RELATION BETWEEN THE SHAPE OF THE HOMOGENEITY REGION OF THE β-PHASE ON THE PHASE DIAGRAM OF THE NIOBIUM-TIN SYSTEM AND THE SUPERCONDUCTING PROPERTIES OF $\mathrm{Nb}_3\mathrm{Sn}$

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RELATION BETWEEN THE SHAPE OF THE HOMOGENEITY REGION OF THE β-PHASE ON THE PHASE DIAGRAM OF THE NIOBIUM-TIN SYSTEM AND THE SUPERCONDUCTING PROPERTIES OF Nb_3Sn

The increased interest in the Nb–Sn system and in the compound Nb_3Sn arose after Matthias and his co-workers first showed that the compound Nb_3Sn, having a crystal structure of the β-tungsten type (A 15), is the highest-temperature superconductor: $T_k = 18.05 \pm 0.1$°K, and Bozorth et al. found an unusually high value of the critical magnetic field for Nb_3Sn. This stimulated further investigations of Nb_3Sn as a promising material for superconducting solenoids.

In developing methods for obtaining wire from Nb_3Sn, it turned out that the superconducting properties of the wire depend substantially on the heat-treatment regime ([2–6]). When the annealing temperature is raised to 850–1000°, the critical temperature and critical current density increase sharply. With a further increase in the annealing temperature these parameters begin to decrease. The need to solve a number of technological problems connected with obtaining wire from Nb_3Sn led to the appearance of a number of works on constructing the phase-equilibrium diagram of the niobium–tin system ([4,7–16]). However, owing to serious difficulties hindering the preparation and investigation of equilibrium alloys, the data of different authors differ substantially, and to this day there is no unified opinion on the character of the Nb–Sn diagram. In particular, there are discrepancies with respect to the concentration and temperature intervals of stability of Nb_3Sn ([4,7–20]). It must be stated that the results of numerous recent investigations of phase equilibria in the niobium–tin system do not explain the deterioration of the superconducting properties when the heat-treatment temperature is raised above 900–1000°. In connection with this, in a number of recent works ([1,6,10,21]) attempts are made to explain the causes of the instability of the superconducting properties of Nb_3Sn on the basis of ideas about changes in dislocation density ([6]), changes in vacancy concentration ([21]), the phenomenon of disordering of atoms in the Nb_3Sn structure ([1]), etc.

Taking into account the substantial discrepancies regarding the concentration

Fig. 1. Dependence of the crystal-lattice parameter of Nb_3Sn on composition. *a*—700°, *b*—1000°, *v*—1400°, *g*—1800°

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and temperature intervals of stability of Nb_3Sn and the absence of a sufficiently clear and logical explanation of the instability of the superconducting properties of Nb_3Sn, we undertook the present investigation.

The starting materials for preparing the alloys were niobium rods of 99.6% purity and tin ingots of 99.9995% purity. Alloys with a tin content up to 40% were melted in an arc furnace with a tungsten electrode and a water-cooled copper hearth in an argon atmosphere, which was purified by melting a titanium–zirconium getter. The alloys were remelted up to 6 times, with the ingots being turned over, to ensure uniformity of composition. During melting, tin evaporated; therefore the final composition of the alloy differed from the initial one. The composition was checked by weighing the ingot obtained and by chemical analysis. The compositions of the alloys are given in Table 1. The cast alloys were annealed at temperatures of 700; 800; 1000; 1400; 1800°. To carry out anneals at 700; 800

and 1000° the specimens were sealed in evacuated and then argon-filled quartz ampoules; the annealing time at these temperatures was 100 h. After annealing, the specimens were quenched in water by breaking the ampoules. In addition, a specimen of an alloy of stoichiometric composition, Nb_3Sn, was annealed in a quartz ampoule at 750° for 350 h. Annealings at 1400 and 1800° were carried out in a -4 furnace in an argon atmosphere for 35 and 5 h, respectively. The specimens were then transferred to a quenching apparatus, again heated to the same temperature in an argon atmosphere, held for 15 min, and quenched in castor oil.

The principal method used in the investigations was X-ray structural analysis. As an additional method, microstructural analysis was employed. X-ray diffraction patterns were taken from rotating powder specimens in cylindrical cameras 142.8 and 57.3 mm in diameter, using unfiltered radiation from a chromium anode ($\lambda K_{\alpha 1} = 2.28962$ Å).

