

THE EFFECT OF HYDROGEN ON THE SUPERCONDUCTING TEMPERATURE IN B.C.C. NIOBIUM-TITANIUM ALLOYS

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Abstract—The dependence of the superconducting temperature, T_k , on the hydrogen concentration in b.c.c. Nb-Ti alloys with 20, 35 and 50 at%Ti have been measured for H content up to H:metal atomic ratio, n , of approx. 0.2. An increase in the H concentration was shown to result in approximately linear lowering of the T_k -values with the same slope, dT_k/dn , of approx. $-15 \text{ K atom H}^{-1}$ for all the Nb-Ti-H solutions under study.

INTRODUCTION

Despite the fact that the superconducting properties of hydrogen solid solutions in transition metals have been intensively studied, correct data concerning the effect of H on the superconducting temperature, T_k , of such well-known superconductors as b.c.c. V, Nb and Ta are absent from the literature. The reason is that, even though at elevated temperatures, V, Nb and Ta metals form, with hydrogen, wide ranges of continuous solid solutions on the base of a b.c.c. metal lattice (the α -solutions), the value n_α of terminal H concentration in these solutions decreases rapidly with decreasing temperature. For example, in the case of Nb-H solutions the n_α -value reaches only $\approx 4 \cdot 10^{-2}$ at 300 K and falls down to $\approx 4 \cdot 10^{-3}$ at 200 K [1]. At the same time, at low temperatures, when the superconducting properties are being studied, the high-temperature homogeneous state of the α -solutions with higher H content cannot be preserved in practice by "quenching", since, due to the large diffusional mobility of H in Nb the hydride precipitation from oversaturated α -solution (and, correspondingly, the depletion of H in the solution) proceeds with a noticeable rate even at 150 K [1]. Besides, the effect of plastic deformation of the α -matrix near to the hydride precipitations on the magnitude of its T_k (an increase of $\approx 0.1 \text{ K}$) proves to be much stronger than the effect of the residual H dissolved in this matrix [2].

In a number of papers [3 and references therein] it has been shown, however, that the value n_α of terminal H solubility in b.c.c. Nb can be considerably increased by means of alloying Nb with Ti (apparently due to H trapping by the Ti atoms). For example, in the case of H α -solutions in the Nb-Ti alloy with 5 at%Ti no hydride precipitations were observed [3] at $T \geq 60 \text{ K}$ for H concentrations up to $n = 0.042$. It therefore seemed quite probable that on a base of Nb-Ti alloys with higher Ti content one could obtain H α -solutions stable at low temperatures in a still wider range of H concentrations and trace the changes in their T_k with increasing n . The results of [4], where with Nb-Ti alloys

containing 45.4–74.4 at%Ti, doped with H up to $n \sim 0.3$ by different methods (mainly, by melting or annealing in a H-containing atmosphere), a monotonous decrease in the T_k -values with increasing hydrogen content was observed, support this assumption. (In the case of hydride precipitation the compositions and, correspondingly, the T_k -values of both phases in the developing two-phase mixture must be nearly independent of the total H concentration of the sample.)

The present paper deals with H solutions on the base of the Nb-Ti alloys with 20, 35 and 50 at%Ti.

EXPERIMENTAL

The alloys were melted from Nb refined by zone melting ($R_{300\text{K}}/R_{4.2\text{K}} \approx 500$) and iodide titanium. The ingots were prepared by levitation melting in an Ar atmosphere and annealed in vacuum $\approx 10^{-6}$ Torr ($\approx 10^{-4}$ Pa) and 1200°C for 24 h with subsequent cooling with the furnace. The weight loss of the ingots during melting and annealing did not exceed 0.3 wt%, which was considered as an upper limit of the uncertainty in the alloy compositions. The specimens were cut from the ingots by a spark cutter. The damaged surface layer, $\approx 0.05 \text{ mm}$ thick, was then removed by chemical etching. The final dimensions of the samples were $4 \times 4 \times 0.5 \text{ mm}^3$.

Hydrogenation of Nb-Ti samples was conducted in an atmosphere of H_2 at $P_{\text{H}_2} = 1 \text{ GPa}$ and $T = 200^\circ\text{C}$, the method is described in [5]. Saturation of the samples with H to different concentrations was achieved by varying the time duration of treatment under these conditions. After hydrogenation was completed, the high-pressure chamber was rapidly cooled to $\approx -20^\circ\text{C}$, the pressure lowered and the samples removed from the chamber and stored in liquid N_2 .

Both the Nb-Ti alloys and H solutions on their base were polycrystalline. An X-ray study of the samples was carried out by a phototechnique at $T = 80 \text{ K}$ using a DRON-2.0 diffractometer with FeK_α radiation. The T_k -values were determined by the induction method at

$T \geq 2$ K from the step midpoint locations, using the temperature dependence of the signal of disbalance of an ac bridge.

