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Phase diagram of the Ti–Ga system

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Abstract

Phase relations in the binary Ti–Ga system have been established experimentally by means of a study of alloy samples in the as-cast and annealed states. The alloys were prepared by arc melting. The investigation was carried out using physico–chemical methods of analyses (metallography, X-ray powder diffraction (XRD), differential thermal analysis (DTA) and electron probe microanalysis (EPMA)) over a composition range 0–75 at.% Ga. The refined phase diagram of the Ti–Ga system is presented as a result of this study.

Keywords: Phase diagram; Compound; Titanium; Gallium; Alloy

1. Introduction

The Ti–Ga phase diagram was previously investigated mainly in the range up to 35 at.% Ga [1–5]. There is only one work devoted to the research of the Ti–Ga alloys over the entire composition range [6]. However, the description of the microstructures given by [6], does not always correspond to the represented phase diagram (Fig. 1). Besides, some of the alloys contained an oxide phase. Therefore results of this investigation were not used by Murray's in the critical assessment of that system [7].

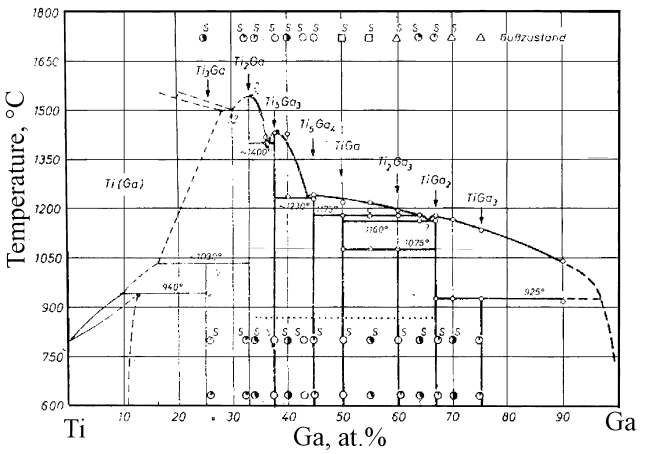

Fig. 1. Phase diagram of the Ti–Ga system [6].

Using experimental data of Gibbs energy of the b.c.c. phases [8] and metallography and X-ray diffraction data [2,3], Kaufman [9] calculated the Ti–Ga phase diagram in the region up to 35 at.% Ga. Murray used this diagram as a basis in the critical review [7]. In this phase diagram the temperature corresponding to the eutectic reaction $L \Leftrightarrow \beta + Ti_2Ga$, as well as a boundary $\alpha/\alpha+\alpha_2$, are represented approximately. The melting point of the compound Ti_2Ga is not given.

Thus it was obvious that it is necessary to undertake a research of the Ti–Ga system over the entire composition range to establish and refine this phase diagram.

2. Experimental procedure

Twenty-four alloys with different compositions were prepared from commercially available component of high purity (iodide titanium (99.96%) and gallium (99.99%))).

Samples were prepared in an arc-furnace using a non-consumable tungsten electrode and a water-cooled copper hearth under a high-purity Ar atmosphere gettered by Ti/Zr. The ingots of ~10 g were inverted and remelted four times to ensure homogeneity. Weight losses were within 0.1–4%, therefore chemical analyses were carried out for some of the alloys. It was found that the composition of the samples with large weight losses did not change.

Most of the samples were annealed under high purity

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argon at different temperatures close to the temperature of the phase transformations. Phase analyses of both the as-cast and the annealed alloys were carried out by means of optical metallography and X-ray diffraction (XRD). The microstructures of the alloys were examined using the optical microscopes MIM-8 M and KONE Jenaphot 2000. Specimens for the metallography were prepared by grinding and polishing followed by etching with a mixture of 2 drops of HF, 4 drops of HNO_3, 20 drops of lactic acid and 10 ml of H_2O to reveal their microstructures. X-ray studies were carried out on powder samples employing the Debye–Scherrer method by means of the URS-2.0 device in a camera with $d=57.3$ mm or a DRON-UM diffractometer with monochromatic CuKα radiation. The lattice parameters were calculated and refined by a computer program called 'Lattice' which uses the least squares method.

The temperatures of the phase transformations were determined by differential thermal analysis (DTA) using only the heating curves because supercooling effects were observed on the cooling curves for both the as-cast and the annealed alloys. The thermal curves were obtained in a DTA-analyzer with W/W–Re thermocouple under a He atmosphere. Al_2O_3 crucibles were used. The heating rate used was 40°C/min. The thermocouple was calibrated using the transformation points of pure Fe and the melting points of pure Au and Pt in order to obtain the exact values of the phase transformation temperatures of the alloys.

The oxygen contents in the samples were less than 0.03 mass% (300 ppm).

The chemical compositions of the phases and the structural constituents of the as-cast and annealed alloys were determined using quantitative electron probe microanalysis techniques (EPMA) by means of a Superprobe 733 (JEOL LTD, Tokyo, Japan) device employing pure Ti and GaP as standards. Errors in the measurements were about ±0.5 at.%. The photographs were obtained using back-scattered electrons (BSE) with this device or with a KONE Jenaphot 2000.

