INVESTIGATION OF THE EFFECTS OF HYDROSTATIC PRESSURE AND PLASTIC DEFORMATION ON THE SUPERCONDUCTING PROPERTIES OF TITANIUM

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The superconducting properties of samples of 99.99% pure titanium iodide are investigated in the region 0.06–0.6° K, and the effects of plastic deformation and hydrostatic pressures up to 26,000 atm are studied. Plastic deformation and the surface states of samples strongly affect the superconducting transition temperature T_c and the critical field H_c of titanium. Nearly hydrostatic pressures up to ~14,000 atm do not affect, or produce only a very small reversible increase of T_c and H_c in single-crystal, plastically deformed, or lathe-turned titanium samples regardless of their superconducting parameters. Between 14,000 and 26,000 atm well reversible increases of T_c and H_c are observed in plastically deformed samples, at the mean rate $\partial T_c/\partial p \approx 0.7 \times 10^{-5}$ deg/atm.

1. INTRODUCTION

WE have previously[1] suggested that the increase in the superconducting transition temperature of zirconium under hydrostatic pressure results from increased density N(0) of electronic d states, which are responsible for superconductivity in transition metals.[2] The density of d states in transition metals and their alloys depends in a complicated manner on the effective number n_v of valence electrons.[2, 3] If we assume that pressure increases the effective number of valence electrons we can expect that all transition metals and their alloys, in which the density of states increases with the number of valence electrons, will exhibit a higher superconducting transition temperature T_c under pressure. As a test of this hypothesis it was of interest to investigate titanium, which is located at one of the minima of the $N(0) = f(n_V)$ curve according to Daunt.[3]

Unfortunately, the literature on the superconductivity of titanium contains inconsistent data. The superconducting transition temperature reported by different investigators lies in the range 0.387–0.49°K.[4, 5] Different authors also give values of $\partial H_c/\partial T$ varying from 89 to 470 Oe/deg. The lowest value of the critical field, determined by extrapolation to 0°K, was about 20 Oe. This disagreement between the data, obtained not only by different authors but even by the same investigators for different samples, indicates a strong dependence of T_c, $\partial H_c/\partial T$, and $H_c(0)$ on the internal state of the titanium samples.

Before investigating irreversible effects associated with hydrostatic pressure, it was therefore important to attempt to determine the causes of irreversible changes in the properties of titanium, especially the effects of surface treatment and plastic deformation.

2. EXPERIMENTAL PROCEDURE

Measurements were performed at temperatures 0.06–0.6° K obtained by adiabatic demagnetization of a pellet of ferric ammonium alum connected to the sample by a cooling duct. The destruction of superconductivity by a transverse magnetic field generated with Helmholtz coils was registered electronically at 22 cps. The experimental setup and measuring technique have been described in detail in [6].

High pressures were produced by two different methods:

Method 1. Pressures from 0 to 26,000 atm were generated by means of an intensifier[6, 7] without transmission through an intermediate medium. Titanium cylinders 2–3 mm in diameter and 4 mm long were cut on a lathe. As in [6], a copper rod 6–8 mm long was positioned between the sample and a piston of VK-6 cemented tungsten carbide.

Method 2. Pressures from 0 to 15,000 atm were generated by a modification of the method described in [8, 9]. The pressure was transmitted through a 50% mixture of dehydrated kerosene and oil. Pressures were produced either at room temperature or in two stages.[9] Figure 1 shows the

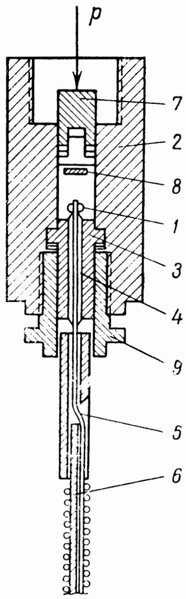

FIG. 1. High pressure chamber. 1 – sample, 2 – chamber, 3 – "mushroom-shaped" fitting, 4 – araldite packing, 5 – cooling duct, 6 – cooling duct pressed into the alum pellet, 7 – piston, 8 – tin manometer.

