High magnetic field transport properties of liquid quenched Nb$_3$Al and Nb$_3$Al(Si,Ge) superconducting compounds

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Critical current behavior and intrinsic superconducting properties of liquid quenched Nb$_3$Al and its pseudobinaries Nb$_3$Al(Si) and Nb$_3$Al(Al,Ge) have been studied in fields up to 29 T. Our results show that flux pinning in these materials is dominated by strong precipitate pinning at low temperatures and by grain boundary pinning at high (> 10 K) temperatures. The best results were obtained in Nb$_3$Al$_2$Ge$_6$ samples with $T_c$ of 20.0 K, estimated $H_{c2}(0)$ of 43 T and $J_c$ (4.2 K) in excess of $10^6$ A/cm$^2$ at 30 T.

Of all the known superconducting materials with $A$ 15 structure only two, Nb$_3$Sn and V$_3$Ga, are currently used for fabrication of high-field superconducting magnets. The maximum limits of these magnets, 16–18 T, are imposed mainly by a rapid decrease of the materials’ critical current density $J_c$ in fields approaching their upper critical field $H_{c2}$. Even with significant alloying improvements, the highest fields attainable are unlikely to exceed 20–22 T.

In other known superconducting compounds with appreciably higher $H_{c2}$’s, high $J_c$’s have either never been achieved (e.g., Chevrel phases) or only in material form unsuitable for magnet fabrication. Examples of this are liquid quenched Nb$_3$Al (Ref. 2) and its pseudobinaries$^3$ Nb$_3$Al(Si) and Nb$_3$Al(Al,Ge) and thin films of the B 1 compound NbN.$^4$ In the latter two cases, $J_c$’s of small laboratory samples of Nb$_3$Al$_{0.75}$Ge$_{0.25}$ and of NbN were reported to exceed $10^6$ A/cm$^2$ at 22.3 and 21.0 T, respectively, suggesting that the maximum fields produced with superconducting magnets could be pushed to higher values.

Recently suggested approach$^5$ of quenching liquid Nb$_3$ Al(Si,Ge) alloy directly onto a rapidly moving hot substrate tape may indeed result in a useful conductor form. At the same time, significant progress in developing Nb$_3$Al based multilaminated composites via powder metallurgy$^6$ provides additional incentive to establish the $J_c$ limits of Nb$_3$Al and its pseudobinaries and the origin of flux pinning in these compounds.

In this letter we report our study of the critical current behavior of rapidly quenched Nb$_3$Al(Si,Ge) alloys in fields up to 29 T. The critical current density in excess of $10^6$ A/cm$^2$ at the highest fields is consistent with our earlier studies$^3$ of these compounds at lower fields. These results also suggest that, other material problems aside, $J_c$ limits should not prevent development of superconducting magnets capable of producing fields in the 25–30 T range.

The details of the sample preparation and measurements can be found elsewhere.$^7,8$ Alloy ingots were melted and levitated by rf induction techniques within a water-cooled, silver-plated copper crucible. Small pieces were then broken off the ingot and inserted into a water-cooled gun.

The molten sample was ejected by a pulse of argon gas from the gun onto the curved edge of a spinning disc where it solidified into a tape, typically 20–40 µm thick and 0.5–2 cm long. The estimated quenching rate for these samples is in the range $10^5$–$10^6$ K/s.

The samples used for $J_c$ measurements were mounted on sapphire substrates. Unlike the as-quenched samples that proved to be extremely susceptible to temperature cycling and had to be imbedded in indium to survive cooling to low temperatures,$^2,3$ the annealed tapes reported on in this letter required no additional mechanical support.

The fabricated Nb$_3$Al and Nb$_3$Al(Si,Ge) tapes have excellent superconducting equilibrium properties as well as high $J_c$’s indicative of strong flux pinning. Transition temperatures are only slightly lower than the best published values,$^{9–11}$ presumably due to disorder and off stoichiometry inherent in the fabrication process. Structural and compositional disorder in the as-quenched samples, resulting from a high degree of undercooling of the $A$ 15 phase, can be greatly reduced by annealing. In fact, $T_c$ increases by about 2 K after annealing at 750 °C for about 200 h. The addition of Ge or Si also increases $T_c$; however, these values (see Table I) are again about 1 K lower than the $T_c$'s of the samples quenched at a much lower rate of $5 \times 10^4$ K/s.$^{11}$ On the other hand, the upper critical field values of our samples are essentially the same as the best published results. This can be attributed to the moderately high residual resistivities ($\rho \approx 50 \mu\Omega$ cm) causing a high critical field slope, $- (dH_{c2}/dT)_T$ (see Table I). In Fig. 1 a large range of linear dependence of $H_{c2}$ on $T$ indicates, as expected in Nb-based $A$ 15 compounds, no apparent paramagnetic limitation.$^{12,13}$ For a comparison among the various $A$ 15 compounds, values of $H_{c2}(0)$ are computed from $dH_{c2}/dT|_{T_c}$. The $T_c$, using the relationship$^{14}$

$$H_{c2}(0) = 0.693 T_c \left( - \frac{dH_{c2}}{dT} \right)_{T_c},$$

which is valid in the dirty limit. The computed results are given in Table I.