Polished sections for microanalysis were prepared mechanically. As an etchant, a mixture of hydrofluoric, nitric, and hydrochloric acids with water in the ratio $1:2:5:20$ was used.

Fig. 1. Dependence of the crystal-lattice parameter of Nb_3Sn on composition. *a*—700°, *b*—1000°, *v*—1400°, *g*—1800°.

X-ray structural analysis of alloys containing from 16.9 to 37.5% tin, annealed at 700, 800, and 1000° for 100 h, at 750° for 350 h, at 1400° for 35 h, and at 1800° for 5 h, showed that these alloys contain either exclusively or predominantly a phase with the crystal structure of the β-tungsten type (A 15), i.e., the Nb_3Sn phase. Thus, the conclusion made in works (9-11, 14) that Nb_3Sn is stable only above 775-860° is not confirmed.

Table 1

Specimen No.	Charge composition	Charge composition	Analysis composition	Analysis composition
	Sn, at. %	Sn, wt. %	Sn, at. %	Sn, wt. %
1	5	6.30	–	–
2	10	12.43	–	–
3	15	18.40	9.3	11.6
4	20	24.21	16.9	20.6
5	25	29.87	22.1	26.6
6	26	31.0	22.2	26.8
7	28	33.2	23.3	28.0
8	30	35.38	26.3	31.3
9	32	37.59	31.4	36.9
10	33.33	38.98	26.9	32.0
11	37.5	43.39	34.9	40.7
12	40	46.0	37.5	43.4

Microstructural and X-ray structural studies show that the compound Nb_3Sn has a concentration interval of homogeneity; moreover, preliminary X-ray patterns taken in the small camera (diameter 57.3 mm) showed that the crystal-lattice parameter of Nb_3Sn depends only weakly on composition. Precision measurements of the dependence of the lattice parameter of Nb_3Sn on composition were performed from X-ray diffraction patterns taken in a camera 142.8 mm in diameter. The (421) reflection was used. The glancing angle was about 83°. It was shown that the lattice parameter depends linearly on composition, increasing with increasing tin content (see Fig. 1). Measurements of the lattice parameter of the β-Nb_3Sn phase in alloys quenched after annealing at different temperatures made it possible to determine the solubility of tin and niobium in Nb_3Sn at 700, 1000, 1400, and 1800° and thus to construct the homogeneity region of the β phase (Fig. 2). It turned out that the solubility curve of niobium in Nb_3Sn is monotonic, whereas the solubility curve ⋯

of the solubility of tin in Nb_3Sn has an inflection at 900°. The maximum width of the β region is 18-19% at 900°. In the phase-equilibrium diagram presented in Fig. 2, the horizontal corresponding to the peritectic equilibrium $\alpha +$ β is drawn at 2130° according to the data of Refs. (13, 15); the liquidus line is shown according to the data of Ref. (15), and the solubility line of tin in niobium according to the data of Refs. (7, 11, 13).

The nonmonotonic temperature course of the solubility curve of tin in Nb_3Sn is apparently explained by the fact that at 900° the solubility curve intersects the

Figure 2-4

Figure 2: Figure 2-4

peritectic horizontal. Their point of intersection, with coordinates 32% tin and 900°, is a nonvariant point, and at this point the solubility curve undergoes a break.

Fig. 2. High-temperature portion of the phase diagram of the niobium-tin system

Fig. 3. Dependence of the superconducting-transition temperature of the Nb_3Sn compound on composition

Fig. 4. Theoretical dependence of the critical temperature of Nb_3Sn on annealing temperature

We shall assume that the characteristic shape of the solubility curve is the cause of the change in the superconducting properties of the Nb_3Sn phase when the annealing temperature is varied. From literature data (1, 15, 17, 18, 21) it is known that an increase in the tin concentration in Nb_3Sn leads to an increase in the critical current density and the critical temperature. However, from the results of Refs. (1, 15, 17, 18) it is not possible to construct a clear dependence of the critical temperature on the composition of the Nb_3Sn compound. There is a scatter of values, evidently associated with inhomogeneity of the specimens and inaccurate determination of the composition. In Ref. (21), the dependence of the critical temperature on composition was likewise not determined, but for each specimen the authors give the value of the critical temperature and the value of the lattice parameter.

