The Effect of Annealing and Gas Content on the Superconducting Properties of Tantalum*

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The superconducting transition temperatures and critical fields of three wires of 99.9+ percent pure tantalum, taken from the same spool, have been investigated to find the effect of annealing and gas content. Annealing the metal at very high temperatures raised the transition temperature from 4.156 to 4.32°K and lowered the initial slope of the critical magnetic field from 1360 to 600 gausses per degree. Much sharper transitions were observed for the annealed specimens. The effect of absorbed gas was slight. Spontaneous fluctuations of resistance on the transition into superconductivity were observed. The effect of the specimen current on the critical field was studied in one of the annealed specimens.

I. INTRODUCTION

EXPERIMENTS on the transition temperatures and critical fields of superconducting tantalum have been noted for their failure to give consistent results for different specimens.[1–5] Transition temperatures have been reported between the extremes of 3.96°K and 4.4°K. The initial slopes of the critical field curves have varied from 310 to 1250 gausses per degree. A more complete summary of the results of the previous investigations will be found in Table I.

In addition to the lack of consistency, tantalum, with one partial exception,[1] has shown considerable evidence of alloy behavior in the form of broad transitions and magnetic hysteresis.

It has generally been supposed that the inconsistencies in the reported superconducting properties of tantalum were due to the presence of small amounts of impurities or to the presence of mechanical strains.[6] There is no question that impurities in the metal have a considerable influence on its behavior. That strains also appear to have some effect was demonstrated by Meissner, Steiner, and Grassman,[7] who lowered the transition temperature of a tantalum wire in zero-magnetic field by 0.017°K by sharply kinking it in many places. A similar conclusion can be drawn from the observation of Brucksch and his co-workers[8] that very fine hard-drawn wires of tantalum have much lower transition temperatures than do larger wires.

The effect of tensile stress was quantitatively studied by Alekseyevski,[9] who found that severely strained wires of tantalum showed sharper zero-field transitions at slightly higher temperatures, and smaller critical field slopes than did the unstrained wires.

The purpose of the work reported here is to investigate the effect of annealing and the effect of gas content on the superconducting properties of tantalum. It is known that tantalum becomes very brittle when heated in high vacuum at temperatures approaching the melting point.[10] The length of the sample under such treatment increases as much as 6 percent, corresponding to the growth of large crystallites. Tantalum also has the property of absorbing gases in large

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[1] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. **A160**, 127 (1937).

[2] W. H. Keesom and M. Désirant, Physica **8**, 273 (1941).

[3] W. Meissner, Zeits. f. Physik **61**, 191 (1930).

[4] K. Mendelssohn and J. R. Moore, Phil. Mag. **21**, 532 (1936).

[5] Francis B. Silsbee, Russell B. Scott, and Ferdinand G. Brickwedde, J. Research Nat. Bur. Stand. **18**, 295 (1937).

[6] For example, D. Shoenberg, *Superconductivity* (Cambridge University Press, Teddington, England, 1938), pp. 89–90, references 1–5 also contain speculations on this matter.

[7] W. Meissner, K. Steiner, and P. Grassman, Physik. Zeits. **36**, 519 (1935).

[8] W. F. Brucksch, Jr., W. T. Ziegler, F. H. Horn, and Donald H. Andrews, Phys. Rev. **60**, 170 (1941); W. T. Ziegler, W. F. Brucksch, Jr., and J. W. Hickman, Phys. Rev. **62**, 354 (1942).

[9] N. E. Alekseyevski, J. Phys. U.S.S.R. **3**, 443 (1940).

[10] B. A. Mrowca, J. App. Phys. **14**, 684 (1943). It is likely that the brittleness is caused by precipitation of impurities at the crystallite boundaries.

quantity.[11] The absorption of these gases causes a slight expansion of the lattice and an appreciable increase in the room temperature resistance.

II. PREPARATION OF SPECIMENS

The three specimens used in this investigation were taken from the same spool of wire supplied by Fansteel Metallurgical Corporation (North Chicago, Illinois). The manufacturer produced the wire by cold rolling, swaging, and, finally, cold drawing down to a diameter of 0.0039 in. The cold working was followed by an "anneal" in high vacuum at about 1000°C. This temperature is well below that necessary for any appreciable recrystallization.[10] An analysis of the product by Fansteel gives a purity of 99.9+ percent, with less than 0.01 percent iron and 0.03 percent carbon present. The wire also contained a small amount (less than 0.1 percent) absorbed gas. The specimens, each about 4 inches long, were treated and mounted by us in the following ways:

Specimen I was taken directly from the spool and mounted without further treatment. The potential and current leads of No. 40 copper wire were attached by means of small clamps.