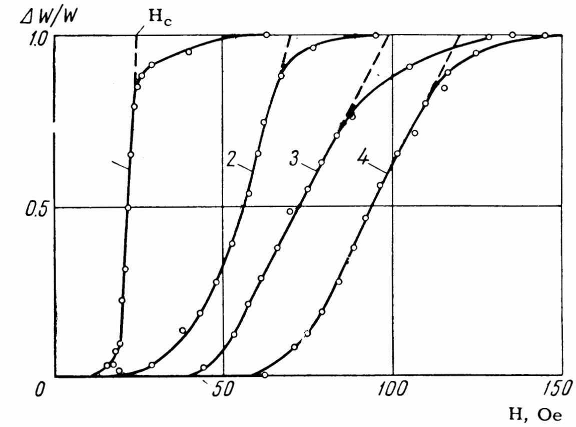

FIG. 2. Superconducting transitions of titanium samples from stock I in a magnetic field. 1 – single crystal at p = 7500 atm and T = 0.105°K, 2 – plastically deformed single crystal at p = 0 and T = 0.128°K, 3 – extruded polycrystalline sample (previously lathe-turned) at p = 23 200 atm and T = 0.154°K, 4 – lathe-turned polycrystalline sample at p = 0 and T = 0.145°K.

changes in the construction of the pressure chamber for measurements at extremely low temperatures. To ensure reliable thermal contact between the alum pellet and the sample 1, a copper cooling duct 5 of 0.5-mm diameter with an araldite packing 4 was introduced into the chamber 2 through a hole of 0.7-mm diameter in the "mushroom-shaped" fitting 3. The sample was cemented directly to the cooling duct by means of BF-2 polymerized adhesive. Along its entire outside length of ~ 100 mm the cooling duct 5 was cemented with BF-2 to another cooling duct 6 pressed into the alum pellet. Both cooling ducts were then covered with the adhesive and an annealed copper wire was wound around them.

The degree of the plastic deformation produced in compressed samples depended on the method used to generate pressure. The deformation was minimal under the pressure of a kerosene-oil mixture at room temperature, increased somewhat in the two-stage method, and was unavoidable in the pressure intensifier without a transmitting medium.

The starting material for the samples was titanium iodide from different stocks (I and II) differing in the composition and concentration of impurities but having 99.99% average purity.[1)] We investigated lathe-turned samples consisting of irregular single crystals produced by dissolving large-crystal titanium blocks in a 50% solution of fluoric and nitric acids; these samples were subjected to severe plastic deformation at room temperature by extrusion or by repeated pressure cycles between steel planes in a press.

3. EXPERIMENTAL RESULTS

Figure 2 shows the variation of the signal W from the amplifier of the electronic circuit as a function of the magnetic field when superconductivity was destroyed in different titanium samples. The critical field H_c was determined by extrapolating the straight portion of each curve to a horizontal line representing a constant value of the signal W following the complete destruction of superconductivity. The values of H_c obtained in this manner for a very sharp superconducting transition in the absence of a magnetic field agree well with ballistic magnetic measurements.[6, 10] It is obvious that if the superconducting transition in zero field is not sufficiently sharp, then the values of H_c determined in this way correspond to the critical-field curve $H_c(T)$ with T_c at $H = 0$, obtained by extrapolating the steepest part of the superconducting transition curve for $H = 0$ to the horizontal axis (Fig. 3). In this case H_c can somewhat exceed the true thermodynamic critical field.

Figure 4 shows the critical-field curves of titanium samples when not subjected to pressure. The curves for single crystals are characterized by the lowest values of T_c that are found in the

1)The electrical resistance of polycrystalline samples from stocks I and II was reduced by a factor of 90 to 70, respectively, when cooled from room temperature to liquid helium temperature.

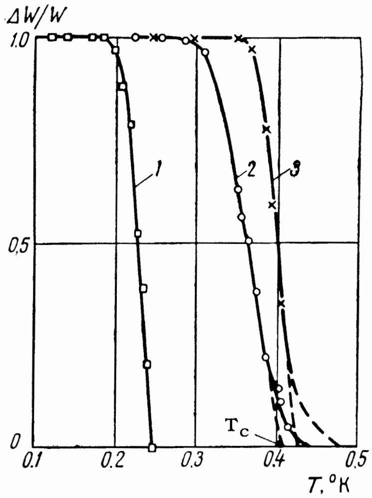

FIG. 3. Superconducting transition for H = 0 in different titanium samples from stock I. 1 – single crystal at p = 14 300 atm, 2 – lathe-turned polycrystalline sample at p = 15 300 atm, 3 – plastically deformed polycrystalline sample at p = 24 000 atm.

