EFFECT OF HEAT TREATMENT TEMPERATURE ON THE THERMAL CONDUCTIVITY OF LARGE GRAIN SUPERCONDCUTNG NIOBIUM*

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Abstract

The phonon peak in the thermal conductivity k_{pp} of high purity niobium is an unknown function of heat treatment temperature T_{h} and RRR, amongst other variables. The relationship between T_{h} and k_{pp} of large grain niobium is investigated using two sets of four specimens each. The specimens of Set 1 were randomly cut from four ingot discs with different RRR. These specimens were subjected to different heat treatments, ranging from 140 °C for 48 hours to 1100 °C for 4 hours. Specimens of Set 2 were cut from the same grain of an ingot disc, with the heat flow direction of each specimen along the same crystal orientation. Each of these specimens was subjected to one heat treatment, at a temperature ranging between 600 °C and 1200 °C, while maintaining a constant temperature for an interval of 2 hours for each specimen. Results from the specimens of Set 1 show that there is no change in k_{pp} after heating at 140 °C for 48 hours. Set 1 specimens also show that for a given heat treatment protocol, the maximum in k_{pp} shows a monotonic dependence on RRR. Results from the specimens of Set 2 suggest that the phonon conduction response to heat treatments for 2 hours shows no increase for $T_{\mathrm{h}} \lesssim 600$ °C and plateaus at $T_{\mathrm{h}} \gtrsim 1000$ °C.

INTRODUCTION

The thermal conductivity k of superconducting metals is a sum of its electron and phonon components. At temperatures cooler than the superconducting critical temperature of niobium (T_c = 9.25 K), the contribution from electrons decreases, due to their condensation into Cooper pairs. The purity of niobium strongly influences electron conduction, and can be correlated at 4.2 K to the residual resistivity ratio (RRR), where RRR is the ratio of the electrical resistivity at 295 K to that at 4.2 K. For $T \gtrsim 3$ K, phonon conduction is relatively minor due to electron-phonon scattering. For $T \lesssim 3$ K, electron-phonon scattering is diminished due to the fewer normally conducting electrons, and phonon conduction becomes the dominant mode of heat conduction. At about 2 K, a local maximum occurs in k, referred to as the phonon peak. Material processing influences the existence and magnitude of this phonon peak, largely through changes in the crystal structure and imperfection density. Heat treatments reduce imperfection density, and hence alter the crystal structure. There is a need for improved understanding of the relationship between thermal conductivity and heat treatment history in niobium to improve the performance of SRF cavities.

Previous studies [1, 2] on the effect of heat treatment temperature on the thermal conductivity at the phonon peak of large grain niobium involved specimens from several ingot discs, with varying RRR, tantalum content, and crystal orientation along the heat flow direction. To reduce the influence of these extraneous factors on the phonon conductivity response, a portion of this study uses single crystal niobium specimens cut from a single grain on an ingot disc with the same crystal orientation in the heat flow direction. Another portion of this study uses partial results from [1, 2] along with results from two new specimens to draw more conclusions.

METHODS

Four large grain niobium specimens (Set 1) were cut from four ingot discs with varying RRR, tantalum content, and crystal orientation along the heat flow direction. These specimens were subjected to different heat-treating protocols ranging from 140 °C for 48 hours to 1100 °C for 4 hours. Also, four single crystal niobium specimens (Set 2) were cut from one grain of an ingot niobium disc manufactured by CBMM, and the heat flow direction was aligned along the same crystal orientation. These specimens reduce the influence of extraneous factors (*e.g.,* RRR, crystal orientation, tantalum content) on the thermal conductivity response of ingot niobium to heat treatments. Each specimen was subjected to a unique heat treatment temperature T_h, while the duration of the constant T_h was maintained at 2 hours for each specimen. Thermal measurements were performed on all of these specimens before and after heat treatments. The thermal conductivity was estimated using temperature and heat flux measurements and a theoretically based model for thermal conductivity.