The H content of the samples was measured with a relative accuracy of $\pm 3\%$ from the amount of H_2 liberated in their thermal decomposition, in a stream of Ar at 900°C , into metal and H_2 . To determine the quantity of the released H_2 a humidity analyser was used [6] in which, between the evaporator and the coulometrical transducer [7], a gas oxidizer (a quartz tube filled with granulated copper oxide heated to 700°C) was installed.

RESULTS AND DISCUSSION

The initial Nb–Ti alloys with 20, 35 and 50 at% Ti had b.c.c. lattices, their parameters, $a(0)$, at atmospheric pressure and $T = 80$ K being equal to 3.289, 3.281 and 3.280 ± 0.003 Å (1 Å = 0.1 nm), respectively, which agrees with the X-ray data listed in [8].

According to [9], at $T \leq 200^\circ\text{C}$ and $P_{H_2} \geq 1$ atm (0.1 MPa), it is the formation of dihydrides on the base of f.c.c. metal sublattice that explains the thermodynamical equilibrium in the Nb–Ti–H systems under study. In fact, having kept the Nb–Ti samples at $T = 200^\circ\text{C}$ and $P_{H_2} = 1$ GPa for more than 6 h, dihydrides with $n = 2.00 \pm 0.05$ were always obtained. At atmospheric pressure and $T = 80$ K the parameters of the f.c.c. metal sublattices of these dihydrides on the base of the Nb–Ti alloys with 20, 35 and 50 at% Ti were equal to 4.545, 4.529 and 4.507 ± 0.005 Å, in agreement with the data of [9]. The dihydrides of all three Nb–Ti alloys under investigation as well as dihydrides of Nb [10] and Ti [11] studied earlier exhibited no superconductivity at $T \geq 2$ K.

In order to synthesize Nb–Ti–H samples with lower H concentrations the following property of Nb and its alloys [12] was exploited. At 200°C , the temperature chosen for the hydrogenation, the ingress of H into the samples is mainly determined by processes on their surfaces, and at any given moment the phase composition of the forming metal/H solid solutions proves to be nearly equilibrium for the total H content achieved inside the sample. Having kept the Nb–Ti samples in a hydrogen atmosphere at $T = 200^\circ\text{C}$ and $P_{H_2} = 1$ GPa for 0.5–4 h Nb–Ti–H samples with H content up to $n \approx 0.2$ were obtained. An X-ray examination showed these samples had b.c.c. metal sublattices with parameters, $a(n)$, monotonically and approximately linearly increasing with H concentration. The values $\Delta V = [a^3(n) - a^3(0)]/2$ of the increment of the volume per metal atom in the obtained Nb–Ti–H α -solutions are shown in Fig. 1A; the T_k -values for these solutions are plotted in Fig. 1B (note that the T_k -values for our Nb–Ti samples without hydrogen agree well with data in the literature [13]).

In favour of the fact that the data presented in Fig. 1 reflect the properties of the homogeneous Nb–Ti–H α -solutions and have not been noticeably distorted due to hydride precipitation or large nonuniformity of the

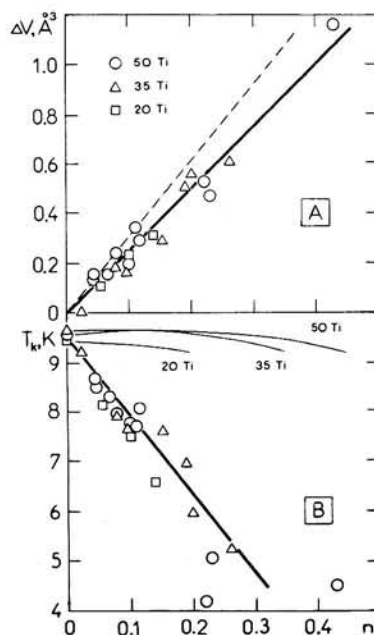


Fig. 1. Dependences of ΔV (A) and T_k (B) on n for H α -solutions in Nb–Ti alloys with 20, 35 and 50 at% Ti.

solutions, the following arguments could be advanced:

(i) The $\Delta V(n)$ dependences for all the investigated H solutions in the transition metals and their alloys are known to be close to each other [14, 5]. The lines in Fig. 1A represent the dependences $\Delta V(n)$ for the H α -solutions in single crystal (dashed line) and polycrystalline and powder (solid line) samples of Nb taken from [14]. As seen from Fig. 1A, the values $\Delta V(n)$ obtained in the present paper for Nb–Ti–H α -solutions lie somewhat lower than the $\Delta V(n)$ dependence for the single crystal Nb–H samples and agree well with the dependence for the polycrystalline and powder samples. Taking into account that the samples were polycrystalline, this may be evidence of the absence of hydride precipitations in the samples, at least in quantities which might result in overestimating the magnitudes of the H content of the α -solutions by values exceeding the experimental error in the determination of the total H content of the samples.

