SUPERCONDUCTING PROPERTIES OF NIOBIUM-BASE ALLOYS

B. G. LAZAREV, O. N. OVCHARENKO, A. A. MATSAKOVA, and V. G. VOLOTSKAYA

Physico-technical Institute, Academy of Sciences, Ukrainian S.S.R.

Submitted September 30, 1967

Zh. Eksp. Teor. Fiz. **54**, 1031–1036 (April, 1968)

The superconducting characteristics T_c and H_{c2} of ternary niobium-zirconium-titanium and binary niobium-titanium alloys were measured in samples that had previously[1] been used in x-ray structure investigations. By varying the superconducting transition temperature T_c of the ternary alloys after annealing we obtained additional knowledge of these technically valuable alloys as two-phase systems. A concentration range (in the middle of the concentration triangle) exists for these ternary alloys such that their critical magnetic field $H_{c2} \sim$ 80 000 Oe does not vary significantly at 4.2°K.

TERNARY and binary alloys of niobium (niobium-zirconium-titanium, niobium-zirconium, and niobium-titanium) are technically valuable superconductors with high critical parameters (critical currents and critical magnetic fields).[2] We have previously performed electron-microscopic investigations of these alloys for the purpose of determining the nature of their high electric conductivity. The experiments showed that an enhanced critical current density in the alloys compared with the single-phase state results from a well-developed system of thin layers and filaments of a second, niobium-rich phase.[3]

In the present work the properties of the ternary and binary alloys are investigated further. To the x-ray structure studies[1] we have added measurements of T_c and H_{c2} in the same samples. These superconducting properties of niobium-zirconium-titanium and niobium-titanium were studied as functions of their composition in a single-phase state (cast) and in deformed states (rolled and drawn) before and after annealing.

1. SUPERCONDUCTING TRANSITION TEMPERATURE

Samples and measuring technique. The alloys were prepared in an argon atmosphere, using an arc furnace on a water-cooled hearth. The results of a chemical analysis of the alloys are given in a table. Samples ~20 mm long with rectangular cross sections of 0.5 to 1.5 mm^2 were cut from ingots. The current and potential contacts (pieces of platinum foil) were attached by spot welding; the instrument leads were soldered on the platinum with tin.

Both the single-phase (cast) and deformed samples were annealed in a 10^{-5} mm Hg vacuum produced by a carbon adsorption pump. Homogeneous alloys (Nos. 1–9) were annealed 24 hrs at 520°C and 120 hrs at 560°C. A rolled strip of the ternary alloy (No. 10) was annealed 3 hrs at 670°C. Wires (Nos. 11–15) were annealed 1 hr at 400°–500°C.

T_c was determined from the return of resistance at the transition from the superconducting to the normal state. The value of T_c was taken to be the temperature accompanied by half of the normal resistance. In the range 4.2°–12°K we used an intermediate-temperature cryostat (an inverted small Dewar in an outer Dewar containing liquid helium). The sample, a platinum thermometer, and a constantan heater were inserted into the inner Dewar. The thermometer and heater were wound around concentric copper tubes to equalize the helium gas temperature.

Superconducting transition temperature T_c, $(\partial H_{c2}/\partial T)_{T_c}$, and critical magnetic field H_{c2} at 4.2°K for niobium-zirconium-titanium and niobium-titanium alloys, in single-phase and deformed states before and after annealing

No. of alloy	Composition, at.%			T_c, °K			$(\partial H_{c2}/\partial T \times 10^3)_{T_c}$, Oe/deg			$H_{c2\perp}$, Oe	
				Single-phase alloy	After annealing		Single-phase alloy	After annealing		Single-phase alloy	After annealing at 560°C
	Nb	Zr	Ti		At 520°C	At 560°C		At 520°C	At 560°C		
1	75	10	15	9.7	—	—	14±2	—	—	57 000	—
2	65	20	15	9.8	—	9.7	14±2	—	16±2	65 000	—
3	62	24	14	9.6	—	—	17±2	—	—	69 000	—
4	52	32	16	9.4	—	9.5	17±2	—	17±2	71 000	72 000
5	47	5	48	8.7	—	8.7	30±4	—	34±4	89 000	=
6	48	22	30	8.9	9.1	9.0	23±4	28±4	31±4	78 000	80 000
7	43	30	27	8.6	9.0	9.1	28±4	28±4	24±4	75 000	77 000
8	41	44	15	8.7	—	9.3	29±4	—	28±4	77 000	76 000
9	35	50	15	8.6	9.2	9.3	26±4	23±4	26±4	79 000	77 000
10**	62	24	14	9.7**	9.6**	—	19±3**	19±3**	—	76 000**	—
11***	57	10	33	9.6***	—	—	14±2***	—	—	78 000***	—
12	53	18	29	9.1***	9.0***	—	24±4***	24±4***	—	81 000***	80 000***
13	41	23	36*	—	—	—	—	—	—	78 000***	77 000***
14	55	—	45	9.4***	—	—	27±4***	—	—	108 000***	—
15	40	—	60*	—	—	—	—	—	—	107 000***	—

*Composition of the original mixture.

