X-RAY STRUCTURE INVESTIGATIONS OF SUPERCONDUCTING ALLOYS WITH NIOBIUM AS THE BASE

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Submitted to JETP editor June 8, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) **51**, 1327–1331 (November, 1966)

Several niobium–zirconium–titanium ternary alloys containing from 5 to 50 wt.% zirconium and 10–20 wt.% titanium are investigated. In the original cast state, all of the investigated alloys possess the structure of the hardened cubic phase. The samples were also investigated after vacuum annealing at 350–600° C. Concentration ranges in which two-phase regions exist, and the compositions corresponding to limiting solid solutions of zirconium in the β-solid niobium–titanium solution and of niobium in the β-solid zirconium–titanium solution, are established on the low-temperature (below 600° C) isothermal sections of the triple diagram. Some details of the kinetics of decay of supersaturated solid solutions during annealing are elucidated.

THE samples of the ternary molybdenum–zirconium–titanium alloy used for the x-ray structure investigations were cut from ingots obtained by melting the components in an arc furnace in an atmosphere of argon. According to the data on the charge from which the corresponding ingots were melted, the samples contained from 5 to 50% zirconium by weight.[2)] In view of the many changes in the composition of the ingot during its melting, and its inhomogeneous composition, a chemical analysis was made of the samples or of ingot material taken from the same section from which the samples were cut. Results of this analysis differed somewhat in many cases from the data on the composition of the initial charge.[3)]

X-ray structure analysis was used to determine the structure of the alloys both in the initial state and after annealing for 20–120 hours in a vacuum oven at 350, 450, 560, and 600° C. The samples were placed in a quartz tube and were annealed in a vacuum of 1×10^{-5} Torr. In the case of prolonged high-temperature annealing, the vacuum at the end of the annealing deteriorated to 1×10^{-3} Torr, owing to the release of hydrogen and inert gases from the samples; these gases could not be effectively pumped out by the adsorption pump with liquid nitrogen cooled adsorbent, which was used in this case. Thus, the samples were annealed either in a vacuum of 1×10^{-5} Torr, or in a rarefied atmosphere of hydrogen and inert gases.

The table shows the concentrations of the components in the samples as obtained from the chemical analysis, their phase composition in the initial state and after the annealing, and the corresponding lattice parameters calculated from the x-ray structure analysis.

As seen from the table (column 2), all the samples have in the initial state a body-centered cubic (bcc) structure, i.e., they consist of a quenched high-temperature β phase. Figure 1 shows the concentration triangle of the molybdenum–zirco-

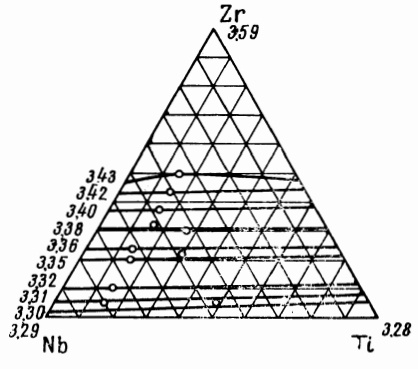

FIG. 1. Equal-parameter curves of bcc lattices of the β phase (in Å) for quenched ternary alloys niobium-zirconium-titanium. Data on the lattice parameters for binary alloys were taken from the literature [1-3].

[1)]E. Sokol took part in the work.

[2)]The ingots were graciously supplied by V. Ya. Solov'ev (Gidredmet), for which the authors are deeply grateful.

[3)]The authors thank E. M. Saenko (Physico-technical Institute, Ukrainian Academy of Sciences), for carrying out the chemical analysis.

Phase composition and lattice parameters of the phase in the ternary-alloy samples.