(ii) According to [1], the process of hydride precipitation from the Nb–H α -solutions slows down essentially at $T \leq 150$ K. In the present work, an X-ray examination of the Nb–Ti–H samples was carried out at 80 K, i.e. at much lower temperature, and it was shown for several different samples that an exposure to liquid N_2 temperature for a few months leads to no changes in the values of the lattice parameters of the α -solutions. It therefore seems quite improbable that hydride precipitation in the samples might occur while cooling them down from liquid N_2 to He temperatures in the process of measuring the T_k -values, especially since the cooling took less than 1 min.

(iii) The width of the diffraction lines in X-ray photographs of the b.c.c. Nb-Ti alloys only slightly increased while saturating the alloys with H up to $n \approx 0.2$. Together with (i) this points to a homogeneous H distribution over the volume of the samples under study at $T = 80$ K.

(iv) The width of the superconducting transition which was equal to ≈ 0.3 K in the initial Nb-Ti samples also hardly increased with increasing H concentration in the alloys. This points to a sufficient homogeneity of the obtained Nb-Ti-H α -solutions at He temperatures as well.

From the above, one may safely deduce that the $T_k(n)$ dependences presented in Fig. 1B refer to the homogeneous Nb-Ti-H α -solutions with H concentrations shown on the abscissa.

It is seen from Fig. 1B that the $T_k(n)$ dependences for all three Nb-Ti alloys studied do not differ from each other within the experimental error and are close to a straight line with slope $dT_k/dn \approx -15$ K atom H^{-1} (thick line in Fig. 1B).

Note, that this value of dT_k/dn is close to that (about -10 to -20 K atom H^{-1}) obtained in [4] for H solid solutions in Nb-Ti alloys containing 45.4–74.4 at% Ti. Consequently, it seems reasonable to admit that the solutions investigated in [4] were the α -solutions as well. If so, then the results of [4] and the present work show that for all the Nb-Ti b.c.c. alloys, from a rather wide interval of concentrations (20 to 74.4 at% Ti), dissolution of H leads to a decrease of the T_k -values with approximately the same slope, ≈ -15 K atom H^{-1} . Thus the H α -solutions in pure Nb and Ti, being stable at low temperatures, may also exhibit a decrease in the T_k -values with increasing H content with the same (at least in order of magnitude) slope.

Referring to the data obtained for the Nb-Ti-H α -solutions, it is worth pointing out that the observed behaviour of the $T_k(n)$ dependences proves to be rather nontrivial. It cannot be explained by considering changes in the degree of filling of the d-band of host metals by electrons as the main reason behind changes in their properties with increasing H concentration, though this describes well the behaviour of many different physical properties (in particular, the magnetic properties) for a great variety of transition metals and their alloys on hydrogenation [5, 15].

In fact, concentration dependences of T_k for the alloys of transition metals, the b.c.c. Nb-Ti alloys included, can be satisfactorily described in the framework of the rigid band model or its slightly modified versions [16], i.e. in wide ranges of alloy compositions the T_k -values prove to be a universal function of the average number N^e of external (s + d) electrons per atom in the alloy. This implies the existence of the universal dependence of T_k -values in the alloys upon the degree of occupation of their d-band by electrons, since the T_k -values are determined by the properties of the electrons near the Fermi surface, and in transition metals the density of d-states at the Fermi level is much higher than that of s-states. Accepting this explanation for the change in

the T_k -value of the alloy saturated with H one could write $T_k(n) = T_k(N^e + \eta \cdot n)$, where $T_k(N^e)$ is the dependence of T_k on the electron concentration of the alloys without H; N^e is the electron concentration of the alloy under hydrogenation; η is the number of electrons supplied by the Hs into its d-band.

$N^e = 4$ el. at^{-1} for Ti and 5 el. at^{-1} for Nb. The $T_k(N^e)$ dependence for the b.c.c. Nb-Ti alloys passes through a shallow maximum at $N^e \approx 4.7$ el. at^{-1} [13, 16], i.e. at the N^e value close to that for the Nb₆₅Ti₃₅ alloy. The N^e values for our alloys with 50 and 20 at% Ti are equal to 4.5 and 4.8 el. at^{-1} , i.e. lie to left and right respectively of the maximum in the $T_k(N^e)$ dependence.

The dependences $T_k(n) = T_k(N^e + \eta \cdot n)$ for the Nb-Ti alloys with 50, 35 and 20 at% Ti calculated for $\eta = 1$ el. at H^{-1} are plotted in Fig. 1B in thin lines labelled 50, 35 and 20 Ti, respectively. These dependences do not agree at all with the experimental ones.