**Rolled strip of cast alloy annealed at 670°C.

***Alloys Nos. 11–15 in the form of wires annealed at 400° – 500°C.

The resistances of the platinum thermometer and the test samples were measured with a potentiometer. The transition-temperature differential of the samples, measured simultaneously in two samples (in the single-phase state and following the anneal) was determined with ±0.05-deg accuracy.

The superconducting transition temperature was measured in a transverse 8000 ± 500 Oe field and also in the absence of the field. We calculated $(\partial H_{c2}/\partial T)_{T_c}$ from the shift of the transition curve in the magnetic field.

Results and discussion. The x-ray structure analysis[1,4] had shown that we initially had single-phase ternary alloys with a body-centered cubic structure (β-phase). The small circles in the concentration triangle of Fig. 1 denote the compositions of the single-phase niobium-zirconium-titanium alloys. The equal critical-temperature curves are labeled with the respective values of T_c. On the sides of the triangle the values of T_c pertain to niobium-zirconium and niobium-titanium alloys.[5]

The figure shows that for ternary alloys in the niobium corner of the concentration triangle (above 50 at.% niobium) T_c is higher than for pure niobium.[6] As the niobium content is reduced (below 50 at.%) the value of T_c decreases independently of the zirconium or titanium content. Dual behavior of the ternary alloys following anneal was observed as a function of composition: Following the anneal T_c either remains unchanged (within error limits) or rises. Constancy of T_c was observed in ternary alloys close to the side of niobium-titanium alloys with 10 at.% and 50 at.% zirconium (Nos. 1 and 5), and also in alloys containing 20–32 at.% zirconium and ~15 at.% titanium (Nos. 2–4).

Figure 2 shows the superconducting transition curves for alloy No. 4, which following the anneal exhibited no change in either the behavior of the transition curve or in its critical temperature.

For the ternary alloys located in the middle of the concentration triangle (Nos. 6–9), the character of the superconducting transition changes following the anneal; a step appears on the curve—the transition begins at the same temperature as in the single-phase sample but terminates at a higher temperature. With further annealing of the same sample the step disappears and the transition to the normal state occurs at a higher temperature than for the single-phase sample. The appearance of the step denotes the existence of two superconducting phases associated with different values of T_c. This is illustrated in Fig. 3, which shows the transition curves of alloy No. 9: in its single-phase state with $T_c = 8.6°K$; represented by the stepped curve after an intermediate anneal; and also after the final anneal with $T_c = 9.3°K$.

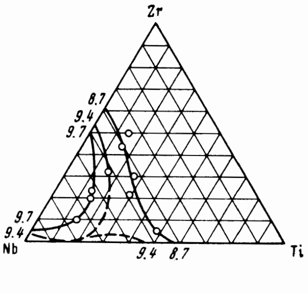

FIG. 1. Equal-temperature curves of the superconducting transition temperature T_c for single-phase ternary niobium-zirconium-titanium alloys (Nos. 1–9).

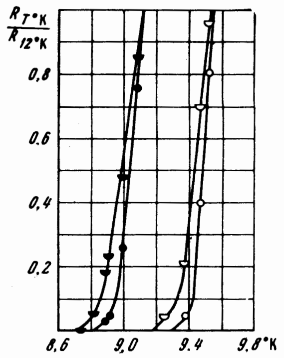

FIG. 2. Curves of the superconducting transition for samples of alloy No. 4: semicircles - single-phase state; circles - after annealing at 560°C. Open symbols - superconducting transition in the absence of the magnetic field; filled symbols - in the magnetic field.

The measured values of T_c for our alloys are given in the table. The higher critical temperatures following annealing result from the precipitation of a new phase and confirm the x-ray structure and electron microscopic investigations.

