Resistance Transitions in Superconducting Tantalum†

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A study has been made of the superconducting to normal transition in outgassed tantalum wires induced by the application of an external longitudinal magnetic field. It was found that in most cases the transition, as determined from resistance measurements, consisted of an almost discontinuous appearance of resistance; followed by a rather gradual rise in resistance until the full residual resistance was restored. Flux measurements showed that the sharp portion of the transition corresponded to the magnetic, or "bulk" transition. The behavior of the broad portion of the transition was of the type commonly associated with superconducting "filaments." Although the "filamentary" properties were found to be extremely sensitive to localized contamination and the thermal history of a specimen, they did not appear to depend exclusively on such inhomogeneities, and a systematic variation with residual resistance could be discerned. Plastic deformation altered the characteristics only in proportion to the corresponding increase in residual resistance. A small amount of supercooling which was independent of the "filamentary" phenomena was sometimes observed in the "bulk" transition.

INTRODUCTION

THE anomalous behavior of the so-called "hard" superconductors, of which tantalum is a good example, has been described on numerous occasions in the literature (see Shoenberg[1]). Characteristically one finds, in varying degrees, (a) large critical fields for the restoration of resistance, (b) small critical currents, (c) broad resistance transitions, (d) an incomplete Meissner-Ochsenfeld effect, (e) separation of the resistance and magnetic transitions, and (f) flux trapping. In many respects the "hard" superconductors resemble some of the superconducting "soft" metal alloys so far investigated, (see reference 1, p. 37) for both exhibit to some degree the above departures from what is considered to be "ideal" thermodynamic behavior. Recently[2–4] there has been some evidence to indicate that in the transition metals these effects are not characteristic of the pure metal, but are due to the presence of interstitial nitrogen, oxygen, and carbon.

In an attempt to explain the appearance of these phenomena in alloys, the concept of the superconducting "filament" was formulated.[5] These "filaments" were believed to be associated with some sort of crystalline imperfections, usually referred to as "flaws"[6] or "strains and inhomogeneities," (see reference 1, p. 37) which could give rise to a negative interphase surface energy in their vicinity.[6–8] Such a negative surface energy could be used to explain the existence of thin threads or laminae in the presence of magnetic fields well above the "bulk" critical field of the material. The nature of these "flaws" and their detailed effect on the superconducting properties of a material remain something of a mystery, however. Pippard[9] has recently proposed a model in which he relates the surface energy to the electronic mean free path in the normal metal. Since, however, it could be a localized mean free path rather than the average mean free path that is the controlling factor, the experimental evidence[10,11] is not conclusive. With the development in this laboratory of more refined techniques for the purification of tantalum, it seemed desirable to conduct a detailed investigation designed to determine the imperfections influencing the superconducting properties of this material.

PREPARATION OF MATERIALS

The growth of single crystals and the purification of single and polycrystals of tantalum has been described previously.[12,13] The specimens were two-inch lengths of 0.010-in. diam wire and were all initially degassed by being heated above 2500°C. in vacua of 5×10^{-8} to 10^{-9} mm Hg. Calculations show that the annealing time employed at these temperatures is sufficient to provide a homogeneous distribution of interstitial contaminants.[13]

The strained specimens were prepared at room temperature by twisting them through 80 revolutions per inch while under a tension, which produced an elongation of about 5%. In addition specimens were strained by being bent sharply along their entire length several times.

For the aging treatment the specimens were attached to a nickel wire and placed in a Pyrex tube which was then sealed onto the vacuum system. A magnet was used to position the specimens in a cool part of the

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[1] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), pp. 9 and 37.
[2] H. Preston-Thomas, Phys. Rev. **88**, 325 (1952).
[3] A. Wexler and W. S. Corak, Phys. Rev. **85**, 85 (1952).
[4] L. C. Jackson and H. Preston-Thomas, Phil. Mag. **41**, 1284 (1950).
[5] K. Mendelssohn, Proc. Roy. Soc. (London) **A152**, 34 (1935).
[6] T. E. Faber, Proc. Roy. Soc. (London) **A214**, 392 (1952).
[7] C. J. Gorter, Physica **2**, 449 (1935).
[8] H. London, Proc. Roy. Soc. (London) **A152**, 560 (1935).
[9] A. B. Pippard, Proc. Cambridge Phil. Soc. **47**, 617 (1951).
[10] P. R. Doidge, Trans. Phil. Soc. **A248**, 553 (1956).
[11] T. E. Faber, Proc. Roy. Soc. (London) **A231**, 353 (1955).
[12] Budnick, Ittner, and Seraphim, *Proceedings of the Kamerlingh-Onnes Memorial Conference on Low-Temperature Physics, Leiden, Holland, 1958* [Suppl. Physica **24**, *S*151 (1958)].
[13] Seraphim, Budnick, and Ittner, Trans. Am. Inst. Mining Met. Petrol. Engrs. (to be published).

