LOW-TEMPERATURE PHYSICS OF PLASTICITY AND STRENGTH

Superconducting properties and structure of vanadium after cryogenic deformation

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The effect of low temperature (77 K) deformation by drawing (80%) on the superconducting properties and structure of vanadium is studied. The structural elements (fragment boundaries) responsible for the observed changes of critical parameters are isolated. The electron-phonon coupling constant and the electron mean free path undergo most significant changes in these regions of rotational deformation localization, which have a high density of defects and are powerful sources of internal stresses. The dislocation density at the fragment boundaries is estimated. © *1998 American Institute of Physics.* [S1063-777X(98)00903-7]

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1. INTRODUCTION

According to the prevailing concepts, the change in the superconducting properties of metals subjected to plastic deformation is associated with the level of defects and the nature of the structural state formed as a result of deformation. This problem has been studied theoretically and experimentally for quite some time, and the maximum progress has been attained for the cases when the structure of the materials is characterized by a uniform distribution of dislocations, a weakly disoriented cellular structure, and the presence of twin interlayers (see, for example, Refs. 1 and 2). The situation was found to be quite different in the studies of the influence of the fragmented structure, one of the most frequently encountered types of structural state, on the properties of superconductors. As a rule, the emergence of such a structure is associated with the growth of large plastic deformations and leads to the fragmentation of the material into a large number of highly disoriented microregions (fragments). Several authors assume that significant changes in the properties of the superconducting state are associated with the onset of rotational plasticity.[3,4] However, the interpretation of the experimental results is greatly hampered due to the absence of suitable models explaining the entire complexity and diversity of this phenomenon. We believe that the separation of contributions from individual elements of fragmented structure in the variation of the superconducting parameters would be an important step towards the solution of this problem and the construction of models conforming to the experimental results.

Earlier, we studied the effect of large plastic deformation by drawing at 77 and 300 K on the magnetic properties of vanadium at 4.2 K.[4] In order to interpret the observed variations, it was proposed by us that one of the main factors responsible for the observed effects is the strength of fragment boundaries which depends primarily on the disorientation angle, the number density of defects, and the level of nonuniform internal stresses caused by them. The strength of boundaries increases significantly as a result of cryogenic deformation, which enables us to study the nature of the phenomenon. In the present paper, which is a continuation of our earlier publication describing the effect of fragmentation on the superconducting properties of vanadium,[4] we endeavor to describe the results of new experimental studies whose analysis makes it possible to isolate the contribution from individual elements of the fragmented structure to the variation of superconducting characteristics of the metal taking into account the internal stress fields.

2. EXPERIMENTAL TECHNIQUE

In the present work, we study the connection between the variations of the lower critical field H_{c_1}, the thermodynamic field H_c, and the upper critical field H_{c_2}, as well as the superconducting transition temperature T_c, the resistivity ρ_n, and the emergence of inhomogeneous dislocation structures as a result of large plastic deformations. As in our earlier work,[4] we chose 99.88% pure vanadium obtained by electron-beam melting as the object of our investigations. Cylindrical bars were first subjected to recrystallization annealing at a temperature of 1300 K in a vacuum of 1.3×10^{-5} Pa for three hours. Subsequent deformation by drawing at 77 K was carried out on a special device.[5] As the deformation attained the level $\varepsilon = 80\%$, samples of wire having a diameter 1.2 mm and a length 12 mm were cut. A structural state of the samples identical to the initial (recrystallized) state was created by repeated annealing.

In order to plot the field dependences of magnetization $M(H)$ for vanadium at 4.2 K, we used a special magnetometer capable of recording the dependence $M(H)$ under a con-

TABLE I. Characteristics of vanadium in different structural states.

State	T_c, K	H_{c1}, Oe	H_{c2}, Oe	$\rho_n \cdot 10^8$, $\Omega\cdot$m
Initial	4.88	90	1660	3.78
Deformed $\varepsilon=80\%$, $T=77$ K	4.98	80	2660	4.18

tinuous variation of the magnetic field. The sample axis was at right angles to the magnetic field. The technique for magnetic measurements was described in detail in our earlier publications.[6,7] With the exception of H_c corresponding to the deformed state, the values of the critical fields at 4.2 K were determined by using the standard technique for processing the $M(H)$ dependences.[8,9] The estimate for the value H_c of the deformed state is presented below. The superconducting transition curves were recorded by the usual resistive technique, and the error in determining T_c was 0.001 K. The structural state was studied by transmission electron microscopy on longitudinal sections of the samples. Note that all investigations in the initial state and in the state deformed by drawing were carried out on the same sample after removing a surface layer of thickness $\simeq 10$ μm.