Sample number	Composition, at. %			Initial samples		Annealed samples							
						350° C		450° C		560° C		600° C	
	Nb	Zr	Ti	Phase	Lattice parameter a, Å	Phase	Lattice parameter a, Å	Phase	Lattice parameter a, Å	Phase	Lattice parameter a, Å	Phase	Lattice parameter a, Å
	1			2		3		4		5		6	
1	80	5	15	β (bcc)	3.310	—	—	—	—	—	—	—	—
2	47	5	48	β	3.302	β	3.300	β	3.302	β	$a = 3.300$	β	$a = 3.299$
3	75	10	15	β	3.326	β	3.324	β	3.322	β	$a = 3.324$	β	$a = 3.326$
4	65	20	15	β	3.346	β	3.347	β	3.348	β	$a = 3.348$	β	$a = 3.348$
										β′	$a = 3.314$	β′	$a = 3.312$
5	48	22	30	—	—	β	3.351	β	3.351	β	$a = 3.351$	β	$a = 3.352$
												β′	$a = 3.321$
6	62	24	14	β	3.361	—	—	—	—	—	—	—	—
7	43	30	27	β	3.375	—	—	s.s.l		β′	$a = 3.324$	β′	$a = 3.324$
												α	$a = 3.225$ $c = 5.224$ $c/a = 1.62$
8	52	32	16	β	3.386	β	3.386	s.l		β′	$a = 3.319$	β′	$a = 3.321$
										α	$a = 3.222$ $c = 5.187$ $c/a = 1.61$	α	$a = 3.223$ $c = 5.221$ $c/a = 1.62$
9	47	38	15	β	3.406	—	—	—	—	—	—	—	—
10	41	44	15	β	3.416	β	3.419	s.s.l.		β′	$a = 3.317$	β′	$a = 3.325$
										α	$a = 3.219$ $c = 5.182$ $c/a = 1.61$	α	$a = 3.226$ $c = 5.226$ $c/a = 1.62$
11	35	50	15	β	3.430	β	3.431	s.s.l.		β′	$a = 3.317$	β′	$a = 3.324$
										α	$a = 3.219$ $c = 5.182$ $c/a = 1.61$	α	$a = 3.220$ $c = 5.216$ $c/a = 1.62$

Note. s.s.l.—strong smearing of lines, s.l.—smearing of lines.

nium–titanium alloys, with the points marking the investigated samples. Using data on the parameters of bcc lattices of these samples and the known published data on the parameters of the lattices of binary niobium–zirconium,[1] molybdenum–titanium,[2] and zirconium–titanium alloys,[3] we drew in the triangle the lines corresponding to the compositions of the quenched ternary alloys with identical lattice parameters (the values of the parameters, in Å, are indicated along the molybdenum–zirconium cannode). The equal-parameter lines are approximately parallel to the molybdenum–titanium cannode, on which are located alloys with lattice parameters that vary little in the entire concentration interval. Figure 2 shows characteristic x-ray patterns of the samples in the initial state, from which we see that these samples are single-phase and that the bcc lattice parameter increases rapidly with increasing zirconium content.

For most investigated alloys, the β phase with the parameters given in column 2 of the table is non-equilibrium at room temperature, and annealing causes it to decay with separation of the hexagonal niobium-poor α phase, and of β'-phase grains which are richer in niobium than the initial alloy. Accordingly, the lattice parameter of such an equilibrium β' alloy is smaller than for the initial

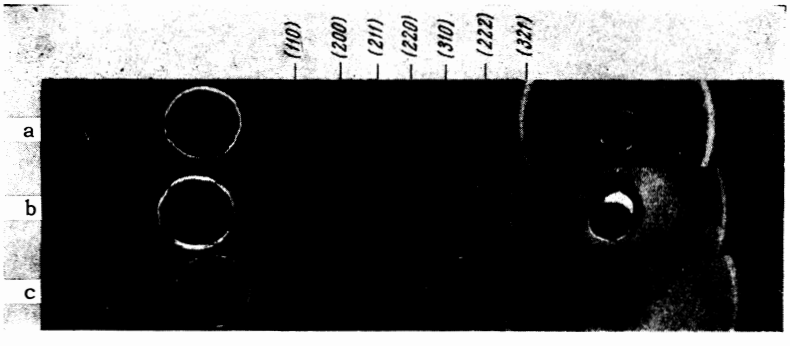

FIG. 2. X-ray patterns of samples of ternary alloys with identical titanium content (~15%) and different zirconium content (a–10%, b–50%, c–50%) in the initial (cast) state.