Specimen II was copper plated on the ends which were then soldered to insulating supports mounted on the brass strip. The distance between the insulating supports was made adjustable to allow compensation for the permanent lengthening of the wire caused by heat treatment. The potential and current leads were soldered to the copper plate.† The whole assembly was then inserted in a vacuum system and heated to extremely high temperatures (2200 to 2500°C) for two hours by passing a direct current through the wire. The heating was then continued at intervals (to allow the pumps to take away the evolved gas) until the room temperature resistance of the specimen reached a minimum. This minimum was about 4 percent below the original resistance of the specimen and indicated[11] a relatively gas-free condition in the metal. The heat treatment resulted in a 2 percent permanent elongation of the sample.

Specimen III was mounted and annealed in the same manner as specimen II. At the conclusion of the anneal the sample was heated for a few minutes at 1200°C in air at a pressure of 10^{-3} mm Hg, causing the specimen to absorb gas. At the end of the treatment the room temperature resistance was 37 percent higher than the resistance of the original hard-drawn specimen. This would indicate [11] the absorption of about 9 volumes of oxygen, a quantity much less than that necessary to cause the formation of the oxide. The wire lengthened slightly over 1 percent as result of the treatment. Specimens II and III were somewhat brittle.

III. APPARATUS

The specimens were mounted vertically in a soft glass Dewar flask 18 in. long and $1\frac{1}{4}$ in. in inner diameter. The space between the walls of this flask contained air at a pressure of about 1 mm of mercury at room temperature. This air

TABLE I. Summary of experimental conditions and results of these and previous investigations of tantalum.

	Measurement method	Purity percent	Annealed	R_n/R_{273}	T_c (°K)	dH_c/dT (gauss/°K)	Tension (kg/cm²)
Specimen I	resistance	99.9+	no	0.152	4.156	1360	
Specimen II	resistance	99.9+	yes	0.07	4.30	600	
Specimen III	resistance	99.9+	yes	0.105	4.32	600	
Daunt and Mendelssohn[1]	susceptibility	99.95+	?	—	4.38	310	
Keesom and Désirant[2]	specific heat	99.95+	?	—	4.075	1230	
Meissner[3] I	resistance	?	yes	0.035	4.38	—	
Meissner[3] II	resistance	?	yes	0.0098	4.36	—	
Meissner[3] III	resistance	?	yes	0.050	4.37	—	
Mendelssohn and Moore[4]	resistance	?	?	0.052	4.4	980	
Silsbee and I	resistance	99+	no	0.26	3.961	1250	
co-workers[5] II	resistance	99+	no	0.26	4.068	1080	
Alekseyevski[9]	resistance	?	?	?	4.250	810	0
					4.375	680	18,000

[11] Mary Andrews, J. Am. Chem. Soc. **54**, 1845 (1932).

† This technique did not prove completely satisfactory as a small contact resistance developed at low temperatures.

allowed the contents of the flask to reach temperature equilibrium with the surrounding bath of liquid nitrogen in a short time. On admitting the liquid helium, the air in the annular region is instantly condensed.

After being filled with the liquid helium, the flask and its shield were placed in the center of a large water-cooled solenoid which supplied a longitudinal magnetic field of intensity up to 1600 gausses. This solenoid consisted of a total of 805 turns of $\frac{5}{16}$-inch hollow copper tubing wound in 9 concentric layers and set in insulating plaster. The nine layers were connected in series electrically, and in parallel, for the purpose of cooling, by means of rubber tubing. The total resistance was 0.4 ohms, and the field homogeneity over the region used was 99.8 percent. The solenoid was 24 inches long, with an outer diameter of 12 inches and an inner diameter of $4\frac{3}{4}$ inches. As far as limited by heating, the solenoid is capable of carrying over 200 amperes, which would yield a field of 3200 gausses. Lack of an adequate current supply limited our investigations to fields of half this intensity.

Fluctuations in this current formed the largest source of error, amounting to a little over 1 percent.

The temperature was measured to an accuracy of 0.002°K by determining the vapor pressure of the liquid helium with a Wallace and Tiernan precision mercury manometer. The 1937 Leiden determinations of the vapor pressures[12] were used.

The potential drop across the specimens was continuously measured with a Brown "Electronik" high speed recording potentiometer. This instrument has a range of 0–50 mv, with an accuracy of 0.125 mv and a sensitivity of 0.06 mv. It proved particularly valuable in this work as it allowed a large quantity of data to be taken with great rapidity.