In our calculations, we used the quantity ρ_D, the contribution to ρ_n from a unit length of the dislocation line. This quantity was determined in supplementary experiments by measuring the increment in ρ_n at 5 K as a result of an increase in the mean dislocation density N registered by an electron microscope after relatively small deformations. It was found that $\rho_D \simeq 1\times 10^{-24}\Omega\cdot$m^3.

3. DISCUSSION OF RESULTS

Table I shows the characteristics of vanadium in various structural states. It can be seen that deformation leads to a decrease in the value of H_{c_1} and an increase in the values of H_{c_2}, T_c and ρ_n, the variation in the value of H_{c_2} being the most significant. While the magnetization of the initial sample is described by a typical hysteresis curve, the nature of magnetization changes significantly as a result of deformation, and a peak effect is observed (Fig. 1).

The initial structural state of vanadium is characterized by a low dislocation density $N \simeq 10^{12}$ m^{-2}, and polygonal structure is practically not observed. The grain boundaries are in equilibrium state and do not cause any internal stresses. Low-temperature deformation leads to the formation of a macroscopically heterogeneous structure over the sample cross section due to different conditions of plastic flow in the core and over the periphery of the bar during drawing. Microhardness measurements show that the ratio of the corresponding regions of the cross section after deformation is about 5:1. The core is characterized by a morphologically homogeneous distribution of dislocations with $N\approx 1.4\times 10^{15}$ m^{-2} (Fig. 2a), and fragments stretched along the direction of drawing are encountered rarely. On the other hand, the periphery abounds in fragmented structure and the fragments are also stretched along the direction of drawing (Fig. 2b). In the region of bulk fragmentation, the density of dislocations uniformly distributed in the fragments is $N\approx 2.6\times 10^{15}$ m^{-2}, the average size of fragments is $d\approx 3.0\times 10^{-7}$ m, and the fragments may be disoriented by up to 15°. The fine structure of fragment boundaries is not resolved, which is apparently due to a very high density of defects at the boundaries, and the presence of internally stress fields in them. This leads to a significant blurring and overlapping of the regions of diffractional contrast between dislocations. Note that strong variations of diffractional contrast and a large number of flexural contours observed frequently in the fragments point towards the existence of quite large and nonuniform internal stresses caused by interfaces. Twinning is not observed after deformation.

Let us compare and analyze the obtained results. It

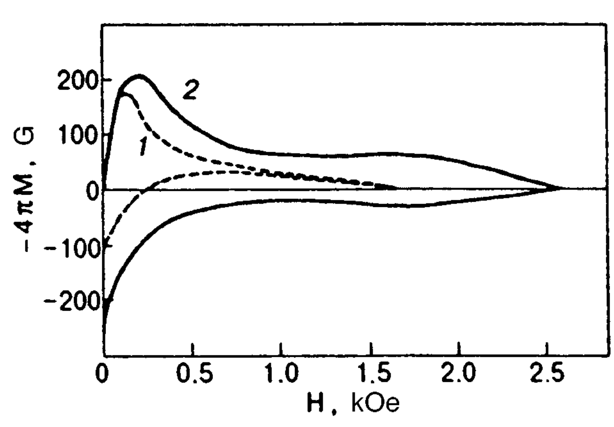
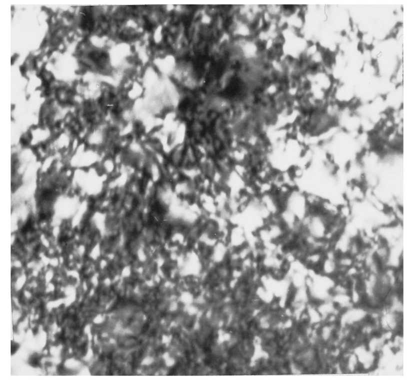


FIG. 1. Magnetization curves for vanadium samples: initial state (curve *1*) and after deformation by drawing (80%) at 77 K (curve *2*).

a



b

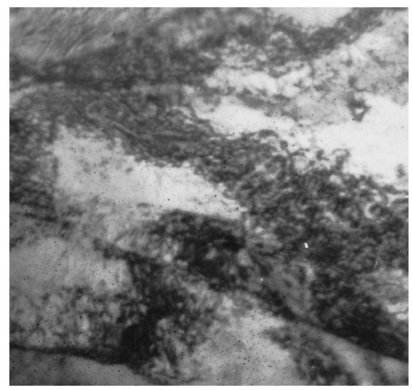


FIG. 2. Vanadium structure after drawing (77 K, $\varepsilon\simeq 80\%$): a—core ($\times$80 000); b—periphery of the sample ($\times$40 000).