3. Results

Data on the constitution of the as-cast and annealed alloys are given in Tables 1 and 2. These data were obtained by means of metallography, XRD, EPMA, and DTA methods. They were used to construct the Ti–Ga phase diagram over concentration range 0–75 at.% Ga (Fig. 2). The results obtained confirm that eight intermediate compounds, titanium with gallium form in the Ti–Ga system: Ti_2Ga, Ti_3Ga, Ti_5Ga_3, Ti_5Ga_4, TiGa, Ti_2Ga_3, $TiGa_2$ and $TiGa_3$ (Table 1). Our results confirm all the structures of these compounds belong to the types, which were established early. Lattice parameters of all phases according to this work show good agreement with literature data.

Microstructure of the as-cast alloys with 5, 10, 20 and 27 at.% Ga consists of polyhedrons of β-phase (β*)[1]. Alloys with 5 at.% Ga annealed at 900 and 1000°C have the similar structure, i.e. at the temperatures higher than 900°C the area of solid solution on the β-Ti base exists. Microstructure of the alloy with 10 at.% Ga annealed at 800 and 900°C formed with polyhedrons of a titanium phase too, but unlike the previous alloy, it does not undergo phase transformations. Hence at the temperatures below 900°C the area of the solid solution on the α-Ti base exists. It is known that the temperature of a β⇔α transformation for pure titanium is 882°C. In the binary Ti–Ga system, the temperature of the formation of the α-phase through a peritectoid reaction $\beta+\alpha_2\Leftrightarrow\alpha$ is equal to 940°C [2,3]. According to the EPMA data for the alloy 80Ti–20Ga the highest solubility of gallium in α-Ti at 940°C is close to 20 at.%. It was found to be 14.6 at.% Ga at 800°C. Therefore it decreases with decreasing temperature.

Microstructure of the alloy 80Ti–20Ga annealed at 930, 900 and 800°C is diphasic. As one can see in Fig. 3a, it formed with α-Ti (dark matrix) and Ti_3Ga (α_2) (clear grains). In that alloy at 1000°C, α_2 coexists with β*. The $\beta/\beta+\alpha_2$ boundary at 1000°C was established to be at ~18.2 at.% Ga. After annealing at 1350°C this alloy consists of polyhedrons of β* and α_2, which has precipitated from β during cooling. The heating curve of the alloy 75Ti–25Ga shows a thermal effect at 1030°C (Table 1), which corresponds to the peritectoid reaction $Ti_3Ga\Leftrightarrow\beta+Ti_2Ga$. The as-cast alloy with 27 at.% Ga is formed of coarse polyhedrons β* with very thin borders of Ti_2Ga. Therefore the highest solubility of gallium in β-Ti was accepted at 27 at.%. The structure of the alloy 75Ti–25Ga annealed at 1350°C is similar to that of the as-cast alloy 73Ti–27Ga, hence the $\beta/\beta+Ti_2Ga$ boundary at 1350°C lies at 25 at.% Ga. Thus the solubility of gallium both in β-Ti and in α-Ti decreases with decreasing temperature.

The boundaries of the Ti_3Ga (α_2) homogeneity range were defined. According to the EPMA data the lower boundary of this range at 930°C is at 22.6 at.% Ga, at 1000°C, 23.9 at.% Ga and at 800°C it is 23.1 at.% Ga (alloy 80Ti–20Ga). Upper boundary at 1000°C goes through 24.3 at.% Ga (alloy 75Ti–25Ga) and at 800°C, through 25.1 at.% Ga (alloy 68.5Ti–31.5Ga). The composition of the α_2-phase which takes part in the peritectoid reaction $Ti_3Ga\Leftrightarrow\beta+Ti_2Ga$ at 1030°C is 24 at.% Ga. The alloy 75Ti–25Ga annealed at 900°C is single-phase (α_2). Thin interlayers of Ti_2Ga appear after annealing of that alloy at 930 and 1000°C. The boundaries of the homogeneity range of this phase according to this work agrees well with experimental data by [3] (Fig. 4). As one can see from this figure, the homogeneity range is located mainly

[1]Solid solution on β-Ti–base, which underwent a β⇔α phase transformation during cooling.

