Contribution to the investigation of the Ti–Dy–Sn system

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A new ternary compound, $Ti_{4.2-4.3}Dy_{0.8-0.7}Sn_{\leqslant3}$ (τ), was found in the Ti–Dy–Sn system. It exists at an almost constant concentration of tin (~36.5 at.%), but has a certain homogeneity region (8.2 to 10.2 at.% Dy) due to mutual substitution of titanium and dysprosium. The crystal system was determined to be hexagonal with preliminary lattice parameters a = 4.94 Å, c = 5.65 Å. The compound melts congruently above 1500°C and coexists with (Ti_3Sn), (Dy_5Sn_3), (Ti_2Sn), and (Ti_5Sn_3).

Ternary compound / Crystal structure / Phase equilibrium

1. Introduction

In the course of our investigation of phase equilibria in the Ti–Dy–Sn system, X-ray diffraction, microstructure and microprobe data indicated the formation of a ternary compound in the vicinity of 37.5 at.% Sn. Literature data on the phase relations in the Ti–Dy–Sn system are absent. Our previous results [1,2] do not involve the concentration mentioned above. Consequently, the ternary compound reported here appears to be a new one.

The aim of the present research was the examination of the crystal structure of the new compound, and the determination of its chemical composition.

2. Experimental

The purity of the starting materials was Ti–99.85%, Dy–99.76%, Sn–99.9995%. The alloys were melted in an arc-furnace with an inconsumable tungsten electrode on a water-cooled copper hearth in an Ar atmosphere purified by a Ti-melt. To achieve homogeneity, the buttons were turned over and remelted three times. The weight losses did not exceed 0.3%, so the composition of the samples was taken according to the initial mixture. The weight of the ingots was ~5-10 g.

The samples were studied, in as-cast and annealed states, by X-ray diffraction, light optical and electron scanning microscopy (LOM and SEM, respectively), transmission electron microscopy (TEM), differential thermal analysis (DTA) and electron microprobe analysis (EPMA). The conditions for the heat treatment are given in Table 1.

X-Ray diffraction was performed by the powder method in a Debye camera (d = 57.3 mm, URS-2.0 device) and from the cross section in a DRON-3.0 device, both equipped with filtered Cu K_α radiation. The lattice parameters were refined by the least-squares method.

Examination of the microstructures and microprobe analysis were performed with a scanning electron microscope Jeol Superprobe-733 using back-scattered electrons. This regime allowed us to identify the phases by their average atomic weight, where light-weight phases appear dark-colored and heavy-weight phases light-colored [3].

DTA was performed in a VDTA-7-type device with a W/W-Re thermocouple in helium. The heating / cooling rate was ~40-80°C/min. Al_2O_3, ZrO_2 and Sc_2O_3 crucibles were used [4].

TEM examination was performed in a JEM-100CXII device. A double-axis goniometer made it possible to tilt the sample ±45° along two mutually perpendicular axes. The samples used for the investigation were mechanically powdered, and fine particles were extracted. Each particle represented a single crystal.

3. Results and discussion

During our examination of the Ti–Dy–Sn system it appeared that the X-ray diffraction patterns and microstructure data for the alloys with 27.5 to 37.5 at.% Sn could be interpreted only if the existence of a ternary compound was accepted. All the patterns contained a new system of reflections, which was more

Table 1 Phase compositions of as-cast and annealed Ti–Dy–Sn alloys and microprobe analysis of the ternary compound τ.