Experiments

A steady-state experimental system [3] was used to measure the temperature and heat flux on the eight specimens. Up to four specimens were placed in an evacuated chamber

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Table 1: Heat treatment histories for the four bi-crystal (Set 1) and four single crystal (Set 2) specimens. Estimated RRR values and tantalum content for the specimens are also tabulated.

				Heat Treatment			
		Est.	**Ta content**	**First heating**		**Second heating**	
	Specimen	**RRR**	**(ppm)**	T_h **(°C)**	t **(hrs.)**	T_h **(°C)**	t **(hrs.)**
Set 1	2	131	668	600	6	1100	4
	3	190	756	750	2	1100	4
	7	174	1375	140	48	1100	4
	8	200	704	140	48	1100	4
Set 2	9	146	1375	600	2		
	10	143	1375	800	2		
	11	151	1375	1000	2		
	12	141	1375	1200	2		

that was surrounded by liquid helium. A temperature gradient was obtained in each specimen by applying a finite heat flux at one end, while the other end was attached to a conflat flange that was exposed to the liquid helium bath. The temperature gradient on each specimen was measured using four temperature calibrated resistors. The thermal conductivities of the specimens were estimated using the temperature and heat flux measurements and an estimation technique described briefly in the next section.

The heat treatment parameters for specimens in Sets 1 and 2 are tabulated in Table 1. The tantalum content [4] and the RRR estimated from $k_{4.2}$ for each of the specimens is also tabulated. The 750 °C heat treatment was performed with a titanium getter in a high-vacuum furnace at Thomas Jefferson National Accelerator Facility, with a temperature ramp rate of 5 °C per minute. The heat treatments at temperatures other than at 750 °C were performed with a titanium getter in a custom built high-temperature, high-vacuum furnace at Michigan State University [5], with a temperature ramp rate of 10 °C per minute.

Thermal Conductivity

A theoretically-based model for thermal conductivity of superconducting metals has been proposed in [6, 7, 8, 9], and was simplified as [10]

$$k(T) = R(y)\left[\frac{\rho_{295}}{L\,\mathrm{RRR}\,T} + aT^2\right]^{-1} + \left[\frac{1}{D\mathrm{e}^{-y}T^2} + \frac{1}{BlT^3}\right]^{-1} \quad (1)$$

where ρ_{295} is the electrical resistivity at 295 K, L the Lorentz constant, a the coefficient of momentum exchange of electrons with the lattice, D quantifies phonon scattering by electrons, B is a value from [6] for scattering at crystal boundaries, and l is the phonon mean free length.

The term quantifying the condensation of normal conducting electrons into Cooper pairs $R(y)$ is calculated in [9] using the BCS theory [11]. The term y within $R(y)$ is defined as

$$y = \frac{\Delta(T)}{k_B T} = \frac{\Delta(T)}{k_B T_c}\,\frac{T_c}{T} \quad (2)$$

where $\Delta(T)$ is the superconductor energy gap, and k_B the Boltzmann constant. For $T/T_c \leq 0.6$ (*i.e.,* 5.55 K for niobium), y can be approximated as

$$y = \alpha\frac{T_c}{T} \quad (3)$$

The parameters within equation (1) can be grouped into new parameters here as [12],

$$\beta_1 = \frac{\rho_{295}}{L\,\mathrm{RRR}} \quad \beta_2 = a \quad \beta_3 = \frac{1}{D} \quad \beta_4 = \frac{1}{Bl} \quad \beta_5 = \alpha \quad (4)$$

Each of the five β_i is associated with a particular contribution to the thermal conductivity, namely: the contribution of the purity of the metal to conductivity is associated with β_1; scattering of electrons by the lattice and phonons with β_2; scattering of phonons by normal electrons with β_3; scattering of phonons by lattice boundaries and sample boundaries with β_4; and the contribution of condensation of electrons due to formation of Cooper pairs to the thermal conductivity with β_5. Thus, equation (1) can be written in terms of the β_i as

$$k(T) = R(y)\left[\frac{\beta_1}{T} + \beta_2 T^2\right]^{-1} + \left[\frac{\beta_3}{\mathrm{e}^{-y}T^2} + \frac{\beta_4}{T^3}\right]^{-1} \quad (5)$$