system while the remainder was thoroughly baked out. The specimens were then dropped into a hot section of the system enclosed by a furnace which was pre-set at a desired temperature. Surface desorption generally caused the pressure to rise to the range of 10^{-6} mm Hg but within a few minutes the pressure decreased to about 10^{-7} mm Hg. During the major portion of the aging process the pressure was less than 5×10^{-8} mm Hg.

There is sufficient evidence that the bulk purity of the specimens did not change significantly during the above treatment. As in previous work[12,13] the resistance ratio $\Gamma=(R_{300}-R_{4.2})/R_{4.2}$ was used as a measure of the impurity content. Γ was found to change but slightly during the treatment. However, the possibility of localized contamination near the surface cannot be excluded.

EXPERIMENTAL PROCEDURE

In all experiments the specimen to be measured was immersed directly in the liquid helium bath. Rough temperature stabilization was accomplished by means of a bellows-operated manostat, which held the pressure above the bath constant to within about 1 mm Hg. For finer control of the temperature of the specimen, a thermoregulator such as described by Sommers[14] was used, with the heater and carbon resistance thermometer mounted on a copper can enclosing the specimen. In this manner the temperature of the specimen could be held to within 10^{-3}°K during the course of a measurement. Temperatures were determined by measuring the vapor pressure above the helium bath at equilibrium (accurate to within 5×10^{-3} °K).

The external magnetic field was provided by a Garrett-type[15] end wound solenoid mounted on the helium Dewar in the liquid nitrogen bath. The fields so obtained were estimated to be uniform to one part in 10^3 over the length of the specimen. Solenoid current, and hence the applied magnetic field could be measured to within 0.25%.

The resistance of a specimen was determined by measuring the voltage developed across a pair of potential leads upon the application of a known current through the specimen. This voltage was then displayed on an X-Y recorder as a function of the solenoid current. Voltages of 0.05 μv were detectable above a noise level of 0.01 μv with this system. Care was taken to minimize stray thermal emf's. The signal to noise ratio appeared to be limited by the noise generated in the silver paste contacts to the specimen.

Magnetic measurements were made in a conventional manner.[10] A coil arrangement, in which the coil containing the specimen is connected to an oppositely wound dummy coil and a ballistic galvanometer, was used. With the specimen normal, the emf's induced across the individual coils by a change in the external magnetic field could be adjusted so as to cancel each other. Thus, the deflection of the ballistic galvanometer caused by a change in external magnetic field was proportional to the flux excluded by the specimen.

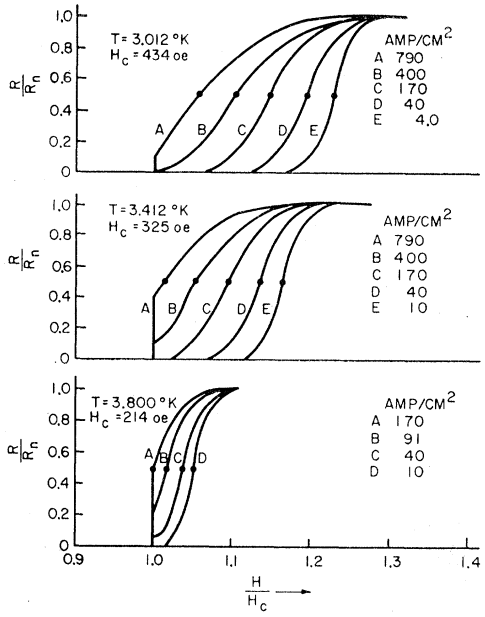

FIG. 1. Resistance transitions for degassed tantalum wire with various measuring currents ($\Gamma=169$).