Alloy, at.%			Heat treatment	Phase composition	Chemical composition of τ, at.%		
Ti	Dy	Sn			Ti	Dy	Sn
65	5	30	1100°C, 30 h + 900°C, 32 h + 1400°C, 30 h	(Ti$_3$Sn)+τ	54.55	9.08	36.37
			1100 °C, 30 h	(Ti$_3$Sn)+τ	53.29	8.61	38.10[a]
					53.92	8.30	37.79[a]
62.5	5	32.5	as-cast	(Ti$_3$Sn)+eutectic ((Ti$_3$Sn)+τ)	55.03	9.87	36.00
					54.92	8.49	36.59
65	1.7	33.3	1100°C, 30 h	(Ti$_2$Sn)+τ +(Ti$_3$Sn)	53.24	8.17	38.59[a]
					53.32	8.40	38.28[a]
63	2	35	1400°C, 30 h	(Ti$_2$Sn)+τ	54.91	9.37	35.72
					53.73	9.56	36.71
					54.91	8.38	36.71
57.5	7.5	35	as-cast	τ+eutectic ((Ti$_3$Sn)+τ)	54.77	8.71	36.52
					53.86	9.63	36.52
					54.36	9.03	36.61
			1400°C, 30 h	(Ti$_3$Sn)+τ+(Ti$_2$Sn)	54.71	9.26	36.02
					54.09	9.57	36.34
55	10	35	as-cast	τ+(Ti$_3$Sn)+eutectic ((Ti$_3$Sn)+(Dy$_5$Sn$_3$))	54.31	9.71	35.98
					54.43	9.28	36.30
					53.45	10.03	36.52
			1400°C, 30 h	(Ti$_3$Sn)+τ+(Dy$_5$Sn$_3$)	53.81	9.49	36.70
					53.91	10.01	36.08
					54.30	9.88	35.82
					53.59	10.27	36.15
52.5	12.5	35	as-cast	τ+(Ti$_3$Sn)+eutectic ((Dy$_5$Sn$_3$)+?)	53.71	9.84	36.45
60.5	2	37.5	as-cast	τ+(Ti$_2$Sn)+(Ti$_5$Sn$_3$)	54.72	9.25	36.04
58.5	4	37.5	as-cast	τ+(Ti$_2$Sn)+(Ti$_5$Sn$_3$)+?	54.61	8.90	36.49
56.5	6	37.5	as-cast	(Ti$_2$Sn)+ τ+(Ti$_5$Sn$_3$)+?+eutectic (τ+(Ti$_2$Sn))	54.63	8.70	36.67
					55.30	8.56	36.15
					54.89	8.86	36.25
54.5	8	37.5	as-cast	τ+(Ti$_5$Sn$_3$)+?	54.16	9.39	36.45
					54.41	9.10	36.49
52.5	10	37.5	as-cast	τ+?	53.20	10.41	36.39
					53.94	9.49	36.57

[a] The content of tin is overestimated.

evident in the alloys along the isoconcentrate 37.5Sn. In the alloys Ti–(8-10)Dy–37.5Sn the reflections of the boundary binary phases were absent. In contrast, in the alloys Ti–(2-6)Dy–37.5Sn additional reflections from Ti$_5$Sn$_3$ were well indexed, showing, thus, Dy solubility in Ti$_5$Sn$_3$ of less than 2%. In the alloys Ti–(10-15)Dy–(32.5-35)Sn the new reflection system was observed together with weak reflections of (Ti$_3$Sn) and of (Dy$_5$Sn$_3$), and in the alloys Ti–(2-5)Dy–(32.5-35)Sn it coexisted with weak reflections of (Ti$_3$Sn) and with well indexed reflections of (Ti$_2$Sn). The chemical compositions of the alloys containing the new reflection system are shown in the partial solidus surface and in the isothermal section at 1400°C, Fig. 1. The phase compositions of the studied alloys are given in Table 1. A partial X-ray diffraction pattern

of the as-cast 52.5Ti–10Dy–37.5Sn sample, containing only the new reflection system, is shown in Fig. 2. The almost single-phase microstructure of this sample, as-cast and annealed at 1400°C for 30 h, is shown in Fig. 3a,b. Attempts to index these reflections in the structure types Mn$_5$Si$_3$, W$_5$Si$_3$ or Cr$_5$B$_3$, typical for 5/3 compositions, failed. These results led us to the conclusion that a new ternary compound τ, containing about 37.5 at.% Sn, exists and its chemical composition can be written as (Ti,Dy)$_5$Sn$_3$.

