Superconducting properties of $V_3Ga$ prepared by rapid liquid quenching and solid-state precipitation

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A modified solid-state precipitation process for the formation of stoichiometric $A$-$15$ $V_Ga$ is presented which results in high values of $T_c = 15.0$ K and $H_{c2}$ (4.2) = 22 T, excellent phase homogeneity, and a high critical current $J_c (4.2)$ K = $3 \times 10^4$ to $6 \times 10^4$ A/cm$^2$ over the field range 0-18 T. We find that grain boundary pinning is dominant, producing a very high specific pinning force $Q'_{pin}$ = $6.4 \times 10^4$ dyn/cm$^2$. The nonparamagnetically limited $H_{c2}$ is needed to explain our high flux-pinning results.

Several $A$-$15$ compounds are excellent materials for superconducting magnets. $V_3Ga$ ranks among the best of them with a high transition temperature ($T_c$ = 15.9 K) and upper critical field [$H_{c2}$ (4.2) K = 22 T]. This material can be made with a microstructure which provides effective flux pinning, and thus it produces very high critical currents. Furthermore, $V_3Ga$ has a stable stoichiometric $A$-$15$ structure, and hence several fabrication methods can be employed. Among these methods are the solid-state diffusion of Ga into V which is widely used in the bronze process and in situ processes, and the solid state precipitation (SSP) of the $A$-$15$ compound from the $A$-$2$ phase. The SSP method has been investigated by Hong et al. In this letter we present a modified SSP process for $V_3Ga$ in which very rapid quenching is employed to form the $A$-$2$ phase with a fine microstructure. The $A$-$2$ phase was completely transformed by heat treatments to the $A$-$15$ phase while maintaining small grain microstructure. Our results show high values for $T_c$ and $H_{c2}$, excellent homogeneity of the $A$-$15$ material as inferred from the extremely narrow superconducting transition widths. Our critical current densities are comparable to the highest reported.

The samples were prepared by first alloying 99.99% pure V with 99.9999% pure Ga, to form $V_3Ga_{25}$ ingots. This mixing was performed by rf induction levitation melting in an atmosphere of Ar (99.98% pure). The loss of Ga through vaporization was compensated for by starting with an extra amount of Ga (30%) and then subsequently weighing the ingot after each melting until the stoichiometric composition was attained.

The tape samples were formed by splat quenching pieces broken off the ingot onto a rotating copper dish. With quenching rates of about $5 \times 10^4$ C/s, a supersaturated bcc structure of the $A$-$2$ phase was obtained with a Ga content at nearly 25 at. %. These tapes are ductile and transform to the brittle $A$-$15$ material by heat treatment. The tapes were then annealed at 700 $^\circ$C for 48 h. This transformed the samples to a single phase of $A$-$15$ material. Lower annealing temperatures can be used but not without much longer annealing times which would make the process impractical and may lead to lower flux pinning.

The as-quenched and annealed tapes were examined by x-ray and electron microscopy. TEM images show a microstructure of $A$-$15$ grains with a mean size of about 1700 $\AA$ in the annealed tapes. The grain boundaries are clean with no evidence of second-phase precipitates. A variation in grain sizes is observed across the cross section of the tape. The splat side has the smaller grains of about 1000 $\AA$ in diameter. The size of the grains across the tape thickness is controlled by the thermal diffusivity of the splatted surface layer, hence larger grains of about 3000 $\AA$ are found near the free surface.

The transport properties are measured by a four-probe resistive technique. The magnetic field measurements were performed at the National Magnet Laboratory in Bitter magnets with fields up to 23 T. The critical current is defined as the current that produces a 1 $\mu$V/cm across the voltage leads.