EXPERIMENTAL RESULTS

Effects of Measuring Current

Initial measurements of the resistance transition showed that in sufficiently pure wires ($\Gamma>150$) the appearance of resistance at 4.2°K was almost discontinuous, i.e., when the magnetic field was raised to a certain critical value, the resistance rose to its full value over a range of field equal to about 1% of the critical field. As the temperature was lowered, however, the resistance *versus* field curves ceased to be completely sharp and assumed a form such as is shown in Fig. 1. The sharp step in the R/R_n *vs* H/H_c curve was found to be relatively insensitive to the specimen impurity content,[16,17] while the broad portion of the curve was found to vary widely from specimen to specimen. These curves were reproducible from run to run for a given specimen, however. The broad portion of the transition showed a marked sensitivity to the current passing through the specimen, as typified by the results shown in Fig. 1. At the lowest temperatures and current densities (see Fig. 1) no sharp step is evident and the transition appears to be continuous.

It was obvious upon comparing the values of the field

[14] H. S. Sommers, Jr., Rev. Sci. Instr. **25**, 793 (1954).
[15] M. W. Garrett, J. Appl. Phys. **22**, 1091 (1951).

[16] A decrease in T_c with increasing residual resistance could be observed. These shifts were of the same order of magnitude as those in dilute Sn alloys as reported by Lynton, Serin, and Zucker, J. Phys. Chem. Solids **3**, 165 (1957), and in most cases could be disregarded in this work.
[17] J. I. Budnick (to be published).

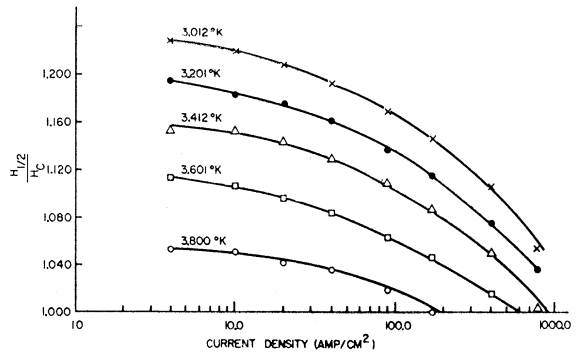

FIG. 2. Current dependence of the filament transition in a degassed and aged tantalum wire. ($\Gamma=530$, $T_{\frac{1}{2}}=3.9°$K.)

at the discontinuity to the known critical field for tantalum[17,18] that the sharp step in resistance coincided with the discontinuities in susceptibility and the specific heat. This fact was further confirmed directly by simultaneous measurements of the resistive and magnetic transitions on several specimens. Within the accuracy of the measurements ($\pm 1\%$) the transition as evidenced by flux measurements coincided with the sharp step in the resistance, and a negligible amount of flux was involved in the broad portion of the transition. In all cases the specimens exhibited a reasonably good Meissner-Ochsenfeld effect.

In view of these facts, it seems justifiable to treat the sharp and broad portions of the transition (as measured resistively) as independent quantities, one characterizing the bulk material, and the other the imperfections present. An equivalent circuit for this model would consist of two different superconductors connected in parallel. One of these fictitious superconductors would have a discontinous resistance transition and a critical field curve corresponding to that of the bulk material. The other would have a broad, continuous, current sensitive resistance transition and a critical field curve defined by the field at which R/R_n assumes a value of one half. In the region where the continuous transition overlaps the sharp transition in field, there is a discontinuity in the resistance of the equivalent circuit, (see Figs. 1 and 4). Henceforth the two will be referred to as the bulk transition and the filament transition, respectively.[19]

The current dependence of the filament transition is shown in Fig. 2, where the field at which the resistance assumes 50% of its normal value, $H_{\frac{1}{2}}$,[20] is plotted as a function of the average current density,[21] defined as the total current divided by the cross-sectional area of the wire.

The behavior here is certainly more complex than the simple power law used by Doidge[10] to describe a similar effect in Sn-In alloys. The interesting feature of Fig. 3 is that $H_{\frac{1}{2}}/H_c$ appears to be approaching a limiting value for sufficiently small current densities. The appearance of the transitions seems to substantiate this observation, for at the lowest current densities, where $H_{\frac{1}{2}}$ is far removed from H_c, the transition becomes relatively sharp. See for example the transitions at 3.010°K in Fig. 1. Here the transition for 4 amp/cm² is much sharper than that for 40 or 790 amp/cm².