For some of the alloys the x-ray structure investigations revealed the precipitation of equilibrium phases following an anneal with no change of T_c, probably because the values of T_c are close in the two phases (Nos. 2 and 3). For No. 10 (ternary) and No. 15 (binary) T_c remains unchanged, within error limits, following deformation; following an anneal T_c is lowered ~0.1 deg by the removal of strains.

2. CRITICAL MAGNETIC FIELDS

The table gives values of $(\partial H_{c2}/\partial T)_{T_c}$ for the test alloys. We can infer therefrom the values of H_{c2} and its dependence on the concentrations of the components. Since precise values of the two quantities are required, measurements were performed in pulsed magnetic fields; the samples were those for which T_c had been determined. Values of H_{c2} obtained in this way are also given in the table.

Measurement technique. For our pulsed technique we used the method developed by Borovik and Limar'[7] to produce magnetic fields of long duration. A multilayer solenoid was wound on a textolite frame; the enamel-insulated copper wire was of 1.75-mm diameter. The inside and outside diameters of the solenoid were 5.27 and 21 cm, respectively; its height was 210 cm; there were 3240 turns. Each layer of the copper winding was covered with a layer of "steklonit" ~0.1 mm

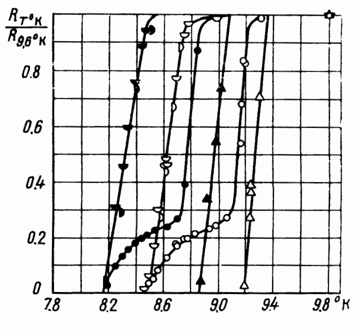

FIG. 3. Curves of the superconducting transition for samples of alloy No. 9: horizontal and vertical semicircles (two separate series of measurements) - single-phase state; circles - after annealing at 520°C; triangles - after annealing at 560°C. Open symbols - superconducting transition in the absence of the magnetic field; filled symbols - in the magnetic field.

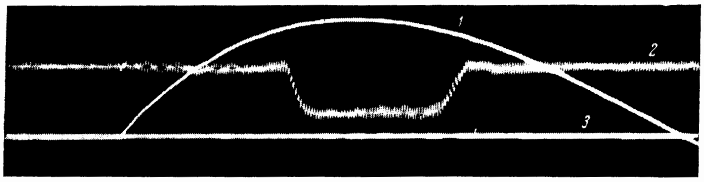

FIG. 4. Oscillograms of (1) the magnetic field pulse, and (2) of the potential difference for single-phase ternary alloy No. 5; (3) zero level of magnetic field pulse.

thick; this was followed by saturation with BF-2 (bakelite) cement and heating for three hours at 150°C. It was shown experimentally that a solenoid prepared in this manner is very strong and long-lived. Our experiments required more than 500 pulses. The rise time of the magnetic field to its maximum was 0.15 sec. The magnetic field H (in Oersteds) within the solenoid was determined from the current I (in amperes):

$$H = cI,$$

where c is the solenoid constant, 134 Oe/A, measured ballistically. The current through the solenoid was determined from the voltage drop, across a known resistance inserted in series in the solenoid circuit.

Our measurements showed that at a distance of ±3 cm from the center of the solenoid the magnetic field homogeneity was 3%. The dimensions of the samples allowed them to fit into a region of the field with better than 3% homogeneity; they were placed into a Dewar containing liquid helium and were oriented either perpendicular to or parallel to the magnetic field. The solenoid was cooled and operated at 20.4°K, the temperature of boiling liquid hydrogen. The current was supplied by a battery of condensers with 1.92 $\times 10^{-2}$ F capacity and a 5-kV maximum.

H_{c2} was the field at which the resistance of a sample was completely restored. The measuring current through the samples was 50–500 mA [(1–10) $\times 10^2$ A/cm^2 density]. The potential drops across the sample and the known resistance in the solenoid circuit were transmitted to a loop oscillograph. The maximum error of the critical field measurements was 2%.

Experimental results and discussion. Figure 4 shows one magnetic pulse oscillogram (1), and a voltage oscillogram recorded when the superconductivity of a sample was destroyed by the magnetic field (2), along with the zero reference line of the magnetic pulse (3). The maximum magnetic field for this pulse was 91 000 Oe; superconductivity was destroyed (resistance was completely restored) at 89 000 Oe.

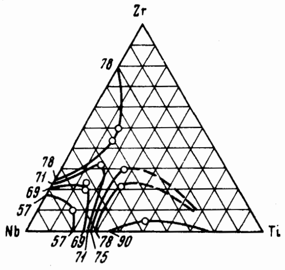

FIG. 5. Curves of equal critical magnetic fields H_{c2} at 4.2°K for single-phase niobium-zirconium-titanium alloys (Nos. 1–9).

