critical field increase with the starting content of Al, and also increase monotonically with aging for times up to 500 hours. The data suggest a gradual increase in the Al content of the Al5 phase, which apparently remains lean in Al since the greatest values of T_c and H_{c2} are significantly below their values for stoichiometric Nb_3Al[3,9].

B. Microstructure

Example microstructures of deformed and aged V-Ga and Nb-Al samples are presented in Figs. 3 and 4.

There are significant differences between the patterns of precipitation in the two materials. In specimens which are not deformed prior to aging, the precipitation of V_3Ga is confined to the grain boundaries of the prior solution, while Nb_3Al nucleates and grows densely within the interior of the grains. After severe warm deformation, both materials contain a high density of dislocations. In the early stages of aging the dislocations organize themselves into low-angle subgrain boundaries. These subgrain boundaries then form a template for nucleation of a network of Al5 precipitates.

As shown in Figs. 3 and 4, the morphological characteristics of the two precipitates are different. V_3Ga precipitates as a set of discrete particles which grow in a lenticular shape away from the boundaries into the interior of the grains. The precipitates tend to be surrounded by matrix phase, suggesting a

Fig. 3. TEM micrograph of V-15.6 at.% Ga aged at 700°C for 108 hrs. Regions A and B are Al5 and BCC phases respectively.

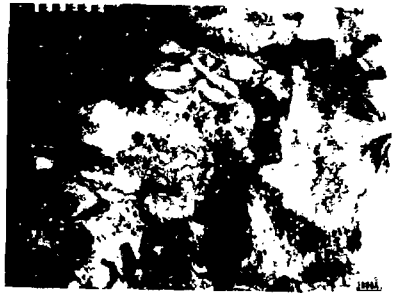

Fig. 4. TEM micrograph of Nb-18.0 at.% Al aged at 750°C for 1.5 hrs. Regions A and B are Al5 and BCC phases respectively.

preferential wetting by the matrix material. As the reaction develops, the grains grow and elongate into particles of relatively high aspect ratio. Alternatively, Nb_3Al precipitates as small, more nearly equiaxed particles which densely coat the subgrain boundaries at an early stage of the reaction. The micrographs reveal good particle-to-particle contact suggesting preferential self-wetting by the A15 phase. As the reaction proceeds, the A15 particles do coarsen somewhat, but the primary process extending the reaction into the interior of grains is the nucleation of new precipitates on the surface of those already present. Significant grain growth occurs only at a relatively late stage in the reaction when the A15 volume fraction is well established and the particles coarsen at the expense of one another.

C. Implicati for Superconducting Properties

From the perspective of establishing a microstructure conducive to good current-carrying properties, the Nb_3Al precipitation pattern revealed in these studies

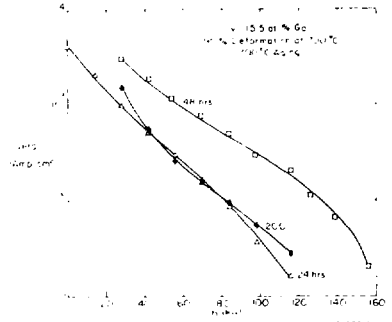

Fig. 5. Critical current versus applied field for V-Ga samples with different aging times.

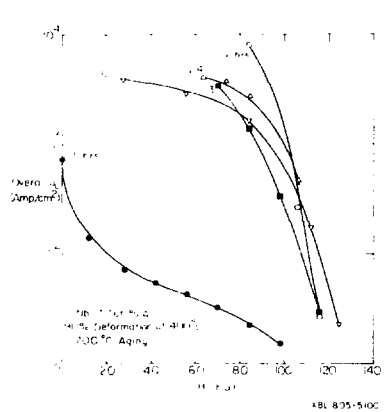

Fig. 6. Critical current versus applied field for Nb-Al samples with different aging times