The parameters defined in equation (5) are estimated from the temperature and heat flux measurements, by applying Gauss minimization with Box-Kanemasu modification to measurements across the range of temperatures. Details of this method are presented elsewhere [12]. Correlation between the different β_i may result in a non-converging minimization [13]. Examining the scaled sensitivity coefficients for β_i, β_2 cannot be reliably estimated using these experiments. Thus, β_1, β_3, β_4, and β_5 are estimated for each of the specimens before and after heat treatment, and the theoretical value of β_2 is used.

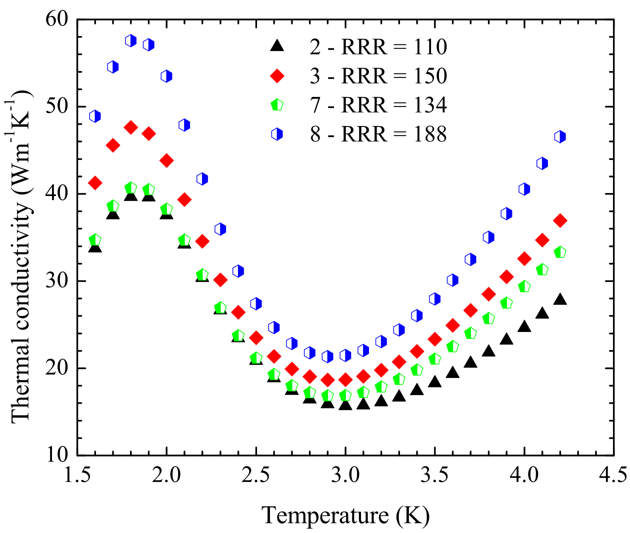

Figure 1: Thermal conductivities of the four niobium specimens in Set 1 after an 1100 °C heat treatment for 4 hours. The estimated RRR for each specimen after the 1100 °C heat treatment is listed in the legend. A dependence of maximum in k_{pp} on RRR is visible.

RESULTS AND DISCUSSION

The estimated thermal conductivities of specimens 2 and 3 in Set 1 before and after the various heat treatments were reported in [1, 2]. The estimated thermal conductivities of specimens 7 and 8 of Set 1 in their as-received condition and after heat-treating at 140 °C for 48 hours follow the trend of specimens 9–12 of Set 2 in their as-received condition plotted in Figure 2 (open symbols). The estimated thermal conductivities of specimens in Set 1 after the 1100 °C heat treatment are plotted as a function of temperature in Figure 1. Also listed in the legend of Figure 1 are the estimated RRR values for each of the specimens after the 1100 °C heat treatment.

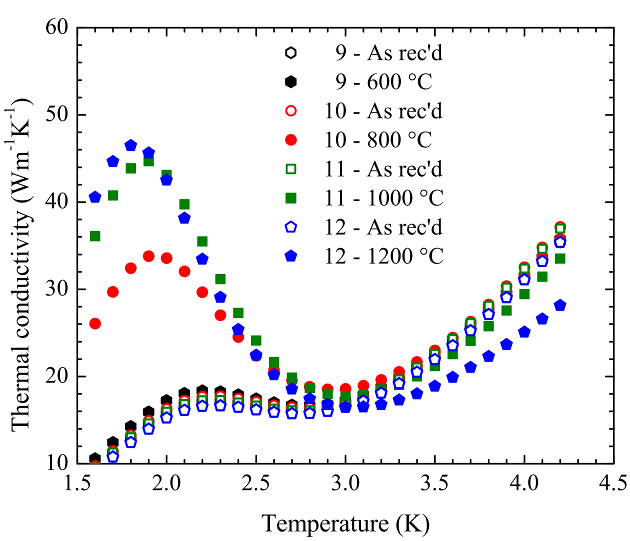

Figure 2: Thermal conductivities of the four niobium specimens in Set 2 in their as-received condition, and after 2 hours heat treatments.