Table 1
Chemical composition, phase composition, structural constituents and temperatures of the phase transformations in the Ti–Ga alloys[a]

Content of Ga. at.%	Primary phase	Structural constituents of as-cast alloys	Temperature (°C) and duration (h) of annealing	Phase composition of annealed alloys	Temperatures of phase transformations, °C		
					$T_{sol.st}$	T_s	T_l
5	β	β*	1000°C, 55 h	β*			
			900°C, 10 h	β*			
10	β	β	900°C, 10 h	α			
			900°C, 1000 h +800°C, 1000 h	α			
20	β	β*	1350°C, 10 h	β*			
			900°C, 12 h+930, 28 h	$\alpha+\alpha_2$			
			1000°C, 55 h	$\beta^*+\alpha_2$	1190[2]	1500[2]	1525[2]
			900°C, 10 h	$\alpha+\alpha_2$			
			900°C, 1000 h +800°C, 1000 h	$\alpha+\alpha_2$			
25	β	β*	1000°C, 55 h +1350°C, 20 h	β*			
			1200°C, 5 h	β^*+Ti_2Ga			
			1000°C, 55 h	$\alpha_2+\langle Ti_2Ga\rangle$			
			950°C, 31 h	$\alpha_2+\langle Ti_2Ga\rangle$	1030	1440	1455
			950°C, 31 h +900°C, 12 h	α_2			
27	β	$\beta^*+\langle Ti_2Ga\rangle$					
30	β	β^*+e_1	1350°C, 10 h	β^*+Ti_2Ga			
			1000°C, 55 h	$Ti_2Ga+\alpha_2$		1420[2]	1435[2]
31.5	Ti_2Ga	Ti_2Ga+e_1	900°C, 1000 h +800°C, 1000 h	α_2+Ti_2Ga			
32.0	Ti_2Ga	$Ti_2Ga+\langle e_1\rangle$					
33.3	Ti_2Ga	Ti_2Ga	1000°C, 55 h	Ti_2Ga		1420[1,2]	1450[2]
34	Ti_2Ga	$Ti_2Ga+\langle e_2\rangle$	1000°C, 30 h	$Ti_2Ga+\langle Ti_5Ga_3\rangle$			
35.5	Ti_5Ga_3	$Ti_5Ga_3+e_2$	1350°C, 33 h	$Ti_2Ga+Ti_5Ga_3$		1425	1455
						1420[2]	1450[2]
			1350°C, 33 h+1000°C, 30 h	$Ti_2Ga+Ti_5Ga_3$			
37.0	Ti_5Ga_3	$Ti_5Ga_3+e_2$	1000°C, 55 h	$Ti_2Ga+Ti_5Ga_3$		1425[2]	1455[2]
37.5	Ti_5Ga_3	Ti_5Ga_3	1000°C, 55 h	Ti_5Ga_3			
40.0	Ti_5Ga_4	$Ti_5Ga_4+Ti_5Ga_3$				1425[2]	1440[2]
42.0	Ti_5Ga_4	$Ti_5Ga_4+Ti_5Ga_3$	1300°C, 33 h	$Ti_5Ga_4+Ti_5Ga_3$		1430[2]	1455[2]
43.5	Ti_5Ga_4	Ti_5Ga_4					
44.4	Ti_5Ga_4	Ti_5Ga_4	1300°C, 33 h	Ti_5Ga_4		1408[2]	1455[2]
47.0	Ti_5Ga_4	Ti_5Ga_4+TiGa	1300°C, 33 h	Ti_5Ga_4	1210[2]	1240[2,3]	1440[2]
			1220°C, 33 h	Ti_5Ga_4+TiGa			
50.0	Ti_5Ga_4	Ti_5Ga_4+TiGa	1200°C, 53 h	Ti_5Ga_4+TiGa		1250	1405
			1100°C, 25 h	Ti_5Ga_4+TiGa			
52.5	Ti_5Ga_4	Ti_5Ga_4+TiGa	1000°C, 30 h	TiGa		1240	1350
55.0	Ti_5Ga_4	$Ti_5Ga_4+TiGa+\langle TiGa_2\rangle$	1100°C, 25 h	TiGa			
			1000°C, 19 h	TiGa		1220	1300
			800°C, 1000 h+900°C, 1000 h	$TiGa+Ti_2Ga_3$			
60.0	TiGa	$TiGa+(Ti_2Ga_3)^{**}+\langle e_4\rangle+TiGa_2^{***}$	1100°C, 25 h	$TiGa_2+TiGa$	1075	1165	1220
			1000°C, 19 h	Ti_2Ga_3			
64.0	$\langle TiGa\rangle$	$TiGa+\langle Ti_2Ga_3\rangle^{**}+\langle e_4\rangle+TiGa_2^{***}$	1100°C, 25 h	$TiGa_2+TiGa$	1080	1165	1205
			1000°C, 19 h	$TiGa_2+Ti_2Ga_3$			
66.6		$TiGa_2$	1000°C, 30 h	$TiGa_2$		1130	1190
73	$TiGa_2$	$TiGa_2+L$	1000°C, 30 h	$TiGa_2+TiGa_3$		1135	1190

[a] $T_{sol.st}$ – temperature of the solid state transformation; * solid solution on the base of β-Ti, which underwent $\beta\Leftrightarrow\alpha(\alpha_2, \alpha')$ transformation during cooling; ** Ti_3Ga_2 formed from TiGa at cooling; $\langle\rangle$ insignificant quantity of the phase; L – liquid; [1] thermal effect which has arisen due to unequilibrium state of the as-cast alloy; [2] thermal effect of as-cast alloy; [3] melting of the unequilibrium γ-phase; e_1, euctic $\beta+Ti_2Ga$; e_2, eutectic $Ti_2Ga+Ti_5Ga_3$; e_3, eutectic $Ti_5Ga_4+Ti_5Ga_3$; e_4, eutectic TiGa+TiGa.