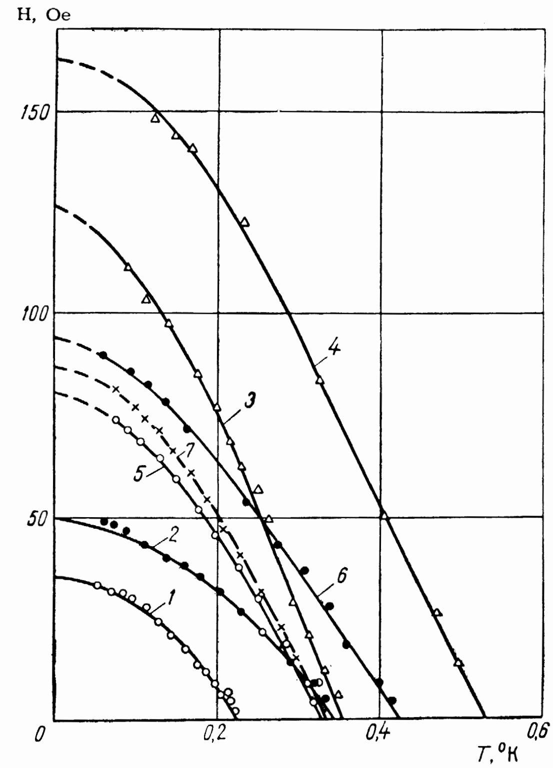

FIG. 4. Critical-field curves of titanium samples at zero pressure. 1 – single crystal from stock I; 2 – single crystal from stock II; 3,4 – lathe-turned polycrystalline samples from stock I; 5,6,7 – plastically deformed samples (5 – single crystal from stock I, 6 – single crystal from stock II, 7 – polycrystalline sample from stock I (lathe-turned in advance) after many pressure cycles).

literature. The critical temperature of lathe-turned samples rises sharply (curve 4) and is located within the range 0.35–0.53°K for some samples. The plastic deformation of single crystals elevates the critical temperature sharply (compare curves 1 and 5, 2 and 6). On the other hand, the plastic deformation of lathe-turned samples lowers their critical temperatures (compare curves 4 and 7). For each of the titanium stocks there exists an equilibrium curve of critical fields (curve 7 for stock I) corresponding to the most extremely plastically deformed material, which is approached from both directions by the critical-field curves of single-crystal and lathe-turned samples when plastically deformed. These "equilibrium" curves differ depending on the titanium stock, evidently because of different concentrations and composition of the impurities.

The strong influence of plastic deformation on the superconducting properties of titanium must be taken into account when investigating reversible changes of T_c and $H_c(T)$ under pressure. In connection with the foregoing discussion it may be stated that a completely reversible pressure effect in titanium can be observed only under pure hydrostatic pressure. Unfortunately, we did not exceed 15,000 atm in applying nearly hydrostatic pressure by the second method. To obtain higher pressures we used a technique[1] whereby plastic deformation could not be avoided during compression.

The results obtained by investigating the pressure effect on the superconducting titanium properties can be summarized as follows. Hydrostatic or nearly hydrostatic pressure up to ~ 14,000 atm induces no change, or only a very weak reversible increase, in the superconducting transition temperature within the critical fields for single-crystal (curves 1 and 2 of Fig. 5), plastically deformed and lathe-turned (curves 3 of Fig. 5) titanium samples, independently of their superconducting parameters.

In samples that were first subjected to strong plastic deformation, at pressures 14,000–26,000 atm we observed a well reversible rise of H_c (curves 4 and 5 of Fig. 5) and T_c (Fig. 6) under pressure. The mean value of $\partial T_c/\partial p$ in this pressure range is $\sim 0.7 \times 10^{-5}$ deg/atm.