The single crystal particles extracted from the as-cast alloys 54.5Ti-12.5Dy-35Sn and 52.5Ti-10Dy-37.5Sn were studied by electron diffraction to examine the crystal structure of the τ compound. A typical view of the studied particles is shown in Fig. 4. The crystals were tilted with the help of a goniometer
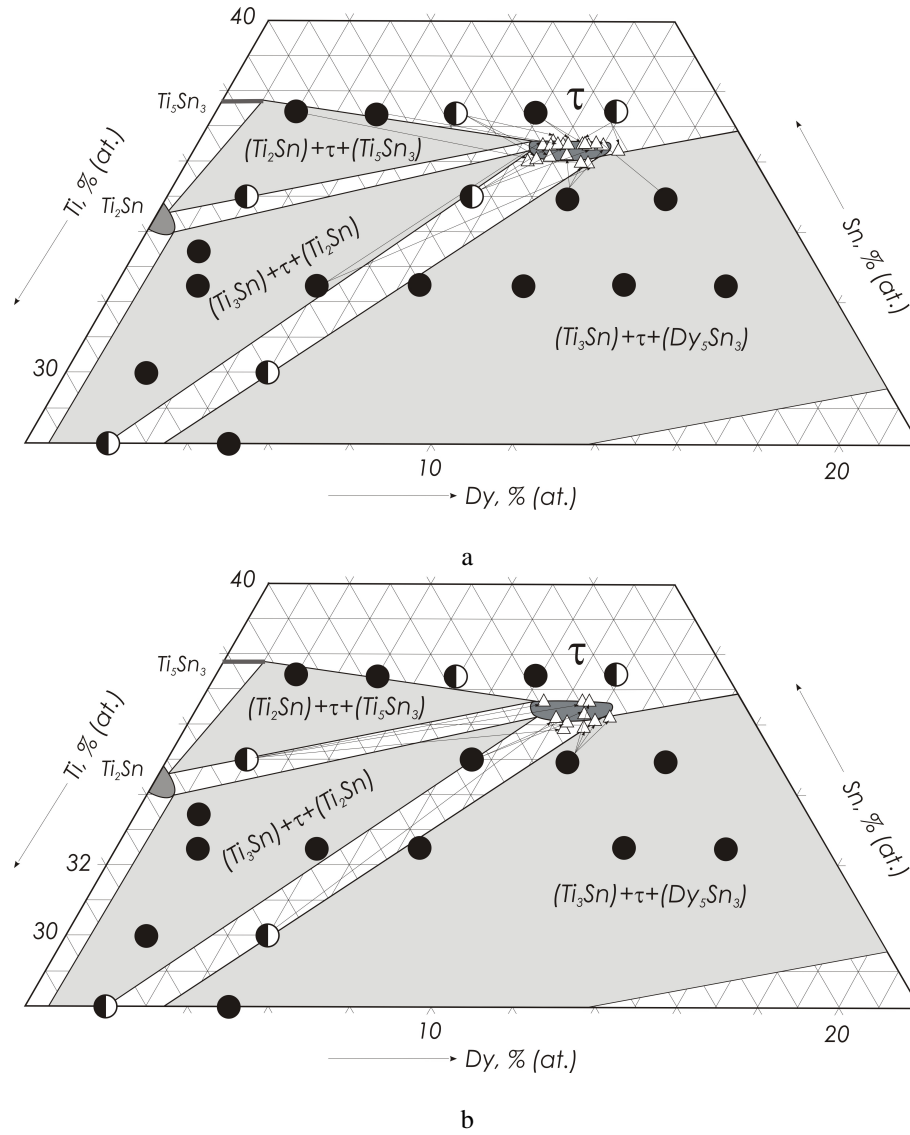
Fig. 1 Partial solidus surface (a) and isothermal section at 1400°C (b) of the Ti–Dy–Sn system in the vicinity of the ternary compound τ based on results of this work: ◐ – two-phase sample, ● – three-phase sample, △ – EPMA data, the arrows indicate the composition of τ in the alloys.
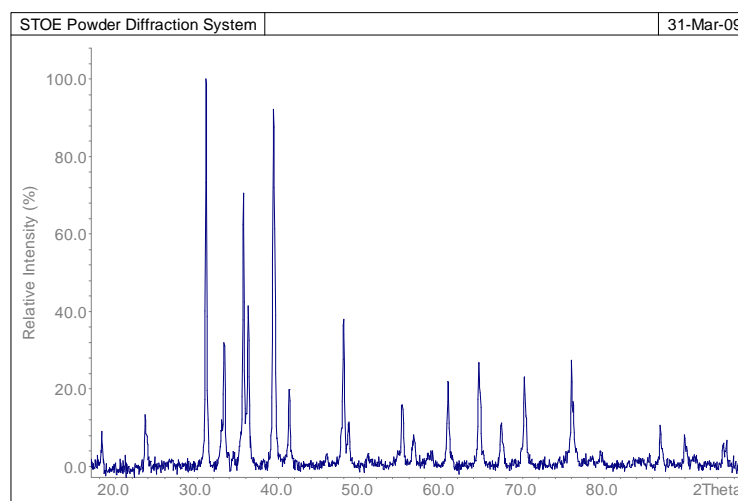