Table 2
Lattice parameters of the intermediate phases in the Ti–Ga system

Phase	Compositions (at.%) and heat treatment of alloy	Pearson symbol	Space group	Strukturber. designation	Prototype	Lattice parameters, nm	
						a	*c*
α	95Ti5Ga, as-cast	hP2	$P6_3/mmc$	$D^4_{6\,h}$	Mg	0.2940(2)	0.4686(6)
Ti_3Ga	75Ti–25Ga, 1000°C, 55 h	hP8	$P6_3/mmc$	$D0_{19}$	Ni_3Sn	5.7447(4)	4.5955(9)
Ti_2Ga	66.7Ti–33.3Ga, 1000°C, 54 h	hP6	$P6_3/mmc$	$B8_2$	Ni_2In	4.5207(2)	5.5222(2)
Ti_5Ga_3	62.5Ti–37.5Ga, as-cast	tI32	$I4/mcm$	$D8_m$	W_5Si_3	10.1906(7)	5.0420(5)
$Ti_5Ga_3O_x$	62.5Ti37.5Ga, 1000°C, 55 h	hP16	$P6_3/mcm$	$D8_8$	Mn_5Si_3	7.6936(4)	5.2792(8)
Ti_5Ga_4	53Ti–47Ga, 1300°C, 33 h	hP18	$P6_3/mcm$		Ti_5Ga_4	7.8456(2)	5.4259(3)
TiGa	47.5Ti–52.5Ga, 1000°C, 30 h	tP4	$P4/mmm$	$L1_0$	AuCu	3.9717(2)	3.9872(3)
	the same	tP4	$P4/mBm$	$L1_0$	AuCuI	2.8089(3)	3.9736(6)
Ti_2Ga_3	40Ti–60Ga, 1000°C, 25 h	tP10	$P4/m$		Ti_2Ga_3	6.2817(3)	3.9991(3)
$TiGa_2$	33.3Ti–66.7Ga, 1000°C	tI24	$I4_1/amd$		$HfGa_2$	3.9405(2)	24.4060(9)
$TiGa_3$	25Ti–75Ga, 1000°C, 30 h	tI8	$I4/mmm$	$D0_{22}$	Al_3Ti	5.5625(7)	8.1178(9)

in the area of compositions, which are less than the stoichiometric composition 3:1.

The as-cast alloy 70Ti–30Ga (Fig. 3b) has a eutectic structure and consists of two phases (β*+Ti_2Ga). The thermal effect at 1420°C on the heating curve in this alloy was attributed to a eutectic reaction L⇔β+Ti_2Ga. The little primary grains of Ti_2Ga appear in the alloy with 31.5 at.% Ga. Therefore the position of the eutectic point is accepted at 30 at.% Ga.

The as-cast alloy of the stoichiometric composition 2:1 (33.3 at.% Ga) as well as annealed at 1000°C is single-phase (Ti_2Ga (χ)) (Fig. 3c). The next alloy 66Ti–34Ga is diphasic (Ti_2Ga+Ti_5Ga_3) with the primary grains of Ti_2Ga in the as-cast alloy. Thus Ti_2Ga congruently melts and takes part in the eutectic reactions with adjacent phases β and Ti_5Ga_3: L⇔β+Ti_2Ga and L⇔Ti_5Ga_3+Ti_2Ga correspondingly. The melting temperature of this compound is established to be 1455°C.

The as-cast alloy of the stoichiometric composition 5:3 (37.5 at.% Ga), as well as annealed at 1100 and 1350°C, is single-phase. Fig. 3d and 3e show the structures of the as-cast alloys with 35.5 and 37 at.% Ga. According to the EPMA data, structural constituents of these alloys are primary grains of Ti_5Ga_3 and interlayers of Ti_2Ga. Two-phase structure of these alloys remained after annealing at 1350°C (Fig. 3f). All of these alloys annealed at 1350°C found out the reflexes of a Mn_5Si_3 structure type phase, which was identified in [6] as $Ti_5Ga_3O_x$. It is possible that a similar phase arises due to the interaction of a melt with the crucible at temperatures above 1500°C and is responsible for an appearance of thermal effects at 1500–1520°C on the DTA heating curves. The thermal effect at 1425°C