The microstructure studies and x-ray analysis show the presence of a small amount of a second phase, Nb$_2$Al$_2$, that is dispersed as equiaxed precipitates along grain boundaries (Fig. 2). This phase is not superconducting above 1.3 K$^{15}$ and competes thermodynamically with the $A$ 15 phase upon so-

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TABLE I. Equilibrium results of some Nb$_3$Al and Nb$_3$Al(Si,Ge) rapidly quenched samples.

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>Sample</th>
<th>at. % B</th>
<th>at. % B'</th>
<th>Treatment ($^\circ$C x h)</th>
<th>$T_c^0$ (K)</th>
<th>$\Delta T_c (K)$</th>
<th>$\frac{-dH_c^0}{dT}$ (T/K)</th>
<th>$H_c^0(0)$ (T)</th>
<th>$\Delta H_c(0)$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb$<em>3$Al$</em>{13}$</td>
<td>A1</td>
<td>24.5</td>
<td>0</td>
<td>750 x 52</td>
<td>18.4 ± 0.1</td>
<td>0.31 ± 0.1</td>
<td>2.49 ± 0.04</td>
<td>32.0 ± 0.5</td>
<td>2.1 ± 0.5</td>
</tr>
<tr>
<td>Nb$<em>3$Al$</em>{13}$</td>
<td>A2</td>
<td>24.5</td>
<td>0</td>
<td>750 x 200</td>
<td>18.2</td>
<td>1.6</td>
<td>2.56</td>
<td>32.0</td>
<td>4.1</td>
</tr>
<tr>
<td>Nb$<em>3$Al$</em>{13}$</td>
<td>A3</td>
<td>24.5</td>
<td>0</td>
<td>750 x 200</td>
<td>18.3</td>
<td>1.7</td>
<td>2.41</td>
<td>31.0</td>
<td>4.6</td>
</tr>
<tr>
<td>Nb$<em>3$Al$</em>{13}$Si$_{1.5}$</td>
<td>AS1</td>
<td>23.9 ± 1</td>
<td>1.4 ± 0.5</td>
<td>750 x 52</td>
<td>18.0</td>
<td>0.3</td>
<td>2.88</td>
<td>36.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Nb$<em>3$Al$</em>{13}$Si$_{1.5}$</td>
<td>AS2</td>
<td>24.5</td>
<td>0</td>
<td>750 x 200</td>
<td>18.7</td>
<td>0.3</td>
<td>2.50</td>
<td>32.5</td>
<td>2.4</td>
</tr>
<tr>
<td>Nb$<em>3$Al$</em>{13}$Si$_{1.5}$</td>
<td>AS3</td>
<td>24.5</td>
<td>0</td>
<td>750 x 200</td>
<td>18.4</td>
<td>0.4</td>
<td>2.74</td>
<td>35.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Nb$<em>3$Al$</em>{10}$Ge$_6$</td>
<td>AG1</td>
<td>17.3 ± 1</td>
<td>6.9 ± 0.5</td>
<td>750 x 52</td>
<td>19.7</td>
<td>0.4</td>
<td>3.06</td>
<td>42.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Nb$<em>3$Al$</em>{10}$Ge$_6$</td>
<td>AG2</td>
<td>20.0</td>
<td>0</td>
<td>750 x 200</td>
<td>20.0</td>
<td>0.3</td>
<td>3.12</td>
<td>43.0</td>
<td>3.8</td>
</tr>
<tr>
<td>Nb$<em>3$Al$</em>{10}$Ge$_6$</td>
<td>AG3</td>
<td>19.7</td>
<td>0</td>
<td>750 x 200</td>
<td>19.7</td>
<td>0.7</td>
<td>3.00</td>
<td>41.0</td>
<td>4.6</td>
</tr>
</tbody>
</table>

$T_c^0$ is the onset $T_c$ taken at 0.98$\rho_0$.
$\Delta T_c$ is the transition width obtained from $T_c^0 - T_c'$. $T_c'$ is taken at 0.92$\rho_0$.
$H_c^0(0)$ is obtained from Eq. (1), using $T_c^0$ and $H_c^0(T)$.
$\Delta H_c$ is the spread of the $H_c$ transition.
$\rho_0$ is the residual resistivity at 21 K.

