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PHASE DIAGRAM OF THE NIOBIUM-TIN SYSTEM

by

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14

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П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

PHASE DIAGRAM OF THE NIOBIUM-TIN SYSTEM

V. N. Svechnikov, V. M. Pan and Yu. I. Beletskiy

In the preceding [1], devoted to the phase diagram of Nb-Sn, we investigated the existing region of this system of β-phase with a crystalline lattice of β-W (A15) type and with a stoichiometrical compositions Nb_3Sn. It was shown that the β-Nb_3Sn phase is stable, apparently, completely to room temperature and has a wide range of homogeneity (nearly 18 atomic, %). The solubility of niobium in Nb_3Sn monotonically decreases with a rise in temperature, but the solubility of tin at first increases with an increase in temperature, attaining almost 32 atomic, % at 900°C, and then decreases. Since the critical temperature of transition in the superconducting state of the β-Nb_3Sn phase increases linearly with an increase in the concentration of tin, then, maximum $T_к$ can be obtained for the β-Nb_3Sn phase, containing nearly 32 atomic, % Sn, for example, in the diffusion layer produced after annealing at 900°C.[1]

From the survey of literature on the niobium-tin[2] system it appears that there are very significant contradictions in the determination of the form of phase diagram of the high-stannous part of the niobium-tin system. The results of new works [2, 3], which were not mentioned

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[1] Below it will be shown that this temperature, apparently, is nearly 960°.

[2] See article "On the Causes of Change in the Superconducting Properties of Nb_3Sn" on p. 100 of this collection.

in our survey of literature[1] also did not satisfy us. The conclusion [2] essentially repeat the conclusions of the well-known earlier work of Ellis and Wilhelm [4], although the compounds present are called differently: Nb_6Sn_5 and $NbSn_2$ instead of Nb_3Sn_2 and Nb_2Sn_3. In [3] Anantharaman proposes the formula, Nb_9Sn_7, for the compound, having, according to his data, a composition of 43-44 atomic % Sn and a tetragonal face-centered cell. However, an analysis of the literature shows that one should prefer the formula, Nb_6Sn_5 (45,45 atomic % Sn) for this compound and that the cell of this compound is the orthorhombic type of β-Ti_6Sn_5 with parameters a = 5.6549, b = 9.2057 and c = 16.814 Å (see [3] and the above-indicated survey of literature). As for the richest tin compound, one can already consider the conventional formula, $NbSn_2$ and the orthorhombic cell of the $CuMg_2$ type with parameters a = 5.6450, b = 9.8576 and c = 19.121 Å (see ibid).

The temperature ranges of the stability of these compounds, and consequently, the overall form of phase diagram equilibriums of the niobium-tin system have been the subject of controversy till now and have not been reliably studied.

In this work the aim was to construct a phase diagram of equilibriums of high-stannous (higher than 40 atomic weight Sn) part of a system tin-niobium and thereby to complete the investigation of this system we started.

Niobium in moldings (99.6% Nb) and tin in ingots (99.9995% Sn) served as source materials for the preparation of the alloys.

Alloys with a content of tin of 40% and more (see table) were prepared from a mixture of powder compounds, Nb_3Sn, melted down in an arc furnace and then ground in a mortar, and chipped of pure tin. This mixture was fused once in an arc furnace, as a result of which a compact ingot was obtained, in which the particles of Nb_3Sn are sufficiently evenly distributed in the tin. Then, for carrying out

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[1] See article "On the Causes of Change in the Superconducting Properties of Nb_3Sn" on p. 100 of this collection.

Composition of the investigated alloys.*

No. of the alloy	According to the charge, % Sn		According to analysis, % Sn	
	atomic	weight	atomic	weight
13	40	46,0	42,9	49,0
14	45	51,11	52,4	58,4
15	50	56,09	53,2	59,2
16	60	65,71	56,0	61,9
17	66,7	71,87	54,4	60,4
18	70	74,88	60,0	65,7
19	70	74,88	63,6	69,1
20	75	79,31	65,0	70,3
21	80	83,63	71,9	76,6
22	85	87,87	79,3	83,0
23	90	92,0	77,6	81,6

*A noticeable scattering of the parallel tests in the chemical analysis of certain alloys was observed. In these cases the average composition was conducted on five parallel tests.

the annealing, the obtained ingots were pressed into niobic glasses with threaded covers. The niobic glasses were placed in a double quartz ampule (evacuated, and then filled with argon). Annealing was conducted at 750°C over 700 hours; during annealing the ampule was continuously revolved with a speed of 2 r/min to prevent liquidation according to the specific gravity.

The basic methods of investigation – differential thermal analysis (construction of the installation is described in [5]) and X-ray diffraction analysis. Microstructural analysis was used as an additional method. X-ray photographs were taken of revolving powder samples in a cylindrical camera, 57.3 mm in diameter, using unfiltered radiation of chrome anode.