The transition temperature of the samples is 15.0 K which is about 0.9 K less than the record value. The width of the transition is very small, about 50 mK. The lower transition temperature in our samples is primarily due to our annealing temperature being higher than the optimal heat treatment of 560 $^\circ$C for two months. In Ref. 1, a $T_c$ = 15.2 K was obtained for stoichiometric $V_3Ga$ with a heat treatment similar to ours. The lower $T_c$ in our samples may be a result of a reduction in the long-range order (LRO) of the $A$-$15$ structure caused by an excess of vacancies created during the higher annealing temperature of 700 $^\circ$C. Furthermore, the samples are slightly off-stoichiometry; electron microscope analysis gave a composition of 24.8 ± 1 at. % Ga. Using the empirical variation of $T_c$ with composition $-1.5$ K/at. % Ga from the ideal of 25 at. % Ga, we find that a depression in $T_c$ of 0.2 K is not unexpected.

The values of $H_{c2}$ ($T$) are as high as can be expected from a homogeneous sample with uniform composition and a high degree of LRO. At 4.2 K, $H_{c2}$ was measured to be 22.0 T with a transition width of only 0.2 T. The experimental results, Fig. 1, show the paramagnetic limitation of $H_{c2}$ which is typical for $V_3Ga$. $H_{c2}$ ($T$) is not linear with temperature except very near $T_c$; with the slope $dH_{c2}/dT = -3.89$ T/K. The $H_{c2}$ ($T$) curve was fitted to our data by using the expression that includes the effects of the electron-phonon interaction. This results in a physically reasonable spin-orbit scattering length of $l_{so} = 500$ $\AA$, and in $H_{c2} (0) = 24.5$ T.

Our critical current densities measured at 4.2 K are displayed in Fig. 2 as a function of the applied field. Included on

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the same figure are the data obtained previously by the SSP process\textsuperscript{b} and recent composite works.\textsuperscript{a} Over the wide field range from 0 to 18 T, \( J_e \) changes only from \( 3 \times 10^5 \) to \( 6 \times 10^4 \) A/cm\(^2\). This persistence of high \( J_e \) up to fields close to the measured \( H_{c2} \) is an attractive feature for a superconducting magnet, and can be attributed to the paramagnetically limited upper critical field and to the high degree of phase homogeneity of the A-15 material throughout the entire sample. Above 18 T, \( J_e \) drops off sharply and diminishes close to the measured \( H_{c2} = 22 \) T. The \( J_e \) values obtained for our modified SSP process are much higher than reported before,\textsuperscript{a} and are close to the best values obtained in Cu-V\textsubscript{7},Ga\textsubscript{5} composites.\textsuperscript{4,10}

The very strong flux pinning observed in our tapes is a result of grain boundary pinning, typical for A-15 compounds. We find, however, that the use of the nonparamagnetically limited \( H_{c2} \) gives closer values of the pinning parameter to the theoretical ones. The maximum specific pinning is obtained from

\[
Q_{\text{p}}^{\text{max}} = F_{\text{p}}^{\text{max}} / N_d,
\]

where \( F_{\text{p}}^{\text{max}} \) is the maximum measured pinning force, \( N_d \) is the average number of flux-pinning sites per unit volume, estimated to be \( 1 / 3 \langle D \rangle \), where \( \langle D \rangle \) is the average equiaxed grain size. For our samples, typical values for \( Q \) are in the range \( 7.5 \times 10^2 - 5.3 \times 10^4 \) dyn/cm\(^2\). This is much higher than the \( Q \) values obtained on other A-15 samples of grain boundary pinning (see Table I) with comparable \( H_{c2} \).

The specific pinning force is related to the elementary pinning force \( F_{\text{p}} \). Ignoring flux line elasticity, the direct summation predicts \( Q_{\text{p}}^{\text{max}} = f_r \). Direct summation seems to be observed in most A-15 materials and we will assume that it is valid in V\textsubscript{5},Ga also.

Assuming that the change of the electron scattering at the grain boundary causes flux pinning, \( f_r \) can be calculated.\textsuperscript{11} Using the measured \( H_{c2} \) value and the results of Ref.