An interesting property was observed when using the first pressure method on samples that were lathe-turned and exhibited higher superconducting parameters before plastic deformation. The magnitude of the variation of T_c at a single given pressure depends on the sequential number of the pressure cycle (Fig. 6). The first compression is accompanied by the maximum shift of T_c; in succeeding cycles the change of T_c diminishes,

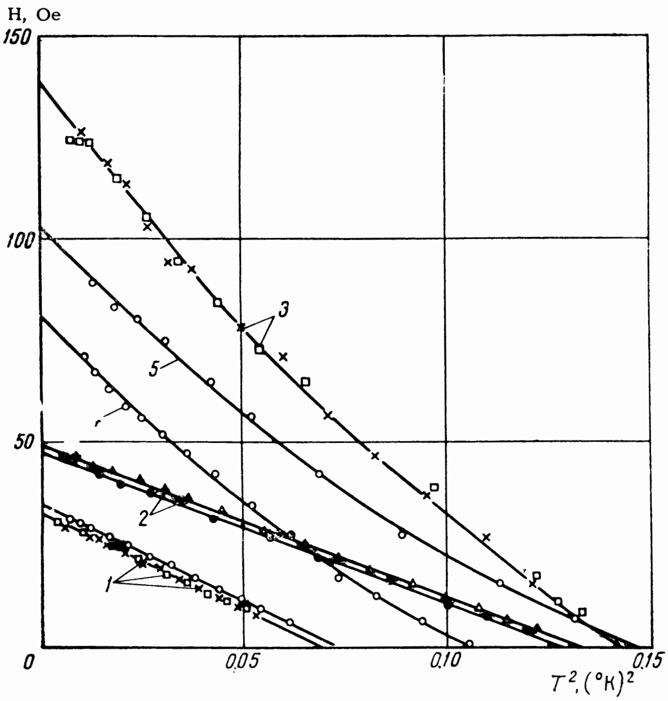

FIG. 5. Critical-field curves of titanium samples under different pressures in the coordinates H_c and T_c^2. 1 – single crystal from stock I, □ - p = 0, ○ - p = 14 300 atm, × - p = 0 (pressure removed); 2 – single crystal from stock II, ● - p = 0, △ - p = 4000 atm; 3 – lathe-turned polycrystalline cylinder, □ - p = 15 300 atm, × - p = 0 (pressure removed); 4 – plastically deformed polycrystalline sample, p = 960 atm (12th pressure cycle, see Fig. 6); 5 – plastically deformed polycrystalline sample, p = 24 400 atm (11th pressure cycle, see Fig. 6).

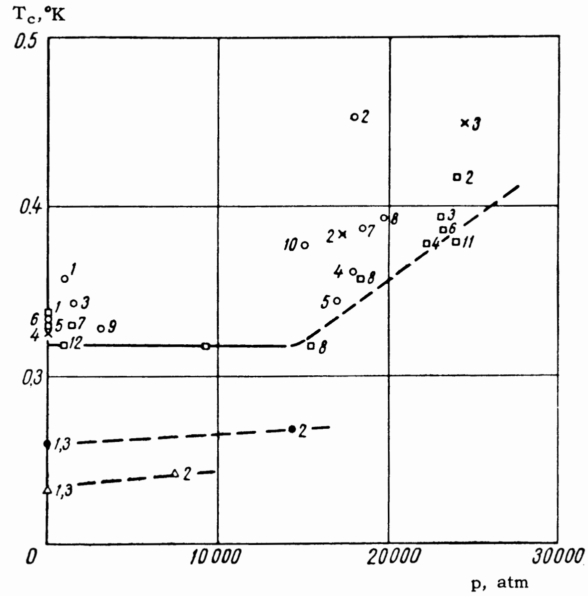

FIG. 6. Pressure dependence of the superconducting transition temperature of titanium samples from stock I. △, ● – single crystals; ×, ○ – lathe-turned polycrystalline samples, □ – extruded polycrystalline sample. The numerals adjacent to the experimental points designate the sequential number of the pressure cycle.

approaching an "equilibrium" limit corresponding to the compression of samples with large plastic deformation. The decrease of $\Delta T_c = T_c(p) - T_c(0)$ in successive pressure cycles is evidently associated with plastic deformation of the sample in each cycle, as a result of which $T_c(0)$ diminishes in each cycle and approaches the "equilibrium" limit. The reduction of T_c is accompanied by decreased slopes $(\partial H_c/\partial T)_T$ of the critical-field curves and increased sharpness of the superconducting transitions in a magnetic field.