A second parameter which could prove useful in describing the continuous portion of the transition is its breadth. A measure of the breadth can be obtained by extrapolating the slope of R/R_n at $H_{\frac{1}{2}}$ to $R/R_n=0$ and $R/R_n=1$. The increment in H between these values of R/R_n can then be defined as the breadth.

The effect of temperature and current density on the breadth of the transition can be observed in Fig. 3. There appears to be a limiting breadth at the lowest current densities. In any case the breadth increases with decreasing temperature and increasing current density.

The approach of the filament transition to some sort of limiting value at the lowest currents suggests that there may be a relatively well defined critical field associated with the substructure. This was, in fact, suggested by Preston-Thomas.[12] Unfortunately the saturation effects become apparent in a range of current densities where the measurement of the voltage drop across the specimens becomes awkward. Therefore in studying the effects of various lattice defects on the filament transition, the current density was arbitrarily fixed at a convenient value (20 amp/cm²) and held constant throughout subsequent measurements.

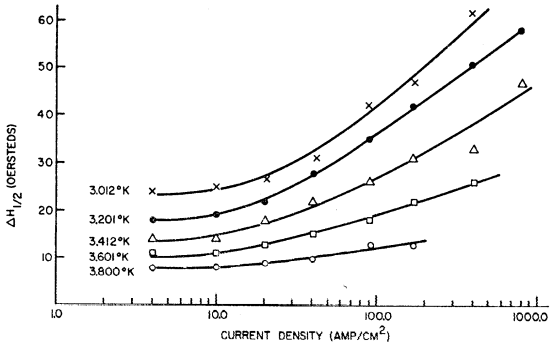

FIG. 3. Current dependence of the filament transition width in a degassed and aged tantalum wire ($\Gamma=530$, $T_{\frac{1}{2}}=3.9°$K).

[18] White, Chou, and Johnson, Phys. Rev. **109**, 797 (1958).

[19] This interpretation was first proposed by M. D. Reeber of this laboratory, in reference to transitions in the resistance of In-Hg alloy specimens, which were of similar disposition to the transitions for tantalum. This work will be published shortly.

[20] If the field values for which $R/R_n>0.5$ are used, the current dependence is proportionately reduced. The increased sensitivity to the shape of the filament transition negates this advantage, however, so the more easily definable $H_{\frac{1}{2}}$ was used.

[21] The use of the current density as a parameter is based on the assumption that the filaments are uniformly distributed throughout the cross section of the wire. While this may be open to question, it does not influence these results, since the wire diameters were always the same.

Effect of Impurities

A group of 15 specimens was degassed above 2500°C in vacua of 5×10^{-8} to 10^{-9} mm Hg and allowed to cool to room temperature in the vacuum system. The variation in treatment between specimens here was mainly the length of time at which they were held at the high temperature and the ultimate pressure of the vacuum system. For these 15 specimens there was no significant difference between single and polycrystalline specimens, but with increasing Γ there was a qualitative decrease in $-\partial H_{\frac{1}{2}}/\partial T$ and the temperature $T_{\frac{1}{2}}$ for which $H_{\frac{1}{2}}=H_c$ at $J=20$ amp/cm^2. The resistance ratios varied from 30 to 500 for these specimens. Therefore there appears to have been a large impurity effect on the filament transition. This was subsequently verified by Ittner and Marchand[22] who added known quantities of nitrogen to the specimens and found a systematic variation of $T_{\frac{1}{2}}$ with the amount of added impurity.

A dependence of $T_{\frac{1}{2}}$ on residual resistance is no assurance that the effect is determined by mean free path, or that it is, in fact, even characteristic of the bulk material. Furthermore, there was sufficient scatter in in the data to indicate that other parameters must be taken into account. For instance, a localization of impurities, such as segregation or precipitation, could certainly explain the observed filamentary behavior. In particular, the mobilities of nitrogen, carbon, and especially oxygen are sufficient in the range of 200°C to 500°C to allow migration of these impurities over significant distances (for example the distance between dislocations) in the tantalum lattice. A number of experiments were thus performed to investigate the disposition of the impurities and other defects.