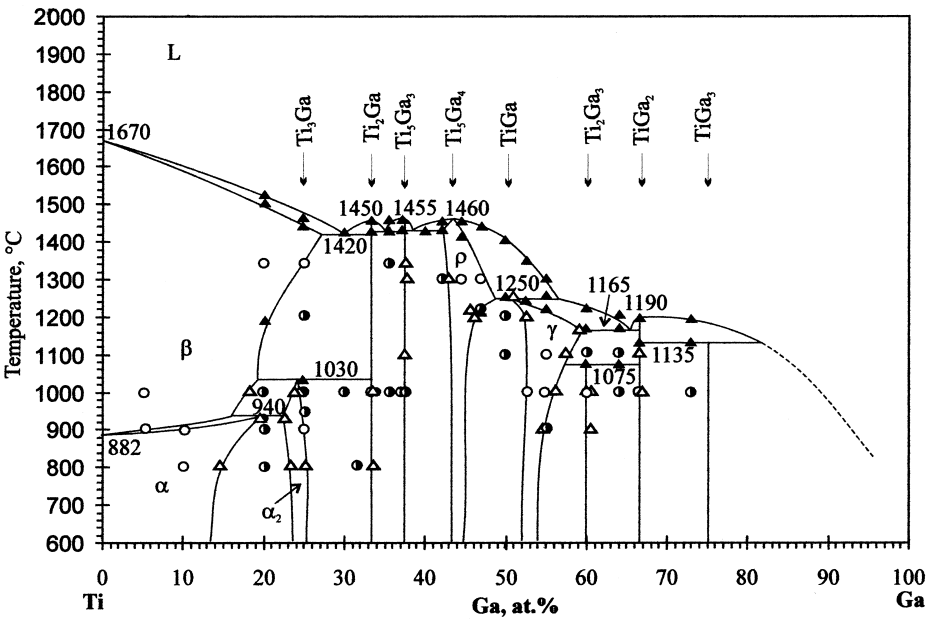

Fig. 2. Phase diagram of the Ti–Ga system.