a, Å	5.289_2	5.239_3	5.288_6	5.287_7	5.284_1	5.287_0	5.286_4	5.287_5	5.285_5	5.282_5
T_k, °K	17.1	17.1	17.5	16.5	6.9	14.3	15.4	15.4	10.8	8.2
a, Å	5.283_9	5.284_6	5.280_8	5.282_5	5.283_2	5.282_8	5.282_3	5.283_2	5.281_9	
T_k, °K	12.4	11.4	7.3	7.9	8.2	8.3	6.9	13.4	6.2	

Using the graph we constructed for the dependence of the lattice parameter on composition (Fig. 1), we determined, from the lattice parameter, the composition of each specimen from Ref. (21), and plotted the dependence of the critical temperature on composition (Fig. 3). An almost rectilinear dependence was obtained. Evidently, the critical temperature T_k for a diffusion layer of Nb_3Sn obtained at each specified annealing temperature is determined by the limiting concentration of tin in the β-Nb_3Sn phase at this temperature. Therefore, with the aid of the graph of the dependence of T_k on the concentration of tin (Fig. 3) and the solubility curve of tin in Nb_3Sn (Fig. 2), it is possible to construct a theoretical curve for the dependence of T_k on the temperature

annealing of wire made of Nb_3Sn. This curve is shown in Fig. 4. When the annealing temperature is increased to 900°C, the critical temperature rises sharply to 18°K, while at annealing temperatures above 900°C it begins to decrease gradually. Such a change in the critical temperature is indeed observed experimentally.

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REFERENCES

1. J. J. Hanak, G. D. Cody et al., *High Magnetic Fields*, N. Y.—London, 1962, p. 592.
2. F. Lange, *Monatsber. Deutsch. Akad. Wiss.*, **1**, 408 (1959).
3. E. Saur, P. Schult, *Zs. Phys.*, **167**, 170 (1962).
4. V. S. Kogan, A. I. Krivko et al., *Fiz. met. i metalloved.*, **15**, 143 (1963).
5. C. L. Kolbe, C. H. Rosner, "Metallurgy of Advanced Electronic Materials," **19**, N. Y., 1963, p. 17.
6. E. Buehler, J. H. Wernick et al., "Metallurgy of Advanced Electronic Materials," **19**, N. Y., 1963, p. 105.
7. M. I. Agafonova, V. V. Baron, E. M. Savitskii, *Izv. AN SSSR, OTN, Metallurgiya i toplivo*, No. 5, 139 (1959).
8. L. L. Wyman, J. R. Cuthill et al., *J. Res. Nat. Bur. Stand.*, **66A**, 351 (1962).
9. T. B. Reed, H. C. Gatos et al., *Superconductors*, N. Y., 1963, p. 143.
10. R. Enstrom, T. Courtney et al., "Metallurgy of Advanced Electronic Materials," **19**, N. Y., 1963, p. 121.
11. R. E. Enstrom, G. W. Pearsall, J. Wulff, *J. Metals*, **16**, 97 (1964).
12. H. W. Schadler, H. S. Rosenbaum, *J. Metals*, **16**, 97 (1964).

13. T. G. Ellis, H. A. Wilhelm, J. Less, *Comm. Metals*, **7**, 67 (1964).

14. H. J. Levinstein, E. Buehler, *Trans. Met. Soc. AIME*, **230**, 1314 (1964).

15. L. J. Vieland, *RCA Rev.*, **25**, 366 (1964).

16. F. J. Bachner, H. C. Gatos, M. D. Banus, *Trans. Am. Soc. AIME*, **233**, 227 (1965).

17. T. B. Reed, H. C. Gatos et al., "Metallurgy of Advanced Electronic Materials," **19**, 1963, p. 71.

18. J. J. Hanak, K. Strater, G. W. Cullen, *RCA Rev.*, **25**, 342 (1964).

19. R. G. Maier, G. Wilhelm, *Zs. Naturforsch.*, **19a**, 399 (1964).

20. H. G. Jansen, *Zs. Phys.*, **162**, 275 (1961).

21. T. H. Courtney, G. W. Pearsall, J. Wulff, *Trans. Met. Soc. AIME*, **233**, 212 (1965).

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