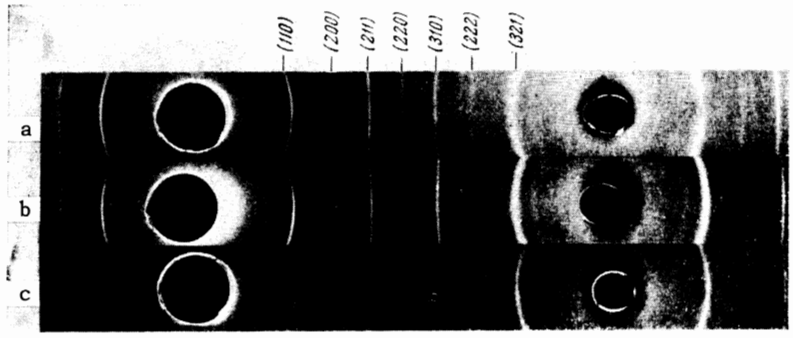

FIG. 3. X-ray patterns of a sample with 10% zirconium and 15% titanium in the initial state (a) and after annealling at 450°C (b) and 600° C(c).

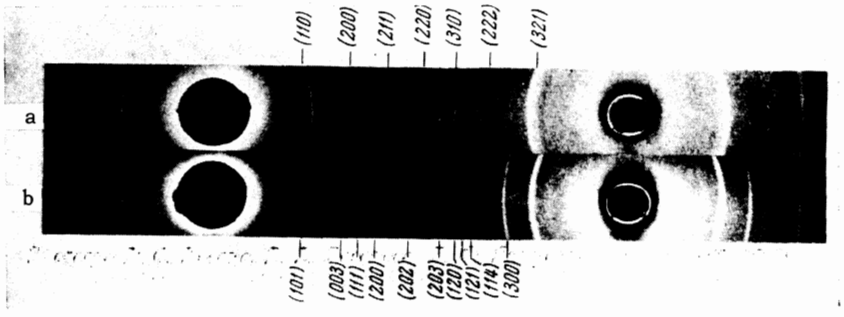

FIG. 4. X-ray patterns of samples of ternary alloys with identical content of titanium (15%) and different contents of zirconium (a–20%, b–50%) after annealing at 600°C.

ones. Only the investigated samples can be separated into three groups relative to the character of the variation of the structure upon annealing.

1. Samples 1–3, containing up to 10 at.% zirconium. Annealing of these samples does not cause a change in the structure; the β phase in them is in equilibrium in the entire investigated temperature interval. The indicated samples lie on the low-temperature isothermal section of the ternary state diagram in the single-phase region of existence of the β phase. Figure 3 shows x-ray patterns of sample No. 3 in the initial state and after annealing at 450 and 600° C.

2. Samples 4–6, containing approximately 20 at.% zirconium. Annealing of these samples at 550–600° C produces in them decay of the quenched β phase. Their composition is apparently such that on the isothermal section of the ternary diagram they are situated near the limit of existence of the β phase, although they are still in the two-phase region. Therefore only a small amount of β phase is precipitated in the decay, and is not registered in the x-ray patterns. Decay at the employed annealing times is not complete, and the x-ray patterns of the annealed samples contain both lines of the equilibrium β' phase with a smaller parameter than for the initial samples, and lines of the quenched nonequilibrium β phase, with the same parameter as in the initial samples. The x-ray pattern of sample No. 4 annealed at 600° C.

3. Samples 7–11, containing 30 at.% zirconium and more. Decay of the quenched β phase begins in this sample even as a result of annealing at 450° C, and is manifest in the corresponding x-ray patterns by a strong smearing of the β-phase lines. Annealing at 560° C leads to the appearance of equilibrium β' and α phases in the samples. The x-ray patterns of such samples show clearly two systems of lines—the lines of the equilibrium β' phase with a lattice parameter smaller than that of the initial samples, and the lines of the β phase, which are the more intense the larger the content of zirconium in the sample. Figure 4 shows an x-ray pattern of sample 11 annealed at 600° C.

Comparison of the foregoing results of the x-ray structure investigations of the ternary alloys of the niobium–zirconium–titanium system with different compositions allows us to express an opinion concerning the contours of the low-temperature (below 600° C) isothermal sections of the ternary diagram of state of this system, the high temperature region of which was investigated earlier.[4] The wide region of β-solid solutions adjacent to the niobium side in the binary niobium–titanium diagram[2] remains apparently the same when up to 10 at.% zirconium is dissolved in them. At large zirconium contents the equilibrium ternary alloys are two-phase at low temperatures. This two-phase region of the ternary diagram goes over into a broad two-phase region of the binary system niobium–zirconium[1] and into a two-phase section near the titanium corner of the binary nio-

bium–titanium diagram.[2] A continuous series of α-solid solutions of the zirconium–titanium system[3] remains only if the niobium is dissolved in them in negligible amounts.

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Translated by J. G. Adashko
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