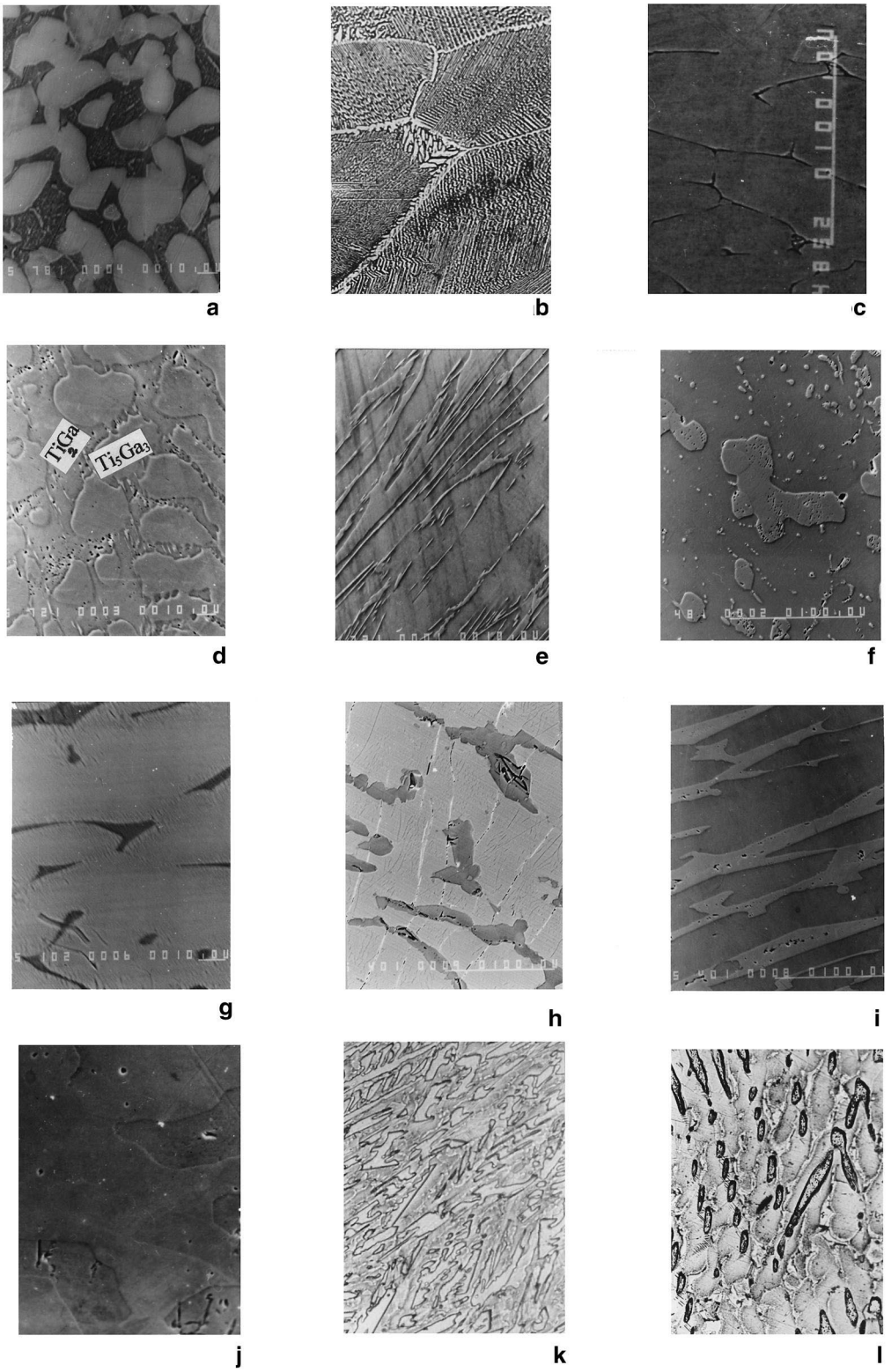

Fig. 3. Microstructures of the Ti–Ga alloys: (a) 80Ti–20Ga, anneal. at 800°C, ×1000, grains of α_2 and matrix α; (b) 70Ti–30Ga, as-cast, ×100, eutectic ($\beta + Ti_2Ga$); (c) 66.7Ti–33.3Ga, as-cast, ×400, Ti_2Ga; (d) 64.5Ti–35.5Ga, as-cast, ×720, Ti_5Ga_3 + eutectic ($Ti_2Ga + Ti_5Ga_3$); (e) 67Ti–33Ga, as-cast, ×720, Ti_5Ga_3 + eutectic ($Ti_2Ga + Ti_5Ga_3$); (f) 64.5Ti–35.5Ga, anneal. at 1350°C, ×480, grains of Ti_5Ga_3 and matrix of Ti_2Ga; (g) 58Ti–42Ga, as-cast, ×1000, coarse primary grains of Ti_5Ga_4 and matrix of Ti_5Ga_3; (h) 58Ti–42Ga, anneal. at 1300°C, ×400, Ti_5Ga_4 and Ti_5Ga_3; (i) 53Ti–47Ga, as-cast, ×400, primary grains of Ti_5Ga_4 and matrix of TiGa; (j) 50Ti–50Ga, as-cast, ×400, primary grains of Ti_5Ga_4 and matrix of TiGa; (k) 47.5Ti–52.5Ga, as-cast, ×250, primary grains of Ti_5Ga_4, matrix of TiGa with precipitations of Ti_2Ga_3 and clear interlayers of $TiGa_2$; (l) 45Ti–55Ga, primary grains of Ti_5Ga_4, matrix of TiGa and clear interlayers of $TiGa_2$; (m) 47.5Ti–52.5Ga, anneal. at 1000°C, ×500, TiGa; (n) 40Ti–60Ga, as-cast, ×500, primary grains of TiGa, precipitations of Ti_2Ga_3, interlayers of $TiGa_2$ and little eutectic ($TiGa + TiGa_2$).

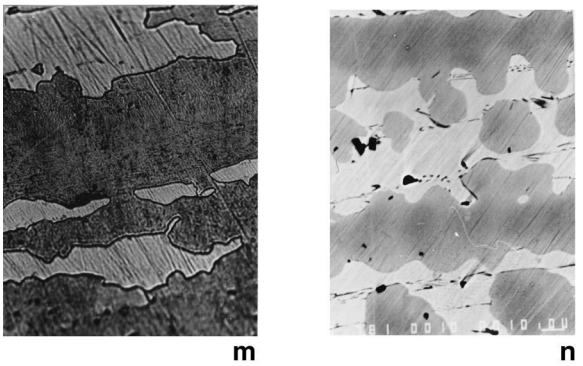

Fig. 3. (*continued*)

in both of the alloys corresponds to the eutectic reaction $L \Leftrightarrow Ti_5Ga_3 + Ti_2Ga$. The alloys with 34 and 35.5 at.% Ga have not shown a eutectic structure (Fig. 3d). The formation of the secondary Ti_2Ga phase occurs on surfaces of the Ti_5Ga_3 grains giving a eutectic of a degenerate morphology. The position of the eutectic point was accepted between the compositions of the alloys with 34 and 35.5 at.% Ga at ~34.5 at.% Ga.

The next phase is Ti_5Ga_4 (ρ). It is the primary phase in the as-cast alloys containing 40, 42, 47, 50, 52.5 and 55 at.% Ga. The as-cast alloys with 43.5 and 44.4 at.% Ga are single-phase (ρ). The alloys with 40 and 42 at.% Ga (Fig. 3g) have a two-phase structure. According to the EPMA data in these alloys, Ti_5Ga_4 primarily crystallizes and then – Ti_5Ga_3 (dark interlayers). We did not observe the typical eutectic structure in the alloys from region Ti_5Ga_4–Ti_5Ga_3. It is possible that the formation of the secondary phase Ti_5Ga_3 occurs on the surface of the Ti_5Ga_4 grains so the eutectic $L \Leftrightarrow Ti_5Ga_4 + Ti_5Ga_3$ is degenerated. According to the DTA data the temperature of this reaction was established to be 1430°C, which is considerably higher than the temperature of this reaction in [6]. The composition in the eutectic point was established on the basis of the metallography data. Since in the alloys with 40 and 42 at.% Ga the primary is the Ti_5Ga_4 grains, the eutectic point should be between 37.5 and 40 at.% Ga. Hence it was shown at ~39 at.% Ga.