The effect of thermal aging ($15\frac{1}{2}$ hours at 290°C) is illustrated by the data in Fig. 4. For clarity the characteristic behavior prior to the aging treatment is shown for only one specimen. For this specimen $H_{\frac{1}{2}}$ intersected the H_c curve at 3.2°K. The intersection temperature increased to 3.9°K after aging, and $-\partial H_{\frac{1}{2}}/\partial T$ increased correspondingly. The remaining data in Fig. 4 show the transition characteristics for aged specimens of various residual resistance ratios. In all cases $T_{\frac{1}{2}}$ and $\partial H_{\frac{1}{2}}/\partial T$ increased greatly with aging, as did the transition width $\Delta H_{\frac{1}{2}}$. The same specimens were subsequently returned to the vacuum system and held at 420°C for $13\frac{1}{2}$ hours. In contrast to the previously observed behavior, the resistance ratios following this treatment decreased slightly (5 to 10%). Nevertheless the transition characteristics improved somewhat, especially for the specimen with the highest Γ; i.e., the aging effect appears to have traversed a maximum. Nevertheless $T_{\frac{1}{2}}$ and $H_{\frac{1}{2}}$ were still well removed from their original values before aging.

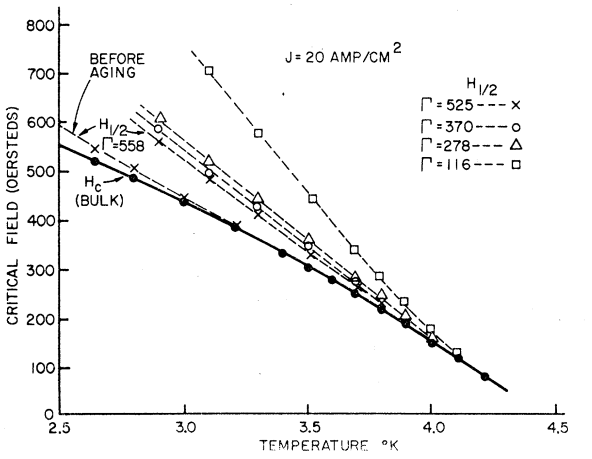

FIG. 4. Filament critical field curves for degassed tantalum wire before and after aging. Included are curves for three other aged samples with various residual resistance ratios.

To ascertain whether exposure to air in the interim between the initial vacuum degassing and subsequent aging could have contributed to the aging effect, several specimens were degassed in the vacuum system and then aged *in situ*. These specimens showed an intersection temperature and a slope $-\partial H_{\frac{1}{2}}/\partial T$ in the general range of values found for unaged specimens with comparable Γ values. Thus exposure to air appears to have had a profound effect on the nature of the filament transition. This was verified by the behavior of a specimen aged briefly in air (2 hours at 150°C). This treatment caused $T_{\frac{1}{2}}$ to increase from 3.05°K to 3.5°K without producing a measurable change in Γ. This specimen also showed an exceptionally broad filament transition. The evidence strongly suggests that one major effect of the thermal treatment was to contaminate the specimens by a mechanism which was sufficiently localized so as not to have changed the residual resistance ratio significantly.

It can be surmized that the contamination may have been confined to regions near the surface of the wire. To check this, several specimens with different thermal histories were etched to various depths and then remeasured. An immediate and obvious effect, which made itself apparent after the removal of less than 0.0001 in. from the surface by a light etching treatment, or more especially by electropolishing, was a sharpening of the broad transition to much smaller values of $\Delta H_{\frac{1}{2}}$. Nevertheless the $H_{\frac{1}{2}}$ curve was still well removed from the bulk critical field curve, and a considerable amount of material had to be removed from the aged specimens before they displayed characteristics comparable to their original behavior before aging. Strangely enough, the unaged specimens also showed a decrease in $T_{\frac{1}{2}}$ and $-\partial H_{\frac{1}{2}}/\partial T$ roughly proportional to the amount of material etched away.

The intricate nature of chemical reactions at surfaces do not allow definite conclusions to be drawn from such treatments at present. What *can* be said is that the removal of a thin surface layer, which should contain all the gaseous impurities (excepting hydrogen) diffusing

[22] W. B. Ittner, III, and J. Marchand, Phys. Rev. **114**, 1268 (1959).