4. DISCUSSION OF RESULTS

A. The elevation of the superconducting transition temperature of titanium under pressure agrees, at least qualitatively, with a hypothesis concerning the relationship between the signs of the derivatives $\partial N(0)/\partial n_v$ and $\partial T_c/\partial p$ for transition metals, based on data obtained in an investigation of zirconium.[1,10] When the behavior of titanium under pressure is compared with that of zirconium we note the following:

a) In both instances plastic deformation induces an irreversible rise of T_c. However, the relative increase of T_c for titanium is approximately twice as great as for zirconium.

b) In unannealed plastically deformed zirconium samples no appreciable rise of T_c was observed up to ~10,000 atm. Practically no pressure effect was observed in similar titanium samples up to about 15,000 atm.

c) For zirconium T_c in a lathe-turned sample did not increase at all above its value in a plastically deformed sample. Since for lathe-turned titanium samples T_c and H_c are sharply reduced after etching and approach the equilibrium curve 7 of Fig. 5 (for titanium from stock I), we can conclude that the properties of these samples depended on the properties of their surface layers. The superconducting properties of this layer possess higher values of the parameters than the interior.

d) The pressure effect in zirconium was enhanced by annealing. A considerably greater pressure effect was observed in titanium upon compressing the surface layer. The specific properties of this layer can possibly result from local heating of the titanium while it is being machined on a lathe.

B. It is of interest to compare the superconducting transition temperatures of different titanium samples with the corresponding densities of states at the Fermi surface. The state density N(0) is given by

$$N(0) \infty \gamma = a_2 \frac{1}{2\pi} \frac{H_0^2}{T_c^2}, \qquad (1)$$

where the coefficient a_2 represents the deviation of the $H_c(T)$ curve from a parabola. Figure 5 shows the critical-field curves for the most characteristic cases in the coordinates H_c and T_c^2. The curves approach parabolas only for single crystals. For plastically deformed and lathe-turned samples we observe a marked negative deviation from the parabolic form. The nearly parabolic dependences of H_c on T for titanium single crystals enable us to calculate the parameter γ for these samples from Eq. (1), assuming $a_2 = 1$. The values obtained for γ are $\sim 6.2 \times 10^{-4}$ and $\sim 7.15 \times 10^{-4}$ cal-mol/deg^2 for samples from stocks I and II, respectively, in quite good agreement with calorimetric measurements[11] that gave $\gamma = 8 \times 10^{-4}$ cal-mol/deg^2. If we assume that the procedure used in calculating γ and N(0) from the given critical-field curves is also valid for plastically deformed samples and for lathe-turned samples (assuming in the latter case that N(0) pertains to the surface layer), we find that for plastically deformed titanium γ is 4–5 times larger, and for lathe-turned samples 8–10 times larger, than for single crystals. These values are evidently highly exaggerated because the derived values of H_c depart from the thermodynamic val-values.

The superconducting transition temperature is related to the state density N(0) by[12, 13]

$$T_c = 0.85\Theta_D \exp\{-1/N(0)V\}, \qquad (2)$$

where Θ is the Debye temperature (429°K for titanium), and V is the electron-phonon interaction parameter. A comparison between the corresponding values of γ and T_c for single crystals and plastically deformed samples above 15,000 atm indicates a definite correlation between T_c and N(0), so that larger values of T_c always correspond to larger values of N(0).

It should be noted that, unfortunately, independently of the accuracy with which N(0) may be determined from the critical-field curves, we cannot simultaneously account for the different values of T_c in different titanium samples and the pressure dependence of T_c (Fig. 6) exclusively on the basis of changes in state density at the Fermi surface. If there were a unique relationship between T_c and N(0), the lowest value of T_c for single crystals would correspond to a minimum of N(0). Since for these samples $\partial T_c/\partial p$ is very small and positive up to 14,000 atm, we can infer that here N(0) is close to the minimum of the N(0) = f(n_V) curve. Then for samples with higher T_c the values of N(0) should lie on the region of this curve with higher values of $\partial N(0)/\partial n_V$, i.e., the pressure effect should be enhanced as T_c increases. The experimental absence of this effect appears to provide evidence that the different superconducting transition temperatures of different titanium samples and their pressure dependences are not determined only by the differences in state density. Variation of the parameter V for titanium could also possibly play a definite part.

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