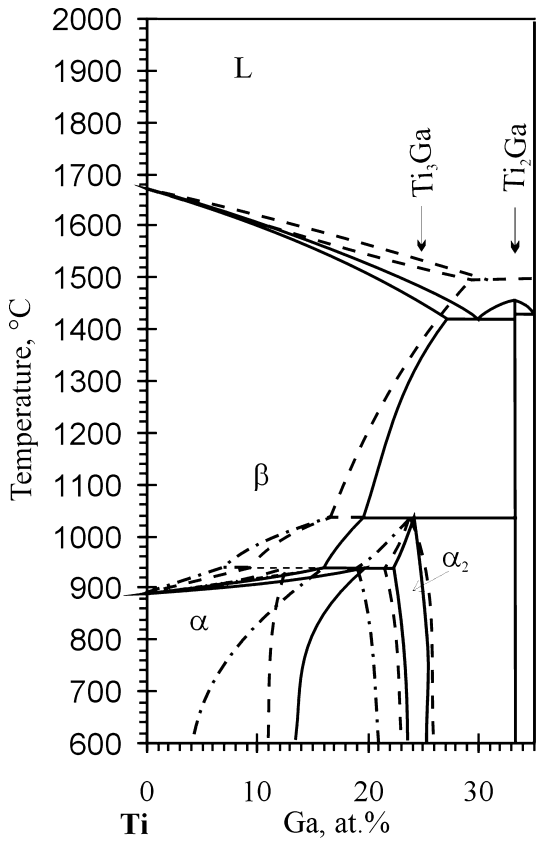

Fig. 4. Phase diagram of the Ti–Ga system in the concentration range 0–35 at.%Ga according to this work and data of [4] and [5].

After annealing at 1300°C the alloy 58Ti–42Ga has remained a two-phase structure $Ti_5Ga_4 + Ti_5Ga_3$ (Fig. 3h). The alloys with 44.4 and 47 at.% Ga at that temperature are single-phase (ρ). The last alloy after annealing at 1230°C was two-phase (ρ + γ). The experimental results as a whole indicate an existence of the significant homogenity range of the ρ-phase. It extends from ~42 at.% Ga at the temperature 1430°C up to 49 at.% Ga at 1250°C. The first temperature corresponds to the temperature of the eutectic reaction $L \Leftrightarrow Ti_5Ga_3 + Ti_5Ga_4$, the second – to the temperature of the peritectic reaction $L + Ti_5Ga_4 \Leftrightarrow TiGa$. The temperature of the latest reaction (1250°C), which was found in this work, considerably exceeds that reported by [6] (1175°C). The width of the homogeneity range of the ρ-phase decreases with temperature. It should be noticed, that the position of the melting point of the Ti_5Ga_4 was found to deviate from the stoichiometric composition 5:4 (44.4 at.% Ga) to the side of lower gallium contents, exactly to 43.5 at.% Ga. This affirmation can be confirmed with the DTA data for the alloys with 42 and 44.4 at.% Ga.

Microstructures of the as-cast alloys containing 47 and 50 at.% Ga are shown in Fig. 3i and 3j. They consist of the primary Ti_5Ga_4 grains and matrix TiGa (γ). As was mentioned above, TiGa (γ) forms through the peritectic reaction $L + Ti_5Ga_4 \Leftrightarrow TiGa$. The first alloy after annealing at 1300°C becomes single-phase (Ti_5Ga_4), but at 1220°C the second phase (γ) has arisen again.

Microstructures of the as-cast alloys 47.5Ti–52.5Ga and 45Ti–55Ga (Fig. 3k and 3l), were found to consist of the primary grains of Ti_5Ga_4, surrounded with TiGa (γ). Precipitates of Ti_2Ga_3 arise within the γ-grains due to the decomposition of the γ-phase during cooling. Thin clear interlayers between γ-grains were identified by means of EPMA as $TiGa_2$. They are formed due to unequilibrium solidification.

The existence of the extended homogeneity range (γ) was established too. Its boundaries have been determined on the basis of the metallography, EPMA and DTA data for the nearby alloys. The alloy 50Ti–50Ga in the as-cast state and after annealing at 1000 and 1100°C has a two-

phase structure (Ti_5Ga_4 + TiGa). The alloy 47.5Ti–52.5Ga annealed at 1000°C (Fig. 3m) and the alloy 45Ti–55Ga annealed at 1000 and 1100°C are single-phase (γ). The latest alloy after annealing at 900°C became diphasic (TiGa + Ti_2Ga_3). Therefore, as it is shown in Fig. 2, the homogeneity range of γ on the solidus extends from 51 at.% Ga at 1250°C to 59 at.% Ga at 1165°C and becomes considerably narrower with decreasing temperature. It deviates from the stoichiometry composition 1:1 to the side of higher gallium contents.

