Journal of Alloys and Compounds 673 (2016) 433–440

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Phase equilibria in the crystallization interval in the Ti–Co–Sn system at above 50 at.% Ti

Iu Fartushna [a], M. Bulanova [a, b], R.M. Ayral [c], J.C. Tedenac [c, *], N. Zhludenko [b], K. Meleshevich [a], Yu Romanenko [b]

[a] I.N. Frantsevich Institute for Problems of Materials Science, Kiev, Ukraine
[b] National Technical University of Ukraine, Kiev Polytechnical Institute, Kiev, Ukraine
[c] ICGM-UMR5253 University of Montpellier, Montpellier, France

ARTICLE INFO

Article history:
Received 13 October 2015
Received in revised form
14 January 2016
Accepted 21 January 2016
Available online 4 March 2016

Keywords:
Phase diagram
Phase equilibria
Titanium alloys

ABSTRACT

Ti-rich corner (above 50 at.% Ti) of the Ti–Co–Sn system was first studied in the crystallization interval by the methods of microscopy, microprobe, DTA, X-ray diffraction. The liquidus and solidus projections, the melting diagram and the reaction scheme were constructed. No ternary compounds form in the concentration interval studied. The liquidus projection is characterized by the fields of primary crystallization of (βTi) and binary-based phases Ti_3Sn, Ti_2Sn, (Ti_5Sn_3), TiCo, Ti_2Co. The solidus projection is characterized by four three-phase fields: $(Ti_3Sn) + (Ti_2Sn) + (Ti_5Sn_3)$, $(Ti_3Sn) + (Ti_5Sn_3) + (TiCo)$, $(\beta Ti) + (Ti_3Sn) + (TiCo)$ and $(\beta Ti) + (TiCo) + (Ti_2Co)$. Three-phase fields form due to invariant four-phase equilibria $L_{U1} + (Ti_2Sn) \rightleftarrows (Ti_3Sn) + (Ti_5Sn_3)$, $L_{U2} + (TiCo) \rightleftarrows (\beta Ti) + (Ti_2Co)$, $L_{E1} \rightleftarrows (Ti_3Sn) + (Ti_5Sn_3) + (TiCo)$ and $L_{E2} \rightleftarrows (Ti_3Sn) + (\beta Ti) + (TiCo)$ at 1230, ~1040, 1210 and 1050 °C, respectively. In the two-phase fields $(Ti_3Sn) + (TiCo)$ and $(\beta Ti) + (TiCo)$ there are temperature maxima at ~1250 and $\gtrsim$1050 °C, respectively, which form by invariant three-phase equilibria $l_{e3} \rightleftarrows (Ti_3Sn) + (TiCo)$ and $l_{e4} \rightleftarrows (\beta Ti) + (TiCo)$ at ~1250 and $\gtrsim$1050 °C, respectively.

1. Introduction

Due to their multiple properties (excellent biocompatibility, low density, good corrosion resistance and balance of mechanical properties etc), Ti-base alloys have been paid more attention in recent years [1,2] in various fields of applications, particularly as biomedical and structural materials. From this point of view, the Ti–Co–Sn system is of both practical and fundamental importance as a background for functional materials based on the intermetallics involved. Particularly, the Ti_3Sn intermetallic was shown [3] to possess extremely low Young's modulus (5 GPa at the room temperature) and a phase transformation at about 50 °C, which is of a martensitic type [3–6]. The TiCo compound is interesting as a shape memory phase, as well. The alloys on its basis simultaneously have high strength, ductility, corrosion resistance, damping ability [7]. Similarly to the Ti–Sn–Ni system [8,9], Ti3Sn–TiCo composites might be interesting as amorphous and damping materials. Many publications are devoted to the Heusler and Half–Heusler compounds, $TiCo_2Sn$ and TiCoSn, which are of interest as thermoelectric and magnetic materials. These data are summarized in a survey [10]. In addition [11], considered rapidly solidified Co–Sn–Ti alloys as cathodic materials for lithium-ion batteries. Thus, the system is of interest in a wide concentration interval for materials of such various applications.