should be remarked at the very outset that a more detailed analysis of the reasons behind observed effects requires a knowledge of not only the characteristics presented in Table I, but also several other theoretical parameters characterizing the superconducting state of the initial and the deformed samples. These parameters are calculated on the basis of the BCS theory and the Ginzburg–Landau theory.[10,11]

Let us consider the properties of the initial state and define its generalized parameter:

$$\kappa_1=\frac{1}{\sqrt{2}}\frac{H_{c1}}{H_c}. \tag{1}$$

An analysis of the magnetization curve shows that $H_c \approx 290$ Oe, which gives $\kappa_1 \approx 4.1$. In order to estimate the ''purity'' of the superconductor under investigation and to select a criterion for correctly determining the variation of κ_1 in the deformed state, we calculate the Sommerfeld constant γ. For this purpose, we use the temperature dependence $H_c(T)/H_c(0)$[12] to estimate the value of $H_c(0)\approx 1.24$ kOe. Using familiar relations,[10,11] we can obtain from here the constant $\gamma=1.1\times10^3$ J/(m$^3\cdot$K^2) and the BCS coherence length ξ_0. The value of $\xi_0 \cong 5.35\times10^{-8}$ m was obtained from a comparison of the characteristics T_c and γ for vanadium which was also analyzed by us in Ref. 12. Having calculated the mean free path $l=9.3\times10^{-9}$ m from the relation $\rho_n l=3.5\times10^{-16}\Omega\cdot$m^2,[12] we obtain the impurity parameter $\alpha=0.882\xi_0/l\approx 5.1$. This means that the metal under investigation is a quite ''dirty'' superconductor.

Let us now consider the possible reasons behind the variation of superconducting properties of a metal as a result of deformation. In the first approximation, these variations may be caused by an increase in the dislocation density in the regions of their uniform distribution (core and the regions inside the fragments), fragment boundaries and macroscopic internal stresses. The latter emerge as a result of any variation in sample shape and must be taken into consideration while estimating the effect of the structural factor on the critical parameters. In the case studied by us, tensile stresses dominate at the periphery, while compressive stresses abound in the core region.[13] For the sake of simplicity, we shall consider the maximum possible effect of these stresses on superconducting characteristics. While evaluating the critical parameters in the core of the sample, we shall assume that the effect of compressive stresses on the chosen volume is similar to the effect of hydrostatic pressure. Considering that fragments are strongly stretched in the peripheral regions, we shall confine ourselves to the case when a trial fragment mainly undergoes an axial elongation. According to Rybin *et al.*,[14] the internal stress field distribution in the fragments is quasiuniform in this case, except in the boundary regions which have a characteristic linear size $\approx 0.05d$.

Let us estimate the most probable variations in the critical parameters in the regions with a uniform dislocation distribution. According to Zaitsev's model[15] and our experimental data,[3] the dislocation part of the growth in T_c satisfies the approximate equality

$$\Delta T_c(N)\cong\frac{\pi}{18}\left(\frac{s_\perp}{s_\parallel}\right)^4\frac{E_F^2 ms}{\hbar k_B G}N, \tag{2}$$

where $s_\perp$ and $s_\parallel$ are the transverse and longitudinal sound velocities, E_F is the Fermi energy, m the electron mass at the Fermi surface, s the velocity of sound, G the shear modulus, $\hbar$ the Planck constant, and k_B the Boltzmann constant. Substituting into (2) the values $s=6\times10^3$ m/s, $G=4.65\times10^{10}$ Pa,[16] $E_F=0.76$ [17] $m\approx m^*\approx 2m_0$ (m^* is the effective cyclotron mass and m_0 the electron mass),[18] and assuming that $s_\perp/s_\parallel$ has the value ~ 0.67 typical of a metal, we obtain

$$\Delta T_c(N)\approx 0.15\times10^{-16}N \tag{3}$$

(ΔT_c is in kelvins). It is well known[19] that for a uniform distribution of dislocations, the stress level can be defined with the help of the expression

$$\sigma=\sigma_0+\alpha G b N^{1/2}, \tag{4}$$

where σ_0 is the yield stress in the initial state, b the modulus of the Burgers vector, and α is a constant. The values $\sigma_0=250$ MPa and $\alpha=0.3$ are obtained from mechanical testing, while Fidel[20] gives the value $b=2.63\times10^{-10}$ m. This gives $\sigma=8.4\times10^{-3}G$. In the first approximation, we shall consider elastic stress fields as the additional additive contribution to the overall increase in the value of T_c. Using formula (3) and the value $dT_c/dp=0.62\times10^{-5}$ K/bar,[21] we find that $\Delta T_c/T_c\approx 0.8\%$, which is smaller than the experimentally observed increase in the value of T_c.