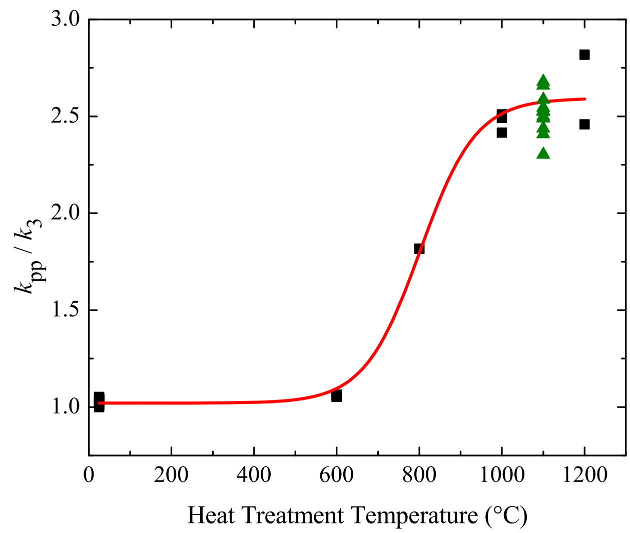

Figure 3: Thermal conductivity ratios k_{pp}/k_3 for the specimens in Set 2 (squares) in their as-received condition, and after 2 hours heat treatments. The solid line represents a sigmoidal curve fit to the k_{pp}/k_3 data for the specimens in Set 2 (squares). The k_{pp}/k_3 for specimens in Set 1 heat-treated at 1100 °C for 4 hours (triangles) is also plotted.

When compared with the RRR of the specimens after the 1100 °C heat treatment, the k_{pp} for specimens in Set 1 illustrated in Figure 1 show a monotonic dependence on the RRR. This implies that the dominant phonon scattering mechanism is now due to impurities, and no longer due to dislocations formed during the differential cooling of the ingot.

The estimated thermal conductivities of specimens in Set 2 before and after 2 hours heat treatment are plotted as a function of temperature in Figure 2. Although there is a significant increase in k in the phonon dominated regime, there is a 10% and 20% decrease in k at $T = 4.2$ K after the 1000 °C and 1200 °C heat treatments, respectively. This indicates introduction of some impurities into the specimen during the 1000 °C and 1200 °C heat treatments.

To reduce the influence of the RRR of heat-treated specimens on their phonon response, the ratio of k_{pp} and k at 3 K (k_{pp}/k_3) is introduced for specimens in Set 2. The ratio k_{pp}/k_3 for these specimens in their as-received condition (25 °C) and after heat treatments is plotted in Figure 3 (squares). A sigmoidal curve was found to best fit the data from specimens in Set 2, and is illustrated as the solid line in Figure 3. Also plotted are the k_{pp}/k_3 for the niobium specimens of Set 1 heat-treated at 1100 °C for 4 hours (triangles).

The ratio k_{pp}/k_3 for specimens in Set 2 displays a sigmoidal dependence on heat treatment temperature, with a plateau above 1000 °C. This suggests that for 2 hour heat treatments there will be little improvement in k_{pp}/k_3 for heat treatment temperatures hotter than 1000 °C.

As-received k for all the specimens display little phonon peak, suggesting a large density of phonon scattering sites, probably formed due to the differential cooling during ingot production. Similar results were reported in [1] for the k of specimens 2 and 3 in their as-received condition.

CONCLUSIONS

The results from the specimens heat treated at 1100 °C for 4 hours suggest that the maximum thermal conductivity at the phonon peak in unstrained large grain niobium has a monotonic dependence on the RRR. This implies that the maximum in phonon conduction is limited by impurities.

The results from the four specimens cut from the same ingot suggest that for 2 hour heat treatments of unstrained large grain niobium, the thermal conductivity at the phonon peak will have a sigmoidal dependence on the heat treatment temperature. The best values for the thermal conductivity at the phonon peak will be obtained after 1000 °C heat treatments, with diminished improvement at hotter temperatures.

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