We confirmed that the γ-phase belongs to the structure type CuAu ($L1_0$). But reflexes of this phase can be attributed to AuCuI type too (Table 2).

The microstructure of the as-cast alloys with 60 and 64 at.% Ga (Fig. 3n) are formed of primary dendritic grains TiGa, interlayers $TiGa_2$ and little eutectic areas. After annealing at 1100°C they have a two-phase structure (TiGa + $TiGa_2$). After annealing at 1000°C the first of them became single-phase (Ti_2Ga_3) and the second – diphasic (Ti_2Ga_3 + $TiGa_2$). The thermal effect at 1075°C on the heating curve was attributed to a peritectoid reaction TiGa + $TiGa_2 \Leftrightarrow Ti_2Ga_3$ and at 1165°C – a eutectic reaction $L \Leftrightarrow$ TiGa + $TiGa_2$.

The alloy with 66.6 at.% Ga ($TiGa_2$) is almost single-phase both in the as-cast state and after annealing at 1000°C. The melting temperature of the $TiGa_2$ compound was established to be 1190°C.

The microstructure of the as-cast alloy with 73 at.% Ga consists of primary $TiGa_2$ grains (EPMA and XRD data) and a heterogeneous matrix. It is diphasic ($TiGa_2$ + $TiGa_3$) at 1000°C. The thermal effect at 1135°C was attributed to a peritectic reaction L + $TiGa_2 \Leftrightarrow TiGa_3$, because we did not observe eutectic constituent in this alloy.

The alloys with gallium contents higher than 75 at.% have not been investigated because of difficulties in sample preparation.

The temperatures of congruent melting and the invariant reactions according to present study and data of authors [6] are given in Table 3.

4. Conclusions

The refined version of the Ti–Ga phase diagram in the composition range 0–75 at.% Ga was constructed taking into account the results of physico–chemical methods of analyses (metallography, X-ray powder diffraction (XRD), differential thermal analysis (DTA) and electron probe microanalysis (EPMA)).

Four eutectic, two peritectic and three peritectoid reactions were established in the range under consideration. The compounds Ti_2Ga, Ti_5Ga_3, Ti_5Ga_4, $TiGa_2$ melt congruently, however the melting temperatures obtained are different from those given in [6]. The temperatures of Ti_3Ga and Ti_2Ga_3 formation obtained coincide with those found by [6]. The temperatures of other reactions also differ from those reported in [6]. Such a large difference of the temperatures can be explained by the not very precise method of the thermal analysis of the previous authors [6]. For the second they used only the thermal curves of cooling in spite of the fact that at high temperatures the samples can interact with the crucible, giving phase $Ti_5Ga_3O_x$.

The gallium solubility in α-Ti and β-Ti as well as the homogeneity range of Ti_3Ga (d_2) were refined by means of the microscopic, EPMA and X-ray diffraction study of the

Table 3
Invariant reactions in the Ti–Gs system

Reaction	Composition of phases, at.% Ga			Temperature of phase transformation, °C		Reaction type
				This work	[6]	
L⇔(βTi)		0.0		1670[a]		Melting point
(βTi)⇔(αTi)		0.0		882[a]	800	Allotropic transformation
L⇔(βTi) + Ti_2Ga	30.0	27.0	33.3	1420	1500?	Eutectic reaction
L⇔Ti_2Ga				1450	~1550	Congruent melting
(βTi) + $Ti_2Ga \Leftrightarrow Ti_3Ga$	18.0	33.3	24.0	1030	1030	Peritectoid reaction
(βTi) + Ti_3Ga⇔(αTi)	~17.0	22.6	~19.0	940	940	Peritectoid reaction
L⇔Ti_2Ga + Ti_5Ga_3	~34.5	33.3	37.5	1425	~1400	Eutectic reaction
L⇔Ti_5Ga_3		37.5		1455	1425	Congruent melting
L⇔Ti_5Ga_3 + Ti_5Ga_4	40.0	37.5	42.0	1430	~1230	Eutectic reaction
L⇔Ti_5Ga_4		~43.5		1460	1235	Congruent melting
L + $Ti_5Ga_4 \Leftrightarrow$ TiGa	~56.5	48.8	51.0	1250±5	1175	Peritectic reaction
L⇔TiGa + $TiGa_2$	~65.0	59.0	66.7	1165	1160	Eutectic reaction
TiGa + $TiGa_2 \Leftrightarrow Ti_2Ga_3$	~57.0	66.7	60.0	1075	1075	Peritectoid reaction
L⇔$TiGa_2$		66.7		1190	~1160	Congruent melting
L + $TiGa_2 \Leftrightarrow TiGa_3$	~81.0	66.7	75.0	1135	925	Peritectic reaction
L + $TiGa_3$ + Ga	?	75	?	?	?	?
L⇔ (Ga)		100		29.7741[a]		Melting point

[a] Data [3].

annealed alloys. The maximum solubility of gallium in β-Ti was established to reach 27 at.% Ga and in L-Ti−20 at.%.

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