Results of investigation are presented in Fig. 1 in the form of a complete phase diagram of equilibriums of the niobium-tin system. Here the horizontal, corresponding to the peritectic equilibrium $\alpha + Ж. \rightleftarrows \beta$, is recorded at 2130°C according to [4, 6], the liquidus curve – according to [2, 6], the solubility curve of tin in niobium – according to [2, 4, 7, 8]. The region of homogeneity of the β phase

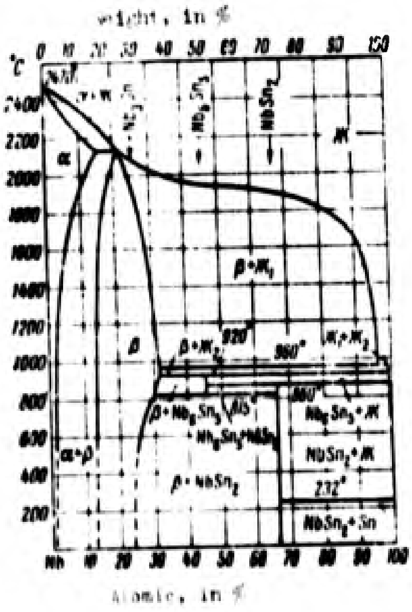

Fig. 1. Phase diagram of the equilibriums of the niobium-tin system.

on a base of Nb_3Sn compound with β-W structure is shown according to our preceding works.

Differential thermal analysis of alloys with a content of tin higher than 40 atomic %, annealed for 700 hours at 750°C, revealed during heating the clear thermal effects at temperatures of 815, 860, 920, and 960°C (see examples of thermograms in Fig. 2), where, if on the thermogram of the alloy with 42.9% Sn (Fig. 2a) there are two effects during heating - at 815 and 915°C, on the thermograms of the alloy with 65.0% Sn (Fig. 2d) there are also two effects - at 860 and 955°C, then, on the thermogram, for example, an alloy with 53.2% Sn (Fig. 2b) four effects are well expressed - at 820, 870, 920, and 970°C. The thermal effect of the melting of tin appears on the thermograms of heating only in alloys 71.9; 77.6; 79,3% Sn (see as an example, Fig. 2e); in alloys with a lower content of tin, such as an alloy with 65.0% Sn, this effect is lacking (Fig. 2d). Two thermal effects are observed in all alloys during cooling and repeated heatings: during cooling - there is a thermal effect at 790-860°C (the position of which generally depends, probably, on the rate of cooling) and there is an effect of the crystallization of tin at 180-200°C; during repeated heating - the effect of the melting of tin is at 230°C and effect is at nearly 860°C.

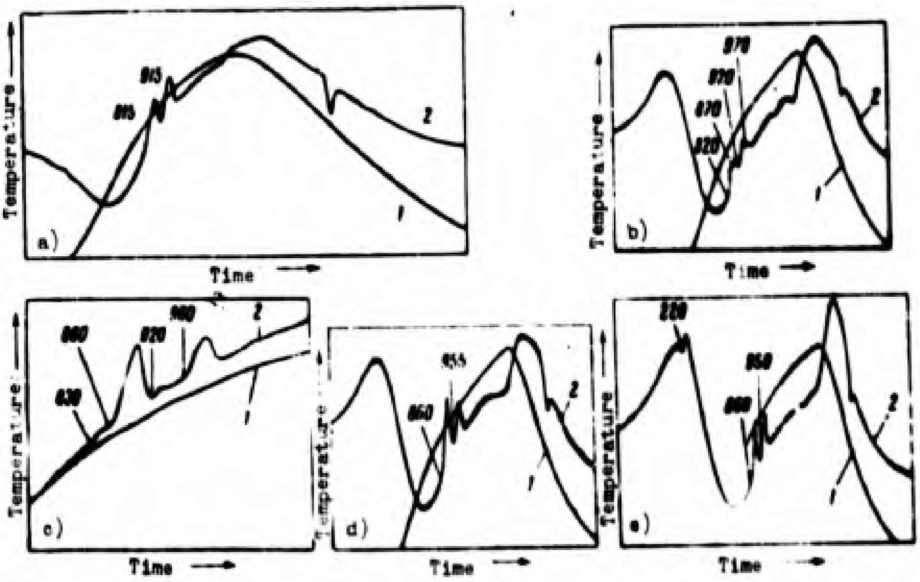

Fig. 2. Thermograms of alloys of the niobium-tin system. Content of tin, atomic %: a) 42.9; b) 53.2; c) 60.0; d) 65.0; e) 71.9. 1 – temperature of the sample. 2 – difference in the temperature of the sample and the standard.