The concentration triangle in Fig. 5 shows the curves of equal critical magnetic fields. The open circles indicate the compositions of the alloys in the single-phase state.

Our results show that the maximum critical magnetic fields of niobium-zirconium-titanium alloys are below those of the binary niobium-zirconium and niobium-titanium alloys.[2] The ternary alloys are characterized by a broad range of concentrations for which H_{c2} at 4.2°K varies only insignificantly at ~80 000 Oe; this occurs in the middle of the concentration triangle (25–50 at.% zirconium, 15–30 at.% titanium). This result is, of course, very important for the practical utilization of these alloys.

It should be noted that H_{c2} was determined in our experiments at quite high densities of the measuring current. For example, the critical field of alloy No. 12 was 78 000 Oe when measured with a current density of 1000 A/cm^2 (measuring current 500 mA, d = 0.25 mm). This field increased to 81 000 Oe when the current density was reduced to 100 A/cm^2 (current 50 mA). Further elevation of H_{c2} will obviously accompany further reduction of the current density.[1)]

Following the annealing of the samples H_{c2} remains invariant within error limits (as seen in the table). However, strong deformation somewhat elevates H_{c2} above the level for the initial single-phase state. For example, in the case of alloy No. 10, which was rolled to a thickness of 0.04 mm, H_{c2} = 76 000 Oe; for No. 3, with the same composition as No. 10 and in its initial state, we obtained 69 000 Oe.

It is known that no great difference exists between the longitudinal and transverse critical magnetic fields of alloys. For example, in the case of our No. 6 we have $H_{\parallel}$ = 82 000 and $H_{\perp}$ = 78 000 Oe.

H_{c2} rises considerably at lower temperatures. For a wire of the ternary alloy that is close to the investigated optimum composition (at the middle of the concentration triangle), when the temperature is reduced from 4.2° to 1.8°K the critical field rises from 78 000 to 99 000 Oe. By using this wire we were able to obtain a magnetic field of 87 000 Oe in the solenoid at 1.8°K.[8]

We should also note that for the binary niobium alloys (having ~50 at.% titanium or zirconium) the critical magnetic field exceeds 10^5 Oe at 4.2°K, but this is reduced by ~20 000 Oe when a third component is added to the alloy, as in No. 5. This effect agrees with results reported by Japanese investigators at the Tenth Low Temperature Conference.[9]

[1)] We shall not discuss here the measurements of critical magnetic fields using minimal current densities.

---

[1] V. S. Kogan, B. G. Lazarev, and L. F. Yakimenko, Zh. Eksp. Teor. Fiz. 51, 1327 (1966) [Sov. Phys.-JETP **24**, 895 (1967)].

[2] C. K. Jones, J. K. Hulm, and B. S. Chandrasekhar, Revs. Mod. Phys. **36**, 74 (1964).

[3] B. G. Lazarev, V. K. Khorenko, L. A. Kornienko, A. I. Krivko, A. A. Matsakova, and O. N. Ovcharenko, Zh. Eksp. Teor. Fiz. **45**, 2068 (1963) [Sov. Phys.-JETP **18**, 1417 (1964)].

[4] N. E. Alekseevskiĭ, O. S. Ivanov, I. I. Raevskiĭ, and N. V. Stepanov, Fiz. Met. Metallogr. **23**, 28 (1967).

[5] J. K. Hulm and R. D. Blaugher, Phys. Rev. **123**, 1569 (1961).

[6] T. McConville and B. Serin, Revs. Mod. Phys. **36**, 112 (1964).

[7] E. S. Borovik and A. G. Limar', Zh. Tekh. Fiz. **31**, 939 (1961) and **32**, 441 (1962) [Sov. Phys.-Tech. Phys. **6**, 683 (1962) and **7**, 321 (1962)].

[8] B. G. Lazarev, L. S. Lazareva, V. R. Golik, and Z. I. Goridov, Trudy Inst. Fiz. Met. AN SSSR, No. 26. Issledovanie v oblasti teoreticheskogo i prikladnogo magnetizma (Research in Theoretical and Applied Magnetism), 1967, p. 82.

[9] S. Maeda, T. Doi, and F. Ishida, Tenth International Conf. on Low Temperature Physics **2**, Sverkhprovodimost' (Superconductivity), VINITI (All-Union Inst. of Tech. and Sci. Information), 1967, p. 63.

Translated by I. Emin
119