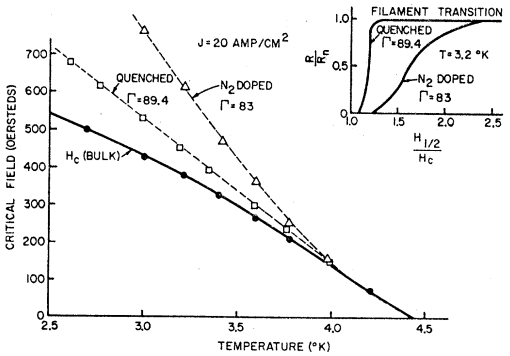

FIG. 5. Filament critical field curves for a tantalum wire quenched from 2800°C to room temperature, and a nitrogen-doped tantalum wire[22] with a comparable residual resistance ratio.

in from the surface by matrix diffusion, does *not* remove all the effects of aging, either in vacuum or in air. The possibility remains, however, that enhanced diffusion along dislocation lines could carry contaminants to the center of these specimens. In any case it seemed clear that the localized impurities were responsible for the effects of aging.

There was thus some hope that quenching from the degassing temperature to room temperature would completely remove the filament transition by preventing localization of the impurities. The quenching experiment was achieved with considerable difficulty but with great success. The specimen was dropped into a bath of liquid gallium with such velocity that the top portion which was not covered by the gallium was white hot while the remainder was completely submerged. The quenching time for the center of the specimen was estimated to be $\sim 0.002/K$ sec at 500°C and $\sim 0.005/K$ sec at 200°C, where K is the thermal diffusivity of gallium in cal/cm² sec. The resistance ratio for this specimen was 95, indicating that the impurity content, even allowing for some contribution from quenched-in vacancies, was rather high.

The behavior of this specimen was unusual, as shown in Fig. 5, where the $H_{\frac{1}{2}}$ *vs* T curve is compared to that of an unquenched specimen with a comparable resistance ratio. Both specimens have a high $T_{\frac{1}{2}}$ (4.05°K) but the quenched specimen has a much lower slope $-\partial H_{\frac{1}{2}}/\partial T$. The transitions at 3.2°K shown in the insert are also quite different. The quenched specimen has a surprisingly sharp filament transition, in contrast to the unquenched specimen. However, since quenching does not eliminate filamentary conduction, this suggests the possibility that dispersed impurities may also have an effect.

With this in mind, detailed experiments were carried out with several high-purity specimens ($\Gamma \simeq 1000$ to $\Gamma \simeq 10\,000$) made from NRC tantalum. The substitutional impurity content in these specimens is approximately a factor of 10 lower than in the Fansteel wire.[13] The data show the intersection temperature occurring as low as 2.6°K. This does not evaluate the "perfectness" of this last group of specimens fairly, however, for at temperatures as low as 1.3°K approximately one-fifth of the normal resistance still returns abruptly, and there are indications that the discontinuity will remain at temperatures close to 0°K.

More recently a careful examination for a group of specimens which has been heavily doped with nitrogen ($\Gamma = 60$ to 130) revealed that the sharp step could also be detected in impure specimens at temperatures below 2.5°K. The fraction of resistance restored at H_c for a fixed current density decreased rapidly with decreasing temperature and decreasing Γ. For example, at $T = 2.59$°K and $J = 100$ amp/cm², only 0.2% of the total resistance was restored at H_c, which at this temperature was separated from $H_{\frac{1}{2}}$ by several hundred oersteds. Nevertheless, extrapolation to even lower temperatures suggests that the resistance may remain finite above H_c at all temperatures, and consequently that the filaments never become completely continuous. Unfortunately the uncertainty involved in this procedure does not allow any definite conclusions.

It seems important at this point to consider the role of dislocations in this phenomenon. Several specimens with various impurity concentrations ($\Gamma \simeq 100$ to $\Gamma \simeq 9000$) were deformed up to 80 revolutions per inch of specimen. In all cases this resulted in a change in Γ of the order of 10^{-3} μ ohm cm and an increase in $T_{\frac{1}{2}}$ of 0.1 to 0.2°K. The above plastic deformation was certainly sufficient to produce orders of magnitude increases in the dislocation densities, although the resultant changes in residual resistance were rather small. The corresponding changes in the filament transition were also small, as would be expected if the residual resistance were increased a comparable amount by changing the impurity level. One must remember of course that the impurities in the specimens were present before the dislocation density was altered. One of the deformed specimens ($\Gamma = 370$) was aged. The intersection temperature increased from 3.1°K to 3.9°K.