For an explanation of the results of the thermal analysis an X-ray diffraction analysis of these alloys was conducted. X-ray photographs were taken after annealing at 750° over 700 hours. In all the alloys, X-ray diffraction analysis revealed a $NbSn_2$ phase. Free tin is disclosed only in alloys with 71.9, 77.6 and 79.3% Sn. The β-Nb_3Sn phase is disclosed in alloys with a content of tin up to 60.0%; at larger concentrations of tin (up to 65.0%) the β phase, obviously, is present in such quantities that X-ray analysis "does not sense" it. These results show that in niobium-tin alloys at 750°C in the equilibrium state only two intermediate phases exist: one of them – β-Nb_3Sn, consisting of a secondary intermediate compound corresponds to the formula, $NbSn_2$. This is confirmed by the data of X-ray and thermal analyses about the fact that tin is absent in an alloy with 65.0% Sn and is present in an alloy with 71.9% Sn, when these alloys are put in a state of equilibrium.

In order to clarify which type, by way of nonvariant equilibriums correspond to the structure, according to thermal analysis, horizontally at 815, 860, 920, and 960 (±10) °C, the quenching of alloys Nos. 13, 14, 15, 16, 18, 21 was conducted from temperatures of 790, 820, 860, 880, 930, and 1000°C. X-ray diffraction analysis of alloys Nos. 14 and 16, quenched from 790°C, showed only some increase in comparative intensity of lines of β-Nb_3Sn phase that indicates an increase in the solubility of the tin in Nb_3Sn at this temperature. In alloys Nos. 13, 14, 15, 16, quenched from 820, 860 and 880°, a new phase is revealed, apparently, an intermetallic compound, Nb_6Sn_5, which is found in equilibrium with β-Nb_3Sn (alloy No. 13), with $NbSn_2$ (alloys Nos. 14, 15, 16, quenched from 820 and 860°C) or with tin (alloy No. 16, quenched from 880°C). The compound $NbSn_2$ disappears in all alloys, quenched from a temperature of 880°C and higher. In alloys, quenched from 930 and 1000°C, only two phases were revealed: β-Nb_3Sn and tin.

On the basis of these data we can conclude that the horizontal at 815°C describes the eutectoid equilibrium $Nb_6Sn_5 \rightleftarrows \beta\text{-}Nb_3Sn + NbSn_2$; the horizontal at 860°C corresponds to the peritectic equilibrium $Nb_6Sn_5 + Ж \rightleftarrows NbSn_2$, the horizontal at 920°C corresponds to the peritectic equilibrium $\beta\text{-}Nb_3Sn + Ж \rightleftarrows Nb_6Sn_5$, and the horizontal at 960°C is of a geometric form of monotectic equilibrium $Ж_1 \rightleftarrows Ж_2 + \beta\text{-} Nb_3Sn$. The existence of monotectic equilibrium was assumed in [7]; however, the authors of all subsequent works rejected it in accord, base on the low solubility of niobium in liquid tin, on the experimentally determined form of the liquidus curve, etc. The data we obtained on the existence of some kind of nonvariant equilibrium at 960°C, characteristics by the fact that the phases, being found in equilibrium above and below this temperature, being the same, turned out to be plausible in explaining only the assumption that this equilibrium is monotectic. In order to tie this assumption with the data of other authors about the low solubility of niobium in liquid tin, and about the shape of the liquidus curve, it was necessary to consider that the dome of stratification of the liquid, $Ж_1 + Ж_2$, is very small (on the order of 2% in width, 30° in height) and is shifted almost up against the tin side of the diagram (see Fig. 1). The last assumption is confirmed by the fact that thermal effect of the monotectic reaction at 960°C on the thermograms of heating increases with an increase in the concentration of the tin in the alloy. Furthermore, for certain alloys (Nos. 12, 17, 19) the thermal analysis was conducted at sufficiently high temperatures (1500-1700°C); at this point, on the thermograms there were no effects above 960°C, and samples appeared to be only partially melted and not completely melted down.

In summarizing the experimental set of facts, we came to the conclusion that in alloys of the niobium-tin system in the equilibrium state, three intermediate phases exist: Nb_3Sn, Nb_6Sn_5 and $NbSn_2$, where Nb_3Sn and $NbSn_2$ are stable from the temperature of formation based on the peritectic reactions (accordingly, $\alpha + \text{Ж} \rightarrow \beta\text{-}Nb_3Sn$ at 2130°C and $Nb_6Sn_6 + \text{Ж} \rightarrow NbSn_2$ at 860°) to room temperature, but Nb_6Sn_5 exists only within the narrow range of temperatures: from 920°C – temperature of formation based on the peritectic reaction $\beta\text{-}Nb_3Sn + \text{Ж} \rightarrow Nb_6Sn_5$ up to 815°C – temperature of eutectoid disintegration, $Nb_6Sn_5 \rightarrow \beta\text{-}Nb_3Sn + NbSn_2$. At 960°C and with nearly 97% Sn monotectic equilibrium $\text{Ж}_1 \rightleftarrows \text{Ж}_2 + \beta\text{-}Nb_3Sn$ apparently occurs.