### Table I. Survey of A-15 grain boundary flux pinning data at 4.2 K.

<table>
<thead>
<tr>
<th>A-15 materials</th>
<th>( H_{c2} ) (T)</th>
<th>( h_p )</th>
<th>( F_{\text{p}}^{\text{max}} ) (10(^2) dyn/cm(^2))</th>
<th>( \langle D \rangle ) (Å)</th>
<th>( Q ) (10(^4) dyn/cm(^2))</th>
<th>( f_r ) (10(^4) dyn/cm(^2))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb\textsubscript{5}Sn</td>
<td>21 ( \pm ) 1</td>
<td>0.3 ( \pm ) 0.03</td>
<td>1900</td>
<td>2500</td>
<td>1.42</td>
<td>1.35 ( \pm ) 0.15</td>
<td>\textsuperscript{a}</td>
</tr>
<tr>
<td>Nb\textsubscript{5}Al</td>
<td>21 ( \pm ) 0.5</td>
<td>0.19 ( \pm ) 0.05</td>
<td>4</td>
<td>( \pm ) 4</td>
<td>12000</td>
<td>1.5 ( \pm ) 0.3</td>
<td>1.12 ( \pm ) 0.07</td>
</tr>
<tr>
<td>Nb\textsubscript{5}Ga</td>
<td>22 ( \pm ) 1</td>
<td>0.23 ( \pm ) 0.03</td>
<td>2.5 ( \pm ) 0.5</td>
<td>11000</td>
<td>0.83 ( \pm ) 0.17</td>
<td>1.26 ( \pm ) 0.14</td>
<td>\textsuperscript{c}</td>
</tr>
<tr>
<td>V\textsubscript{5}Ga</td>
<td>22 ( \pm ) 0.2</td>
<td>0.74 ( \pm ) 0.02</td>
<td>1200 ( \pm ) 5</td>
<td>1700 ( \pm ) 300</td>
<td>6.4 ( \pm ) 1.1</td>
<td>1.5 ( \pm ) 0.03</td>
<td>\textsuperscript{d}</td>
</tr>
<tr>
<td>V\textsubscript{5}Ga\textsuperscript{+}</td>
<td>36 ( \pm ) 0.6</td>
<td>0.45 ( \pm ) 0.02</td>
<td>9120 ( \pm ) 50</td>
<td>1800 ( \pm ) 300</td>
<td>6.4 ( \pm ) 1.1</td>
<td>5.1 ( \pm ) 0.2</td>
<td>\textsuperscript{e}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Results obtained by using the nonparamagnetically limited \( H_{c2} \).


\textsuperscript{c} See Ref. 7.
11, we find $f_p = (1.5 \pm 0.3) \times 10^4 \text{dyn/cm}^2$. This is markedly smaller than the measured $Q^{\text{max}}$ values. Also the value of field at which $Q$ is maximum is $h_p = H_p / H_c2 = 0.74$, which is much higher than $h_p$ values due to grain boundary (gb) pinning in other A-15 compounds (see Table I). However, using the nonparamagnetically limited $H_c2 (4.2 \text{K}) = 36 \text{T}$ in our samples, we find $f_p = 5.1 \times 10^4 \text{dyn/cm}^2$ and $h_p = 0.45$, in closer agreement with the measured $Q$ values and the other $h_p (\text{gb})$ values.

The excellent overall $J_c$ values are due to the stability of the A-15 compound and the small grains. Our modified SSP method produced small composition fluctuations and fine microstructure. The absence of a second phase and Ga segregation at the grain boundaries would lead to a sharp $\Delta \kappa / \kappa$ profile over a distance comparable with the electron mean free path, and this may contribute to the stronger pinning.

In conclusion, the modified SSP process which uses an initial rapid liquid-quenching step followed by a heat treatment is a well-controlled process which produces $V_3 \text{Ga}$ with excellent critical properties. This process can be scaled up by continuously quenching the superconducting tape onto a copper ribbon which would serve as mechanical support as well as a thermal sink.

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