For the relative deviation of H_{c2}, we obtain from Eq. (1)

$$\frac{\Delta H_{c2}}{H_{c2}}=\frac{\Delta k_1}{k_1}+\frac{\Delta H_c}{H_c}. \tag{5}$$

Since vanadium which was the object of our investigations is a very ''dirty'' superconductor and κ_1 is defined in the vicinity of T_c, we obtain

$$\Delta\kappa_1\approx 2.37\times10^6\gamma^{1/2}\Delta\rho_n. \tag{6}$$

In subsequent calculations, we can disregard the small increase in γ associated with an increase in T_c. The dislocation contribution to the increase in the electrical resistance is estimated from the relation $\Delta\rho_n\approx N\rho_D$. Nearly the same increase in electrical resistance is caused by the point-type scatterers accumulated as a result of deformation.[22] Further, we consider that the scale of effects associated with the connection between H_{c2} and elastic stresses is mainly determined for $T\sim T_c$ by the quantity $dH_c/dp\approx 1.85\times10^{-3}$ Oe/bar.[23] In this case we obtain from Eq. (5) the value $\Delta H_{c2}/H_{c2}\approx 8\%$, which is also much lower than the experimentally determined variation of H_{c2} in vanadium after low-temperature deformation.

A practically similar result is obtained from analogous calculations for the quasiuniform core region of the fragment, since a certain increase in the critical parameters associated with an increase in the dislocation density will be compensated by the competing effect of tensile stresses.

Thus, the analysis carried out by us shows that even the maximum possible values of T_c and H_{c2} in regions with a uniform dislocation distribution are smaller than the experimentally recorded values, which can be naturally associated with the fragment boundaries that are narrow unrelaxed zones of localization for rotational deformation.

According to the prevailing concepts, the main variations in the critical characteristics of vanadium observed after deformation are caused by an enhancement of the electron-phonon interaction and a decrease in the electron mean free path. Using McMillan's formula[24] and assuming[25] that an equal increase in the value of T_c is accompanied by an insignificant decrease in the Debye temperature, we obtain the value $\Delta\lambda/\lambda \approx 1.5\%$ for the relative increase in the electron-phonon interaction constant. This value is close to the estimates for the increase in λ at the regions of plastic deformation localization.[1]

Let us now evaluate the parameter κ_1 and the characteristic electrical resistance ρ_b of the boundary by using the experimental values of H_{c2} and T_c and disregarding possible distortions of the dependence $H_c(T)/H_c(0)$ introduced by the stress field. Considering that the increase in γ as a result of deformation of vanadium correlates with the increase in T_c,[25] and using relations from the Fetter-Hohenberg theory,[11] we obtain $H_c(0) \approx 1.27$ kOe, $H_c \approx 330$ Oe, and $\kappa_1 \approx 5.8$. This gives the required value of $\rho_b \approx 5.88 \times 10^{-8} \Omega \times \mathrm{m}$. Since the measuring current flows through the circuit element with a resistance lower than ρ_b, we find that $\rho_b > \rho_n$. Naturally, the electron mean free path in the deformation localization region is smaller than in the surrounding volume.

The value of ρ_b can be used to calculate approximately the dislocation density at deformation boundaries. Assuming that scattering at the cores of individual dislocations is a dominating factor, we obtain $N \approx 2 \times 10^{16}$ m^{-2} from the relation $\rho_b = \rho_n + N\rho_D$. This value of the dislocation density is an order of magnitude larger than at the core of the fragment.

CONCLUSION

Thus, an analysis of the experimental data allows us to differentiate the contribution from individual elements of the fragmented structure to the variation of the critical parameters of deformed vanadium. The dominating contribution is made by boundaries of fragments that are unrelaxed zones of localization of rotational plasticity and are regions of high density of crystal structure defects as well as powerful sources of internal stress fields. The variations of superconducting characteristics observed at fragment boundaries are associated with the combined effect of an increase in the electron-phonon interaction constant and a decrease in the electron mean free path in such structural formations. The dislocation density at fragment boundaries causing a disorientation of about 15° may attain values up to $\approx 2 \times 10^{16}$ m^{-2}.

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