Lidification, thus limiting the atomic percent of Al to less than the stoichiometric 25 at. % in the ideal $A15$ phase. The higher degree of stoichiometry of the $A15$ phase in the pseudobinaries is due to the presence of a miscibility gap between the second phase $Nb_2Al(Ge)$ and $Nb_3(Ge,Al)_3$, and also between $Nb_2Al(Si)$ and $Nb_3Al(Si)$, which allow the $A15$ phase boundary to advance closer to the stoichiometric composition at the appropriate Al to Ge and the Al to Si ratio, respectively.\(^\text{10}\)

In addition, plate precipitates were found within the $A15$ grains in some regions of the tapes for all compositions. To the best of our knowledge, this is the first observation of plate precipitation in any $A15$ material. Further study of this will be published elsewhere.

The critical current densities measured at 4.2 K for some annealed Nb$_{33}Al_{13}$, Nb$_{33}Al_{22.5}Si_{1.5}$, and Nb$_{33}Al_{10}Ge_6$ samples are plotted in Fig. 3. Although the values of $H_c(4.2$ K) of Nb$_{33}Al_{13}$ and Nb$_{33}Al_{22.5}Si_{1.5}$ are not very different (see Fig. 1), $J_c$ of the Nb$_{33}Al_{13}$ sample decreases rapidly in a magnetic field exceeding 18 T while Nb$_{33}Al_{22.5}Si_{1.5}$ retains a $J_c$ of the order of $10^4$ A/cm$^2$ at fields close to 26 T. This is believed to be due to the greater compositional inhomogeneity of the binary $A15$ phase as inferred from the transition widths $\Delta T_c$ and $\Delta H_c(0)$ which are included in Table I. Nb$_{33}Al_{10}Ge_6$ has an extremely high $H_c(0) \approx 38$ T at $4.2$ K and high $J_c$ of the order of $10^3$ A/cm$^2$ in fields up to 30 T. In the intermediate field range, higher values of $J_c$ than the ones reported in this letter have been achieved.\(^\text{2,3,5}\)

The compositional inhomogeneity of the $A15$ phase and the observed wide distribution of the size of the pinning centers both contribute to a decrease in the critical current at high fields and to an overall decrease of $J_c$ at higher temperatures. We find relatively small $A15$ grains of the order 2000 Å on the splat side of the tape, where the growth process is inhibited by rapid solidification. In the remainder of the cross section, the growth is controlled by the thermal diffusivity of the solidified splat side, thus producing grains that are as large as 1 μm. In general, the microstructural features depend very sensitively on the quenching rate, degree of melt superheating, and other experimental parameters that are difficult to control. As a result, the microstructural scale was found to vary from 50 to 100 Å in very thin, as-quenched Nb$_{33}Al_{22.5}Si_{1.5}$ samples\(^\text{3}\) to several thousand angstroms in thicker or annealed samples, with $J_c$ varying accordingly. It should be possible to reduce the overall microstructural inhomogeneity and improve reproducibility by forming thinner samples. Such a process might be better achieved by quenching onto hot substrates.\(^\text{5}\)

In general, flux pinning in $A15$ compounds is attributed to grain boundary pinning. In our samples we find that flux pinning results from a superposition of two pinning mechanisms: grain boundary (gb) pinning which can possibly be attributed to electron scattering mechanism (ESM),\(^\text{16,17}\) and precipitate (ppt) pinning due to fluxoid core pinning. The range of the effectiveness of the gb pinning versus ppt pinning is temperature dependent, with the ppt pinning contributing less as the temperature increases. Above $T \approx 13$ K the gb pinning dominates. Grain boundary pinning produces a peak in $F_p(h)$ at about $h_p = 0.10-0.28$, which is in the $h$-

![FIG. 1. Upper critical field $H_c^0$ vs temperature for the Nb$_3$Al(Si,Ge) samples.](image-url)
range reported in the literature for gb pinning in Nb$_7$Ge$^{18}$ and Nb$_7$Sn.$^{19}$ The peak in $F_p$ due to ppt pinning is observed in the $h_p$ range 0.58–0.67. A more detailed report on the flux pinning characteristics of these samples will be published elsewhere.

In summary, we find that melt-spin quenching with subsequent annealing produces Nb$_7$Al and Nb$_7$Al (Ge, Si) tapes with excellent equilibrium properties. Flux pinning in these materials is dominated by strong precipitate pinning at low temperatures and by grain boundary pinning at high temperatures. Critical currents in excess of 10$^4$ A/cm$^2$ at 29 T in annealed Nb$_{51}$Al$_{49}$Ge$_{6}$ tapes suggest that the maximum fields attainable with the present generation of superconducting magnets can be pushed to much higher limits.

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