Phase equilibria in the Ti–Co–Sn system were experimentally studied in only one paper [12], where partial isothermal sections at 600 °C (above 50 at.% Sn) and at 800 °C (below 50 at.% Sn) were reported. Thermodynamic optimization of the system was performed by Refs. [13], which was based on experimental results [12] and few complementary experiments. The liquidus projection and a number of isothermal sections were presented. Up to now no experimental data on phase equilibria at crystallization are available. A lack of experimental data didn't not allow [13] to use the Compound Energy Formalism in their thermodynamic description, and the thermodynamic functions were treated by a classic Redlich–Kister model.

* Corresponding author.
E-mail address: tedenac@univ-montp2.fr (J.C. Tedenac).

http://dx.doi.org/10.1016/j.jallcom.2016.01.160
0925-8388/

Table 1
Chemical composition of individual phases and of eutectics in Ti–Co–Sn system according to microprobe measurements in as-cast samples.

№	Alloy, at. %	Phase composition at the solidus surface	Microprobe results, at.%			
			Phase	Ti	Co	Sn
1	2	3	4	5	6	7
1	90Ti–5Co–5Sn	(βTi)	–	–	–	–
2	85Ti–5Co–10Sn	(βTi)	(βTi)	84.5	4.5	11.0
3	80Ti–5Co–15Sn (79.4Ti–5.3Co–15.3Sn)[a]	(βTi) + (Ti_3Sn) + (TiCo)	(Ti_3Sn)	76.3 ± 0.5	0.2 ± 0.3	23.5 ± 0.2
			(βTi)	83.6	5.8	10.6
4	75Ti–5Co–20Sn (74.0Ti–5.5Co–20.5Sn)	(βTi) + (Ti_3Sn) + (TiCo)	(Ti_3Sn)	75.0 ± 0.2	0.0	25.0 ± 0.2
5	70Ti–5Co–25Sn	(Ti_3Sn) + (Ti_5Sn_3) + (TiCo)	(Ti_3Sn)	72.9 ± 0.1	1.2 ± 0.4	25.9 ± 0.3
6	65Ti–5Co–30Sn (64.7Ti–5.0Co–30.3Sn)	(Ti_3Sn) + (Ti_2Sn) + (Ti_5Sn_3)	(Ti_5Sn_3)	58.5 ± 0.4	8.2 ± 0.1	33.3 ± 0.3
			(Ti_2Sn)	66.7 ± 0.3	3.9 ± 0.4	29.4 ± 0.2
7	57.5Ti–5Co–37.5Sn	(Ti_5Sn_3)	–	–	–	–
8	74.5Ti–1Co–24.5Sn	(Ti_3Sn) + (Ti_5Sn_3) + (TiCo)	(Ti_3Sn)	73.7 ± 0.6	0.7 ± 0.6	25.3 ± 0.7
9	73.5Ti–2Co–24.5Sn (73.2Ti–2.1Co–24.8Sn)	(Ti_3Sn) + (Ti_5Sn_3) + (TiCo)	(Ti_3Sn)	74.1 ± 0.2	0.9 ± 0.1	25.0 ± 0.2
10	72.5Ti–3Co–24.5Sn	(Ti_3Sn) + (Ti_5Sn_3) + (TiCo)	–	–	–	–
11	71.5Ti–4Co–24.5Sn	(Ti_3Sn) + (Ti_5Sn_3) + (TiCo)	–	–	–	–
12	70.5Ti–5Co–24.5Sn	(Ti_3Sn) + (Ti_5Sn_3) + (TiCo)	–	–	–	–
13	80Ti–10Co–10Sn	(βTi) + (Ti_3Sn) + (TiCo)	–	–	–	–
14	70Ti–20Co–10Sn	(βTi) + (Ti_3Sn) + (TiCo)	(Ti_3Sn)	74.3 ± 0.2	0.8 ± 0.2	24.9 ± 0.0
			(TiCo)	50.7 ± 0.3	49.0 ± 0.3	0.3 ± 0.1
			(βTi)	85.6	7.2	7.3
15	60Ti–30Co–10Sn	(Ti_3Sn) + (TiCo)	(TiCo)	49.8 ± 0.2	49.5 ± 0.2	0.6 ± 0.1
16	50Ti–40Co–10Sn (50.5Ti–39.0Co–10.5Sn)	(Ti_5Sn_3) + (TiCo)	(TiCo)	49.2 ± 0.1	48.9 ± 0.2	1.9 ± 0.0
17	60Ti–20Co–20Sn	(Ti_3Sn) + (Ti_5Sn_3) + (TiCo)	(Ti_5Sn_3)	57.3 ± 0.4	9.2 ± 0.2	33.5 ± 0.3
18	60Ti–35Co–5Sn	(βTi) + (Ti_3Sn) + (TiCo)	(TiCo)	50.1 ± 0.4	49.6 ± 0.4	0.3 ± 0.1
			(Ti_3Sn)	74.3	1.4	24.3