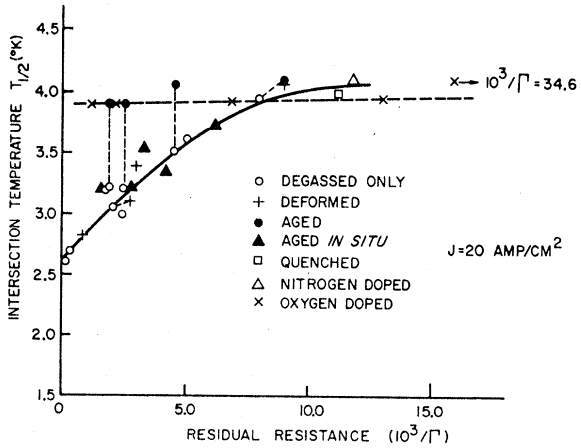

FIG. 6. Dependence of the intersection temperature $T_{\frac{1}{2}}(H_{\frac{1}{2}} = H_c$ for $J = 20$ amp/cm²) as a function of residual resistance.

The values of $T_{\frac{1}{2}}$ for all the specimens investigated are plotted as a function of $1/\Gamma$ in Fig. 6. One can discern two distinct curves, the lower characteristic of well outgassed and vacuum cooled tantalum, and the upper characteristic of specimens which were either aged or doped with oxygen.[23] In both groups filamentary conduction remains in specimens so pure as to have Γ between 10^3 and 10^4. More importantly, the small amount of oxygen sufficient to provide $\Gamma \simeq 10^3$ is also sufficient to raise $T_{\frac{1}{2}}$ from below 3°K up to 3.9°K. The scatter of data in the lower curve can thus be explained in terms of a pronounced sensitivity of the specimens to contamination by oxygen and perhaps by other similar interstitial contaminants. The effect of aging can be explained simply by the contamination of the specimens from the few monolyaers of oxide which form on the specimens upon exposure to air. It appears from the data in Fig 6 that there is a saturation effect occurring with very minute quantities of oxygen. It should be stressed that there is no assurance that the oxygen is dispersed. Rather it seems more probable that in having such a large effect it may be localized in spite of all efforts to achieve homogeneity.

DISCUSSION

A result of particular practical importance in this work was the identification of the sharp step in the restoration of resistance with the bulk transition, and the realization that in such cases the critical fields determined from resistance measurements can be meaningful. It is interesting to note that increasing the current density will move the toe of the broad filament transition towards lower fields until the sharp step, or flux exclusion point, can be seen. In situations where it is inconvenient to measure the magnetic transition directly, the above observations can be of great importance. The major limitation in determing the critical field by the method lies in the necessity of keeping the power dissipation in the specimen and the current leads to the specimen sufficiently small to avoid heating effects. In the present work this limitation affected us only when dealing with specimens where $\Gamma < 50$.

The large effect of the measuring current on the filament transition must somehow be related to the fact that the current is actually localized, and the high-energy density of the current in localized superconducting regions is thus able to produce a profound effect. Little can be said at this time concerning the details of this situation, which can be described only through a knowledge of the geometry of the filaments. The size, shape, and orientation of the superconducting regions, as well as their number, can all influence the current distribution within the specimen, and simple theoretical models prove to be of little use in describing the observed results. From the sharpness of the transitions at the lowest current densities, one might infer that most of the filaments in a given specimen are equivalent insofar as their "critical fields" are concerned, but there is nevertheless a wide variation in current sensitivity among the filaments, as evidenced by the increasing breadth with increasing current.

The temperature dependence of the filament transition is amenable to a qualitative interpretation in terms of the interphase surface energy. The absence of any sign of filamentary conduction in the purer specimens at temperatures close to T_c might be inferred to indicate that the interphase surface energy, α_{ns} is everywhere positive. As the temperature is lowered, α_{ns} should decrease in value, and it may become negative in certain regions. At this point the filament transition should become observable. This would correspond to the temperature $T_{\frac{1}{2}}$ for which $H_{\frac{1}{2}}=H_c$, (neglecting for the moment the spread in the transition, which possibly indicates the spread in composition throughout the specimen).

Unfortunately, a calculation of the dependence of $T_{\frac{1}{2}}$ on the residual resistance, based on an expression for the surface energy derived by Bardeen,[24] and using the mean-free-path dependence of the penetration depth as given by Pippard,[25] did not agree even qualitatively with the experimental data shown in Fig. 6. The cause of this disagreement is not clear, but it very likely lies in the assumption that the surface energy can be influenced by the mean free path of the normal electrons in such a simple manner.