Fig. 2 Reflection system of the τ compound in a partial X-ray diffraction pattern of the as-cast 52.5Ti–10Dy–37.5Sn alloy.
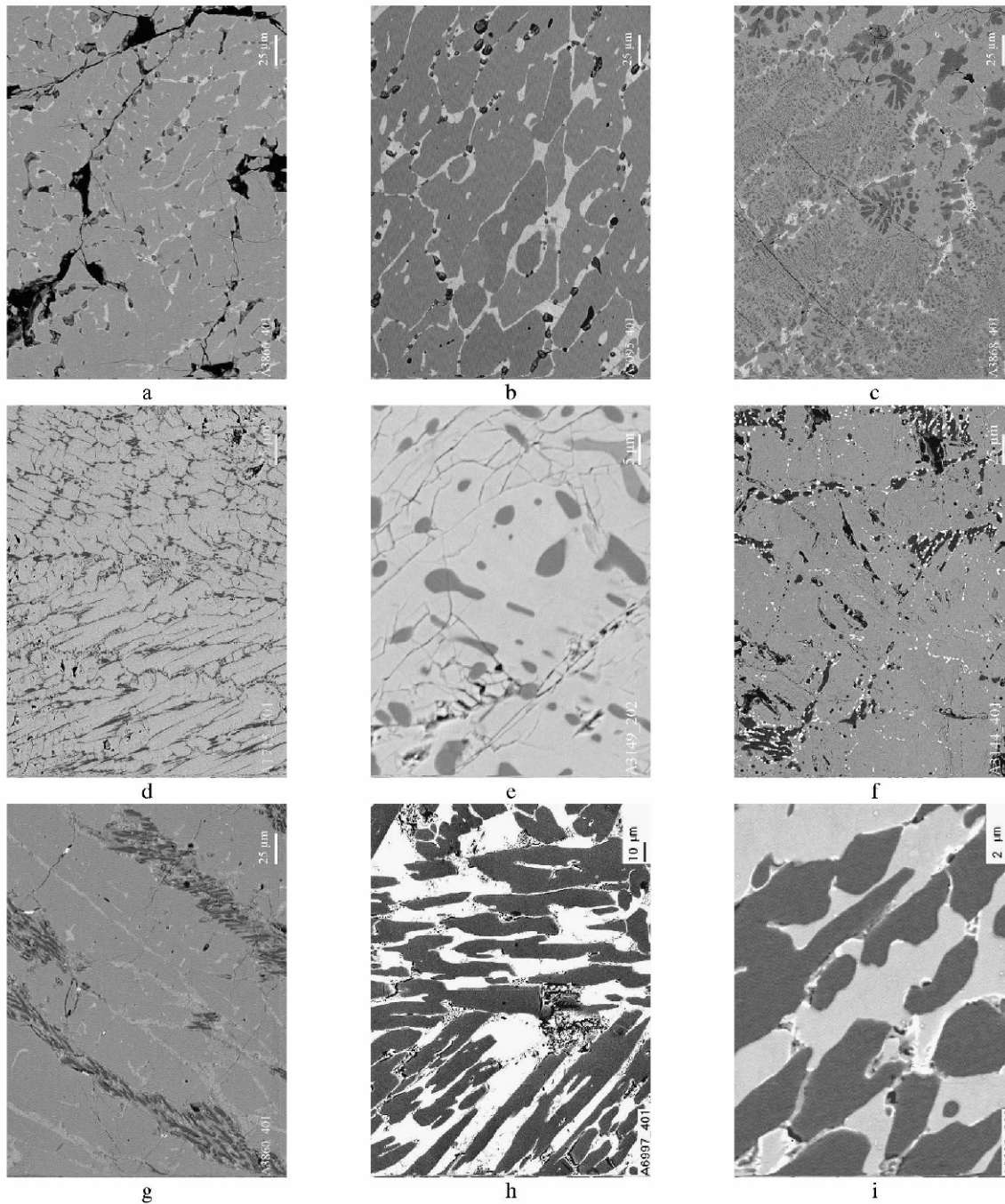
Fig. 3 Microstructure of Ti–Dy–Sn alloys: a) 52.5Ti–10Dy–37.5Sn, as-cast, ×400, τ+?; b) 52.5Ti–10Dy–37.5Sn, 1400°C 30 h, ×400, τ+?; c) 56.5Ti–6Dy–37.5Sn, as-cast, ×400, (Ti_2Sn)+τ+(Ti_5Sn_3)+?