[a] In brackets composition of the samples according to SEM analysis of their surfaces is given.

The goal of the present research was to study phase equilibria with participation of liquid in the part of the system with Ti concentration over 50 at.%.

2. Experimental

The purity of the starting materials was Ti - 99.85, Co - 99.86 and Sn - 99.995.[1] The alloys were melted in an arc-furnace with a nonconsumable 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 0.1%, so the composition of the samples was taken according to the initial mixtures. For few alloys chemical analysis of their surfaces was performed in S.E.M., which has shown good correspondence with those of initial mixtures. Selective analysis of samples for oxygen showed that its content does not exceed the original content in titanium. So, nominal samples compositions were accepted.

The samples were studied in as-cast state by DTA, X-ray diffraction, metallography and microprobe analysis.

DTA was performed in a VDTA-7-type device with a W/W-Re thermocouple in helium. The rate of heating/cooling was ~40 °C/min. Mo was used as the reference sample. Alumina crucibles were used. The liquidus temperatures were taken from the heating curves as the beginning of a return to baseline. However, these could be overestimated by the false interval of crystallization. Other temperatures were taken as beginning of deviations from baseline.

X-ray diffraction was performed by the powder methods in Debye cameras ($d = 57.3$ *mm*) and from cross sections in a DRON-3.0 diffractometer with CuKα-filtered radiation. The X-ray patterns were identified with the WinXpow and Powder Cell 2.4 softwares. The lattice parameters were calculated by least–squares refinement.

The samples for microstructure examination were polished with a water suspension of Cr_2O_3. No chemical etching was used. Examination and Microprobe analysis of the microstructures were performed with SEM JEOL JSM-6490LV and FEI Quanta FEG 200 using back-scattered electrons.

[1] Weight %. For the alloys compositions at.% are used.

3. Results and discussion

In this study the Ti–Co and Ti–Sn systems are accepted from Refs. [14] and [13], respectively.

3.1. Solid phases

Any ternary compound was not found in the concentration interval under discussion. Table 1 shows chemical composition of individual phases resulting from the microprobe measurements. According to these data, the binary compounds have limited solubilities of the third element. Thus, Ti_5Sn_3 and Ti_2Sn dissolve up to 10 and 5 at.% Co, respectively; Ti_3Sn dissolves no more than 1 at.% Co. Solubility of Sn in Ti_2Co was estimated as below 1 at.%, as well. TiCo has wide homogeneity domain, however, it is outside the considered interval. The phase (βTi) forms the widest homogeneity range.

Microstructures of single-phased or nearly single-phased samples are shown in Fig. 1 a–c, and the limits of the homogeneity regions are given in the solidus projection, Fig. 2 average.

Note, that in Table 1 compositions of the phases together with standard deviations are presented, while Fig. 2 contains the results of all the measurements.

One should note the typical morphology of the primary grains of Ti_2Sn (sample 65Ti–5Co–30Sn, # 6, Fig. 1 b. They contain long precipitates of (Ti_5Sn_3). Such morphology of Ti_2Sn grains is observed in other Ti–Sn based systems: Ti–Zr–Sn [15], Ti–Dy–Sn [16]. Except these two phases, alloy # 6 has very few amounts of (Ti_3Sn) at the grain boundaries of the primary phase.

A single-phase nature of sample 60Ti–5Co–35Sn (# 7, Fig. 1 c), is associated with an interesting way of formation of the homogeneity region of the phase (Ti_5Sn_3). Thus, the binary compound contains 62.5 at.% Ti and one would expect that the cobalt and titanium atoms replace each other in the crystal lattice. The