It has by no means been conclusively established that filamentary effects will appear in homogeneous materials. The treatments given the unaged specimens were probably sufficient to create a random distribution for the interstitial contaminants, but there is no assurance that this was true for the slower moving substitutional components. Those substitutional components with substantial vapor pressures can, in fact, be expected to be more densely distributed near the center of the wire. The gradual increase in Γ with increased degassing time[13] that was observed is indicative that substitutional impurities were indeed diffusing to the surface. There is, moreover, a remote possibility that some tightly bound intermetallic compounds or otherwise insoluble contaminants are present in precipitates which are too small to be observed with normal microscopy techniques. Certainly localized contamination by interstitials, as evidenced in the aging experiments, can play a dominant role. Nevertheless, the rather consistent dependence of $T_{\frac{1}{2}}$ on $1/\Gamma$ for quenched, unquenched, and deformed specimens, as shown in Fig. 6, would indicate that some sort of mean free path effect cannot be ruled out en-

[23] The oxygen doping was accomplished by heating the tantalum wires to 2500°C in oxygen atmospheres ranging in pressure from 5×10^{-5} to 5×10^{-7} mm Hg. This work is a part of a comprehensive program for adding known quantities of oxygen, nitrogen, hydrogen, and carbon to high-purity tantalum which has recently been initiated by Seraphim, Budnick, and Novick. A more complete report on this work will be published at a later date.

[24] J. Bardeen, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. 15, pp. 327–330.

[25] A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).

tirely. If the existence of inhomogeneities is not a necessary condition for filamentary effects, and if in turn the explanation of their occurrence in terms of a negative interphase surface energy is correct, one is led to the possibility that it can be negative everywhere, for sufficiently short mean free paths.[26] A local theory is incapable of handling such a situation without arbitrary restrictions on the minimum size of the superconducting and normal regions into which the material could subdivide. It is possible that treatment of this problem in terms of a nonlocal theory[26] could resolve this difficulty, but to date no computations of this sort have been completed.

Another interesting feature of the resistance transitions of these specimens is that in almost all cases a certain amount of hysteresis was observed for the sharp transition. No hysteresis could be seen in the filament transition. While the amount of hysteresis varied from about 2% to 8% of the critical field in going from specimen to specimen, its behavior for a given specimen was rather consistent, showing a gradual increase in magnitude as the temperature was lowered. The fact that the amount of hysteresis was independent of measuring current, ruled out the possibility of a heating effect being responsible for the observed behavior. Since it was impossible to stabilize the specimen on the normal-superconducting transition, the behavior seemed to indicate the presence of supercooling. Hysteresis effects of this type were also observed by J. I. Budnick in the magnetization curves of high-purity tantalum. That this was indeed supercooling was confirmed by performing an experiment of the type described by Faber,[6] whereby a small coil wound on a portion of the specimen was used to lower the field locally, thus inducing the normal-superconducting transition throughout the entire specimen.

[26] Such a condition would favor the subdivision of the material into arbitrarily small superconducting and normal regions, with no exclusion of the magnetic field. For reference see F. London, *Superfluids* (John Wiley and Sons, Inc., New York, 1950), Vol. 1.

In the model proposed by Faber[6] to explain the occurance of supercooling, he postulates that there always are "flaws" in the material which are superconducting even at very high fields. These superconducting nuclei cannot immediately grow when the magnetic field is reduced below H_c, since their small size makes their surface to volume ratio unfavorable for growth in regions of positive interphase surface energy. It is not until the field has been lowered to some value $H_c' < H_c$ that the ratio becomes favorable for growth, and the entire specimen becomes superconducting.

Significantly, supercooling could be observed not only at temperatures close to T_c where the transition was entirely sharp, and the interphase surface energy was presumably positive throughout the bulk of the specimen, but also at temperatures below $T_{\frac{1}{2}}$, where there was pronounced filamentary conduction and consequently no scarcity of superconducting nuclei. Indeed, the supercooling in all respects seemed to be almost completely independent of the filamentary conduction. This is rather surprising, in view of the fact that the phenomenological description of both the superconducting nuclei and filaments in terms of negative surface energy are almost identical. Furthermore, the existence of supercooling as explained in terms of surface energy is incompatible with the idea of a simple mean free path effect, where the surface energy could become negative everywhere. It is evident that considerably more work on impurity effects is needed before these questions can be answered satisfactorily.

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