The specimen current in all cases was 25-ma d.c., except in the case of specimen II where data was also secured for a current of 100 ma.

IV. RESULTS AND DISCUSSION

The resistance of specimen I was observed to fluctuate markedly as the temperature was lowered slowly through the transition point in zero field. The fluctuations were completely irregular, and their maximum amplitude was about 5 percent of the total resistance. These fluctuations are similar to, but much smaller than, those reported by Silsbee, Scott, and Brickwedde.[5] The amplitude of the fluctuations in our annealed samples was smaller still (maximum of $1\frac{1}{2}$ percent), lending support to the

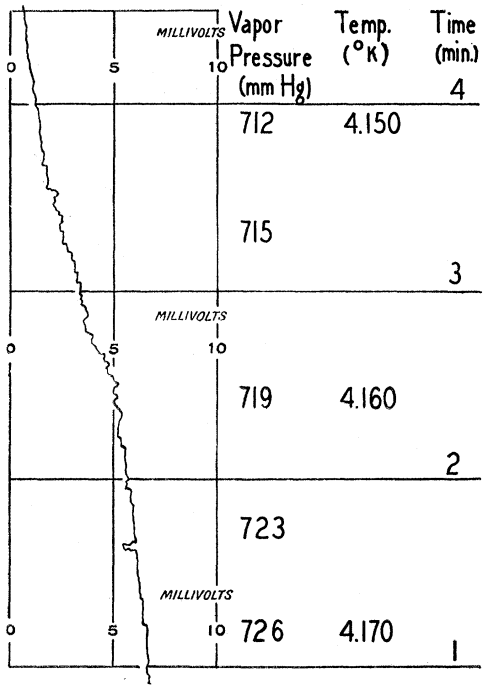

FIG. 1. Potentiometer record of the zero-field transition of tantalum specimen I, showing spontaneous fluctuations of resistance as the temperature is slowly lowered.

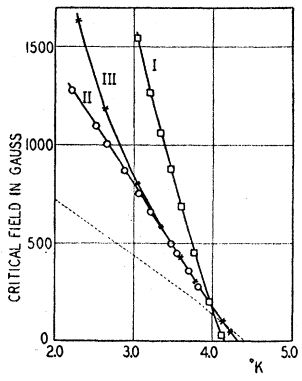

FIG. 2. Critical field curves of the three tantalum specimens. The numbering of the curves corresponds to the specimens as described in the text.

[12] G. Schmidt and W. H. Keesom, Physica 4, 971 (1937).

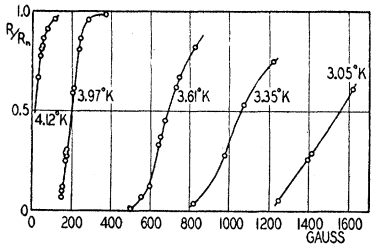

FIG. 3. Isothermal transitions of tantalum specimen I (hard drawn) in magnetic fields.

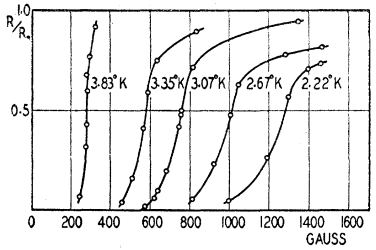

FIG. 4. Isothermal transitions of tantalum specimen II (annealed and outgassed) in magnetic fields.

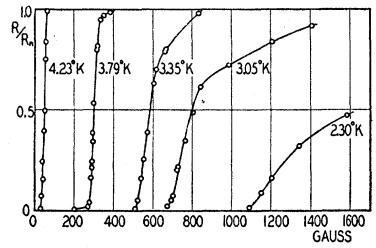

FIG. 5. Isothermal transitions of tantalum specimen III (annealed and gassy) in magnetic fields.

contention of Misener[13] that the phenomenon is of a secondary nature associated with imperfections in the metal. Figure 1 may be of interest as it shows what we believe to be the first published recording of the fluctuations. The square-sided dip occurring at a vapor pressure of 724 mm of mercury was caused by the automatic calibration of the potentiometer.

Figure 2 gives the critical field curves for the three specimens. The ordinates of the points correspond to the magnetic field necessary to restore one-half of the normal resistance. Curves I through III correspond to the three specimens as described above. The dotted curve represents the data of Daunt and Mendelssohn.[1]

[13] A. D. Misener, Proc. Camb. Phil. Soc. **34**, 465 (1938).