+eutectic $((Ti_2Sn)$+$\tau)$; d) 57.5Ti–7.5Dy–35Sn, as-cast, ×400, τ+eutectic $((Ti_3Sn)$+$\tau)$; e) 57.5Ti–7.5Dy–35Sn, 1400°C 30 h, ×2000, τ+(Ti_3Sn)+(Ti_2Sn); f) 55Ti–10Dy–35Sn, 1400°C 30 h, ×400, τ+(Ti_3Sn)+(Dy_5Sn_3); g) 52.5Ti–12.5Dy–35Sn, as-cast, ×400, τ+(Ti_3Sn)+eutectic $((Dy_5Sn_3)$+?); h) 65Ti–5Dy–30Sn, 1100°C 30 h, ×400, τ+(Ti_3Sn); i) 65Ti–5Dy–30Sn, 1100°C 30 h + 900°C 32 h, ×2000, τ+(Ti_3Sn)+(Dy_5Sn_3).
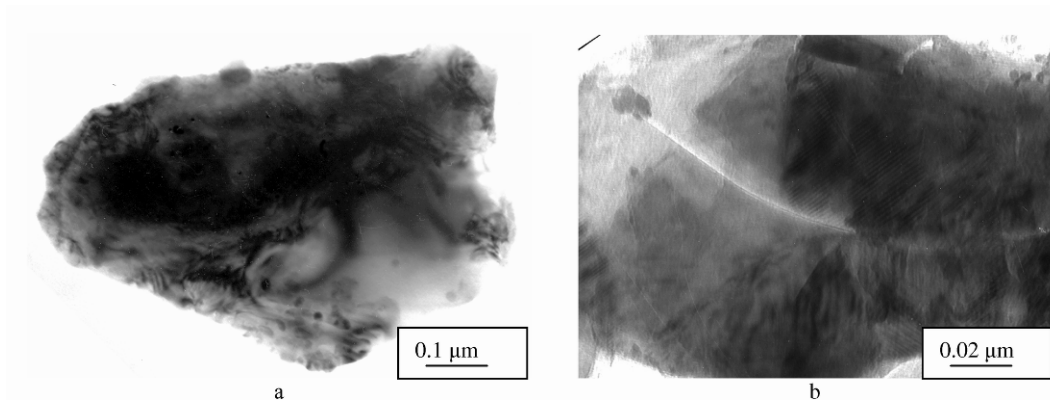
Fig. 4 Typical view of a particle extracted from the as-cast 52.5Ti–10Dy–37.5Sn alloy for TEM examinations: a) ×100000, b) ×400000.
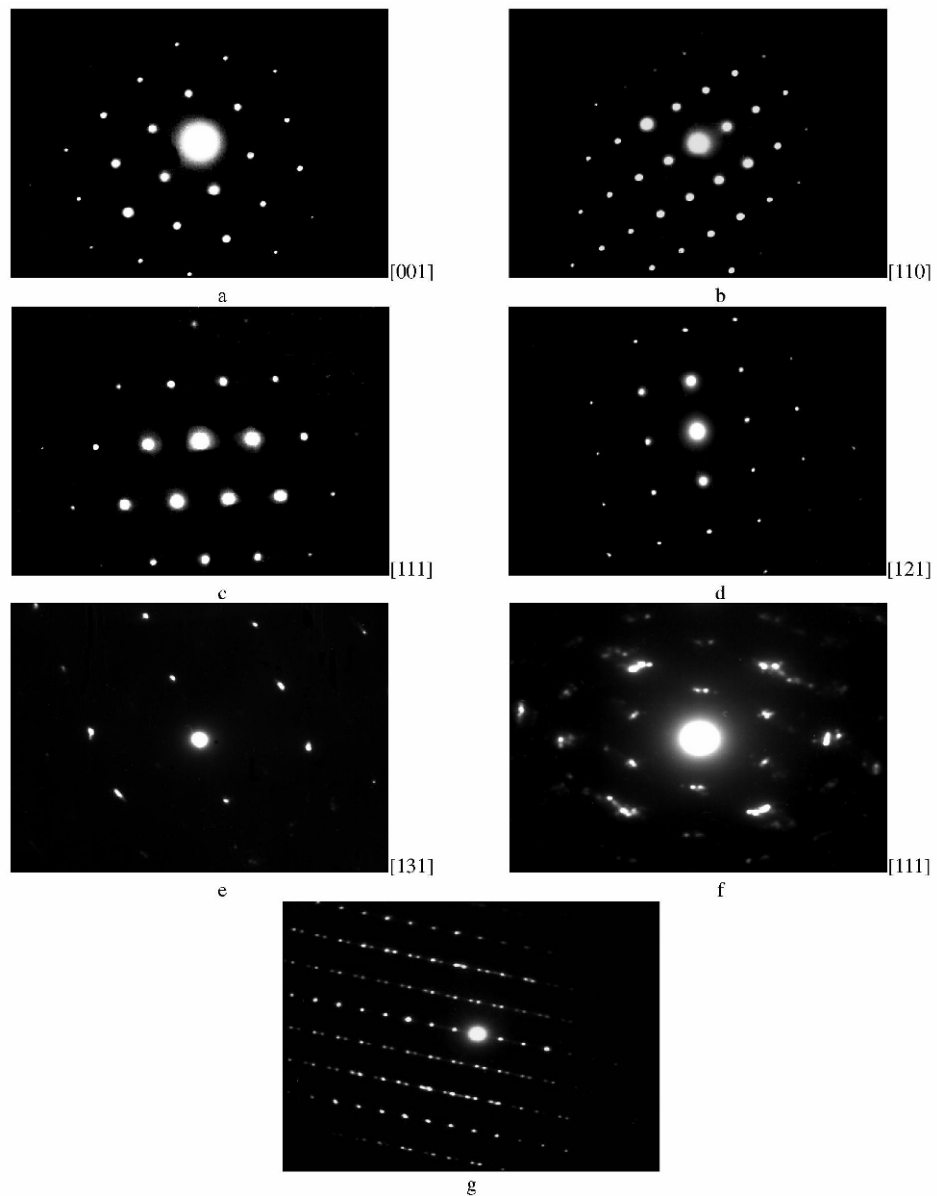