For cast alloys of niobium with tin, obviously, a diagram of the metastable equilibriums can be built; although the compounds of $NbSn_2$ and Nb_6Sn_5 are lacking, the monotectic reaction $\text{Ж}_1 \rightarrow \text{Ж}_2 + Nb_3Sn$ can be recorded. Actually, on the thermograms the heating of the cast alloys (i.e., heated above 960° and then cooled) is noted only by the thermal effect of the melting of tin to nearly 230°C and the thermal effect, at 850-860°C. Since X-ray analysis does not reveal alloys of other phases, besides Nb_3Sn and tin in castings (i.e., heated above 960°C) then we assumed that the effect at 850-860° corresponds to the monotectic reaction $Nb_3Sn + \text{Ж}_2' \rightarrow \text{Ж}_1'$. Obviously, in connection with the fact that equilibriums metastablely, in consisting of a monotectic alloy, the temperature of equilibrium for the stable diagram can also differ from the observed one. The diagram from [7], probably, is such a meta-stable diagram, where the temperature here of the monotectic reaction was obtained even still lower – at 730°C.

The nonmonotonic nature of the temperature march of the solubility curve of tin in Nb_3Sn is explained, thus, by the fact that 960° the solubility curve intersects with the monotectic horizontal, at 920° – with the peritectic horizontal and at 815°, with the eutectoid horizontal. At each of these three intersections the curve of solubility should have a break, and at one of the breaks the sign of solubility changes. Apparently, the sign of the change in solubility changes at the intersection of the monotectic horizontal at 960°C for an alloy containing nearly 32% Sn (see Fig. 1).

Conclusions

1. A full phase diagram of equilibriums of the niobium-tin system was constructed.

2. It was shown that besides Nb_3Sn in niobium-tin alloys, there are still two intermetallic compounds Nb_6Sn_5 and $NbSn_2$, but they will form only during prolonged annealing. The compound $NbSn_2$ can form according to the peritectic reaction $Nb_6Sn_5 + \text{Ж} \rightarrow NbSn_2$ at 860°C and stablely down to room temperatures. The compound Nb_6Sn_5 can form according to the peritectic reaction $\beta\text{-}Nb_3Sn + \text{Ж} \rightarrow Nb_6Sn_5$ at 920°C, stabely to 815°C and at this temperature, disintegrates according to the eutectoid reaction $Nb_6Sn_5 \rightarrow \beta\text{-}Nb_3Sn + NbSn_2$.

3. It is assumed that in niobium-tin alloys monotectic equilibrium $\text{Ж}_1 \rightleftarrows \text{Ж}_2 + \beta\text{-}Nb_3Sn$ takes place at 960°C. The monotectic point lies at nearly 97% Sn.

4. For niobium-tin cast alloys, where the compounds Nb_6Sn_5 and $NbSn_2$ are absent monotectic reaction $\text{Ж}_1 \rightarrow \text{Ж}_2 + \rightarrow Nb_3Sn$, does occur one can, apparently, build a diagram of the metastable equilibriums. In connection with the equilibrium, metastabely, as well as the temperature of the monotectic equilibrium and concentration, conforming to the monotectic point, can differ from that observed for the stable diagram. The metastable diagram is, probably, the niobium-tin diagram in [7].

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ABSTRACT

(U) The phase diagram of the high tin portion of the niobium-tin system was constructed. The temperature range of stability of the various intermetallic compounds was determined. Ten alloys were arc melted, cast, and annealed at 750 degrees centigrade for 700 hr. On the basis of x-ray, thermal and microstructural analysis, a phase diagram was constructed. Differential thermal curves are given, and the various temperature peaks are analyzed. Besides Nb(subscript 3)Sn, two other intermetallic compounds, Nb(subscript 6)Sn(subscript 5) and NbSn (subscript 2), exist in the niobium-tin system. However, they only form upon protracted annealing. For case niobium-tin alloys, in which the compounds Nb(subscript 6)and NbSn(subscript 2) are absent but in which the above monotectic occurs, a metastable equilibrium diagram can be constructed. In the metastable diagram, the equilibrium monotectic temperature and composition may differ from that obtained for a stable diagram. Apparently, the niobium-tin diagram obtained by Agafonov, et al (Izv. AN SSSR, OTN. Metallurgiya i Toplivo, 1959, No. 5, 139) is a metastable one. Orig. art. has: 2 figures, 1 table.