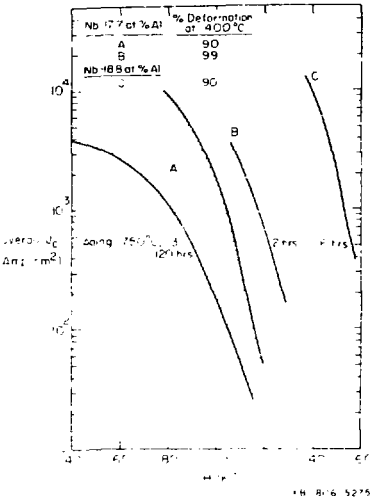

Fig. 7. Critical current versus applied field for Nb-Al samples with different compositions (curves A and C) and different amounts of deformation (curves A and B).

is clearly preferable to that of V_3Ga. The Nb_3Al reaction establishes a good interparticle contact between small precipitates which are dense on the network of subgrain boundaries, hence yielding good continuity with fine grain size at a reasonable volume fraction. The V_3Ga pattern yields particles which tend to be isolated from one another by buffer films of the matrix solution and which grow to relatively large size before good continuity is achieved. On the other hand, the inherent superconducting properties are better in the V_3Ga case. The A15 phase in V-Ga achieves a critical temperature and upper critical field reasonably near the best obtainable in V_3Ga, while the Nb-Al A15 phase has a critical temperature and field well below the best found in Nb_3Al. The two materials we have produced to date hence include one having a basically good A15 phase in an undesirable morphology and one having a less attractive A15 in a very promising morphology. These features are reflected in their relative critical current characteristics.

Critical Current Characteristics

The variation of overall critical current with applied magnetic field was measured for a number of V-Ga and Nb-Al specimens. Examples of the data are given in Figs. 5, 6 and 7. Figures 5 and 6 show the variation of properties with heat treatment time for examples of V-Ga and Nb-Al, respectively.

In the V-Ga case represented in Fig. 5, the current-carrying properties improve over the whole range of fields studied as the heat treatment time is increased to 48 hours but deteriorate thereafter. The improvement apparently reflects both the better intrinsic characteristics of the A15 precipitates, which particularly determine high-field properties, and the increasing continuity and volume fraction of the A15 phase. The subsequent deterioration presumably re-

flects the low of intrinsic properties (Fig. 1) coupled with the increasing grain size of the A15. The critical current is relatively low at all fields (compared with multifilamentary V_3Ga[10] and increases only slightly as the field is decreased. Both these features may be due to the tendency of the A15 phase to form in isolated particles[9]

In the Nb-Al case represented in Fig. 6, the low-field properties improve for heat treatment times up to 12 hours and deteriorate thereafter, while the properties at the highest fields continue to improve. The latter effect is almost certainly due to the enhancement of the intrinsic superconducting properties at long aging times documented in Fig. 2. The former probably reflects the competition between increasing continuity and volume fraction, which cause the critical current to increase, and grain growth of the A15 precipitates, which causes J_c to decline. The very rapid increase in the overall critical current of the 12 hr specimen for decreasing field below H_{c2} suggests a very good balance between A15 grain size, continuity and volume fraction. The relatively slow increase in J_c of the 1.5 hr specimen presumably reflects the poor continuity of the A15 phase at this early stage of the precipitation process.

The microstructural considerations discussed in the previous section suggest that the overall critical current characteristic of Nb-Al will be improved by either increasing the deformation of the sample prior to aging, which should refine the size of the subgrain network on which the precipitates form, or by increasing Al content of the starting alloy, which should improve the intrinsic properties of the A15 phase. The data presented in Fig. 7 show that both of these processing modifications enhance the critical current characteristics.

Given the results of this investigation, the development of a competitive Nb-Al superconducting wire through the direct precipitation process will necessarily require a substantial improvement in the intrinsic properties, and hence the stoichiometry of the A15 precipitate phase. There are metallurgical techniques which may lead to a more stoichiometric A15 precipitate, and these are now under investigation.

Acknowledgement

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