Figures 3, 4, and 5 show some of the isothermal transition curves for the three specimens at various temperatures. The ordinates give the ratio of the resistance, R, to the resistance just above the normal transition temperature, R_n. All three specimens exhibited fairly sharp transitions at temperatures near the zero-field transition temperature. At lower temperatures the transitions become increasingly broad, indicating the existence of a considerable amount of intermediate state. A comparison of the isothermal transitions of the three specimens at a given temperature (at 3.35°K, for example) shows that the two annealed specimens have much sharper transitions at lower magnetic fields than those exhibited by the hard-drawn specimen. No hysteresis was observed in any of the specimens.

Specimen III (annealed and gassy) proved to be somewhat anomalous. At temperatures above 3°K it exhibited the sharpest transitions of the three specimens. Below this temperature, however, the transitions degenerate rapidly, corresponding to the break upward of curve III of Fig. 2. Whether this difference in the behavior of specimens II and III is due to the difference in gas content, or to minor differences in annealing technique, is impossible to say. In any case, we can conclude that gas content is not a major factor contributing to the diversity in the properties of superconducting tantalum reported previously.

A summary of the numerical results of these and previous investigations is given in Table I.

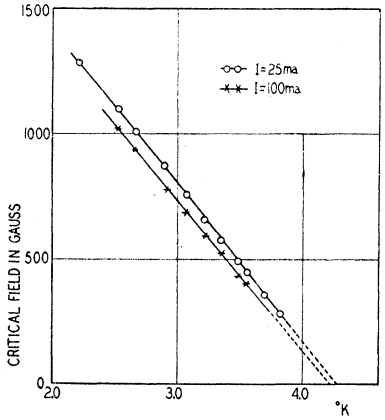

FIG. 6. Critical field curves of tantalum specimen II for currents of 25 and 100 milliamperes.

In the cases where information on annealing is given it is clear that the ratio of the resistance at helium temperatures to that at 0°C (R_n/R_{273}), the transition temperature and the initial critical field slope are strongly affected by the heat treatment. In view of this, the poor characteristics of the sample of Keesom and Désirant[2] are probably explained as being due to severe strains in their specimen. The influence of kinking the tantalum wire[7] and reducing the wire diameter[8] on the superconducting characteristics are probably similarly explained.

The influence of current on the critical fields of the annealed and outgassed specimen is shown in Fig. 6. The critical fields are 50 to 70 gausses lower for the higher current, an amount considerably in excess of what would be expected from the hypothesis of Silsbee.[14]

The author is particularly indebted to Professor C. T. Lane for his frequent advice and encouragement. He is also indebted to Dr. Henry A. Fairbank and Mr. William Fairbank for their assistance in the collection of data.

[14] F. B. Silsbee, Sci. Pap. Bur. Stand. **14**, 301 (1917).

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Ultrasonic Velocity and Absorption in Liquid Helium*

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Measurements are given on the velocity and attenuation of ultrasonic energy in liquid helium at a frequency of 15 megacycles per second as a function of temperature from 1.57°K to 4.5°K. The velocity at 15 Mc/sec. was found to agree with results obtained at 1.3 Mc/sec. by previous investigators, and hence there is no dispersion in this frequency range. The attenuation measurements exhibit three important features: (a) in the upper temperature range of He I the measurements agree very well with classical theory, (b) at the λ-point the attenuation coefficient rises abruptly, presumably to infinity, indicating complete absorption of the ultrasonic energy, (c) just below the λ-point the attenuation (first sound in He II) has its smallest value and with lowering temperature the attenuation increases.

I. INTRODUCTION

THE experiments described in this paper give the velocity and attenuation of sound in liquid helium at a frequency of 15 megacycles per second as a function of temperature from 1.57°K to 4.5°K. The object of these experiments is twofold: (a) to check experimentally the theory of sound absorption for a monatomic liquid, and (b), to probe into the nature of liquid helium in its low temperature phase and at the transition point. The experiments were made possible by two recent developments: the ultrasonic pulse technique which grew out of radar research[1] and the Collins Cryostat[2] which can produce relatively large amounts of liquid helium.

II. EXPERIMENTAL

The special advantages and capabilities of the pulse technique originally developed for radar have made measurements of the type conducted in this research possible. By using short pulses absorption measurements may be conducted at relatively high frequencies (15 Mc/sec. in this case), for which the attenuation is sufficient to

FIG. 1. Transducer-reflector system.

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*** Now at The Rice Institute, Houston, Texas.

[1] Radiation Laboratory, Massachusetts Institute of Technology Report 963, March 1946.

[2] S. C. Collins, Rev. Sci. Inst. **18**, 3 (1947).