The value of $\eta = 1$ el. at H^{-1} was chosen because it just permits a quantitative description of the behaviour of magnetic susceptibility of the Nb-Ti-H α -solutions at 180°C in [17] and because approximately this value of η was calculated in [18] for the V-H α -solutions, close analogue of the Nb-Ti-H solutions. In principle, however, it could not be excluded that the η -values for the Nb-Ti-H α -solutions might essentially differ from 1 el. at H^{-1} . In particular, an analysis of the conditions for the proton screening in transition metals [19] has shown that for the VI–VIII group metals one might expect $\eta \geq 0$ whereas for III–V group metals and, hence, for Ti and Nb $\eta \leq 0$ is more probable. In our case, the uncertainty in the η -values is of no significance, since no choice of η -value from the possible interval +1 to -1 el. at H^{-1} , could describe the experimental dependence of $T_k(n)$ shown in Fig. 1B. Indeed, even if $\eta = -1$ el. at H^{-1} and the dependences $T_k(n) = T_k(N^e + \eta \cdot n)$ change strongly compared to those plotted in Fig. 1B (the T_k -values for the alloys with 50 and 35 at% Ti must then decrease with increasing n and the $T_k(n)$ curve for the alloy with 20 at% Ti must pass through a maximum at $n \approx 0.1$), the calculated changes in T_k -values at $n \leq 0.2$ do not exceed ≈ 1 K, while the experiment has shown these values to decrease by ≈ 3 K.

The totality of available theoretical [18] and experimental [5, 15] data evidence a very weak deformation of the d-bands of transition metals in the vicinity of the Fermi level. The obvious conclusion is that the rapid and approximately identical decrease in the T_k -values of the Nb-Ti alloys, with a slope $dT_k/dn \approx -15$ K at H^{-1} , is not solely associated with the changes in the density of states at the Fermi level with increasing H content of the alloys, but is due to another and moreover, common reason. At present, it seems most probable that it is due to changes in the phonon spectrum of the alloys brought about by the dissolved H.

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REFERENCES

1. D. G. Westlake, *Trans. Metal. Soc. AIME* **245**, 287 (1969).
2. Ch. V. Kopetsky, V. A. Marchenko and G. I. Salnikov, *Fiz. Metall.* **59**, 62 (1985).
3. G. Cannelli, R. Cantelli and M. Koiwa, *Phil. Mag. Appar. Mfrs* **46**, 483 (1982).
4. U. Zwicker and W. Böhm, *Z. Metallkde.* **69**, 600 (1978).
5. E. G. Ponyatovsky, V. E. Antonov and I. T. Belash, *Usp. fiz. Nauk* **137**, 663 (1982) [*Soviet Phys. Usp.* **25**, 596 (1982)].
6. V. A. Orlov *et al.*, USSR Patent 979977 (1982).
7. V. A. Orlov and N. M. Gordik, USSR Patent 545913 (1977).
8. W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys*. Pergamon Press, Oxford (1958).
9. B. Stalinski and B. Nowak, *Bull. Acad. pol. Sci. Sér. sci. chim.* **25**, 451 (1977).
10. C. B. Satterthwaite and D. T. Peterson, *J. less-common metals* **26**, 361 (1972).
11. B. T. Matthias, T. H. Geballe and V. B. Compton, *Rev. mod. Phys.* **35**, 1 (1963).
12. J. Völkl and G. Alefeld, Topics in applied physics. In G. Alefeld and J. Völkl (eds), *Hydrogen in Metals I*, Vol. 28, p. 321. Springer, Berlin (1978).
13. J. K. Hulm and R. D. Blaugher, *Phys. Rev.* **123**, 1599 (1961).
14. H. Peisl, Topics in applied physics. In G. Alefeld and J. Völkl (eds), *Hydrogen in Metals I*, Vol. 28, p. 53. Springer, Berlin (1978).
15. E. Wicke, *J. less-common Metals* **101**, 17 (1984).
16. S. V. Vonsovsky, Yu. A. Izyumov and E. Z. Kurmaev, *Superconductivity of Transition Metals, Their Alloys and Compounds*. Nauka, Moscow (1977). (In Russian).
17. W. Baden, P. C. Schmidt and A. Weiss, *J. less-common Metals* **88**, 171 (1982).
18. A. C. Switendick, Topics in applied physics. In G. Alefeld and J. Völkl (eds), *Hydrogen in Metals I*, Vol. 28, p. 101. Springer, Berlin (1978).
19. J. Friedel, *Ber. Bunsenges. physik. Chem.* **76**, 828 (1972).