Fig. 5 Electron diffraction patterns in as-cast 52.5Ti–10Dy–37.5Sn sample from the atomic planes: a) (001), b) (110), c, f) (111), d) (121), e) (131), g) not determined.

to obtain electron diffraction patterns from the planes with minimum deviation from the primary beam. Thus, a few electron diffraction patterns of different orientations were obtained from each extracted crystal, Fig. 5a-d. Analysis of the patterns allowed us to establish the hexagonal system for the τ compound. The lattice parameters were determined as $a = 4.94$ Å, $c = 5.65$ Å.

It should be noticed that most of the studied particles revealed a layer-like structure, resulted both in moiré fringes in the images, Fig. 4b, and in double reflections of electron diffraction, Fig. 5e, f. Some of the electron diffraction patterns show reflections corresponding to twin orientations of neighboring crystals. This makes us believe that the structure is probably more complex consisting of clusters. The lattice parameters determined here should thus be considered as preliminary and a more precise examination of the space group and determination of the atomic positions by X-ray diffraction is necessary. The crystal structure is under investigation at present.

The chemical composition of the new compound was determined by EPMA, the results are given in Table 1, and Fig. 1. A number of representative microstructures are shown in Fig. 3. At the solidus temperatures the ternary compound was found to contain 36.5 at. % Sn, rather than 37.5 at.% Sn, as we supposed previously. The compound has a homogeneity range, with limits corresponding to 8.2 and 10.2 at.% Dy, formed by mutual substitution of Ti and Dy atoms. Consequently, the composition of the compound can be written as $Ti_{4.2-4.3}Dy_{0.8-0.7}Sn_{\leqslant 3}$. A decrease of the temperature down to 1400°C does not significantly change the width of the homogeneity range. The compound was observed also in alloys annealed at 1100 and 900°C.

According to the results of the microstructure analysis, the compound melts congruently. The

melting temperature determined by DTA is above 1500°C. The τ compound is in equilibrium with (Ti_3Sn), (Dy_5Sn_3), (Ti_2Sn), and (Ti_5Sn_3), as shown in Fig. 1.

4. Conclusions

1. A new ternary compound τ ($Ti_{4.2-4.3}Dy_{0.8-0.7}Sn_{\leqslant 3}$) was found in the Ti–Dy–Sn system. The compound exists at an almost constant concentration of tin of about 36.5 at.%, and has a homogeneity range along this isoconcentrate. The compound melts congruently above 1500°C.

2. The hexagonal translation lattice of the τ compound was determined by the TEM method. The preliminary lattice parameters are: $a = 4.94$ Å, $c = 5.65$ Å.

3. At the solidus temperatures and at 1400°C the τ compound was shown to be in equilibrium with (Ti_3Sn), (Dy_5Sn_3), (Ti_2Sn), and (Ti_5Sn_3).

References

[1] M.V. Bulanova, Yu.N. Podrezov, Yu.V. Fartushnaya, R.A. Danilyuk, K.A. Meleshevich, *Teor. Prakt. Metallurg.* 4-5 (2006) 4-6.

[2] M.V. Bulanova, Yu.N. Podrezov, Yu.V. Fartushnaya, A.N. Rafal, S.A. Firstov. *Dopov. Nats. Akad. Nauk Ukr.* 6 (2007) 95-104.

[3] E.V. Panchenko, Yu.A. Skakov, B.I. Krimer, P.P. Arsentiev, K.V. Popov, M.Ya. Tsviling. *Laboratoriya Metallografii*, Metallurgia, Moscow, 1965, 439 p.

[4] Yu.A. Kocherjinsky, N.A. Bezshtan'ko, V.I. Vasilenko, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* 4(9) (1974) 32-35.