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Structure and mechanical properties of the Ti-Ga-Si alloys in the Ti-rich corner

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The structure and mechanical properties (bending strength and bending deflection) of three alloys with high content of eutectic constituents were investigated. The formation of the structure is considered according to the Ti-Ga-Si phase diagram presented by the sections through the points of compositions of the alloys investigated. The mechanical properties have been determined by means of bending test of the samples by a scheme of the three-point bend in the air in the temperature interval of 20–800 °C. The correlation between the structure and mechanical properties is considered.

1. Introduction

Ti-based superalloys have a broad application in different areas of an up-to-date engineering [1]. Eutectic alloys, which are relevant to the group of the natural (*in situ*) composites [2–8] attract the particular attention among them. In such materials the mechanism of strengthening is caused by the considerable volume content of the refractory phase included in a ductile matrix. Both phases take part in the congruent type reaction, due to which the alloys have refined composite structure. For example, in the Ti-Si system, the silicide Ti_5Si_3 which forms congruently at 2130 °C and Ti-based phase jointly take part in the eutectic reaction $L \Leftrightarrow \beta + Ti_5Si_3$ [9] at 1355 °C [10]. Owing to the high thermodynamic stability and high melting temperature the Ti_5Si_3 compound and the solid solutions on its base can be effective reinforcements. Such systems as Ti-Al-Si [2–6], Ti-Al-Si-Cr [7], Ti-Al-Si-Zr [8] have been studied during last time. The new heat-proof materials based on them are being developed.

The aim of present study was to investigate the structure and to evaluate mechanical properties of eutectic Ti-Ga-Si alloys in the Ti-rich region. The system on the Ti-base containing gallium was chosen due to the fact that gallium, as well as aluminium, is an α-stabilizer of titanium. In spite of low melting point (29.8 °C) [9], gallium rises the temperature of $\alpha \Leftrightarrow \beta$ transformation from 882 up to 940 °C [9]. The high solubility of gallium in titanium (up to 13 at % in α-Ti and up to 28 at % in β-Ti) does not result in a significant decrease of the titanium melting temperature. In the Ti-rich region gallium forms the stable gallide Ti_2Ga with the sufficiently high melting temperature equal to 1460 °C ±. So we supposed, that it is expedient to investigate strength and ductility properties of the Ti-Ga-Si alloys.

2. Experimental

The samples were prepared from commercially available metals of high purity (iodide titanium (99.98%), silicon semiconductive monocrystals (99.999%) and gallium (99.99%)) in an arc-furnace with a nonconsumable tungsten electrode on a water-cooled copper hearth under an argon atmosphere gettered by titanium.

The ingots of ∼35 g were inverted and remelted four times to obtain homogeneous alloys. The weight losses were within 0.1–1%.

The samples were annealed at 1350 ± 5 °C for 70 h under a high purity argon atmosphere, that is about 50 °C below of solidus temperature. A phase analysis of the both as-cast and annealed alloys was made by means of microscopy (MSA) and X-ray diffraction. The microstructure of the alloys was examined by means of an optical microscope KONE Jenaphot 2000 with polished cross-cuts of samples, which were etched in 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 the microstructure of the alloys. X-ray studies were carried out with powders of the as-cast and annealed samples employing the Debye-Scherrer method by means of URS-2.0 device in a camera with $d = 57.3$ mm or DRON-UM diffractometer with monochromic CuK_α radiation. The lattice parameters were calculated and refined by a computer program "Lattice" using the least squares fit.

The contents of oxygen in the samples was less than 0.03 mass%. The mechanical properties have been determined by testing of the samples by scheme of the three-point bend in the air over the temperature interval of 20–800 °C. The tests have been carried out with the specimens of 2 × 5 × 35 mm which were cut out by means of electrodischarge machining and subsequently polished.

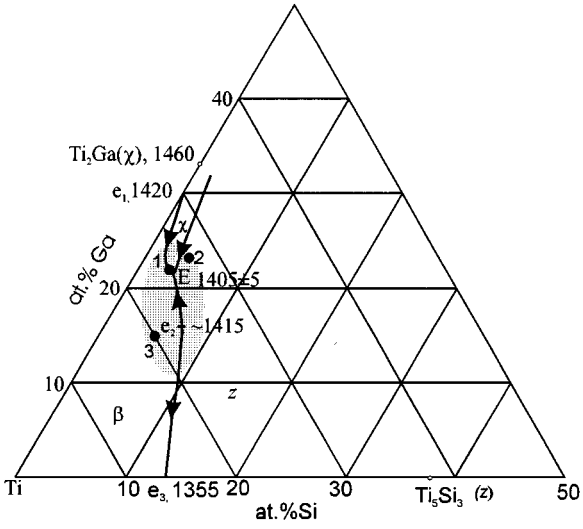

Figure 1 Liquidus surface projection of the Ti-Ga-Si system in the Ti-rich corner. (⬭): area of the investigated alloys; (●): compositions of investigated alloys.

3. Results

3.1. Structure of Ti-Ga-Si alloys in the region of >70 at % Ti

The projection of liquidus surface of the Ti-Ga-Si system in the Ti-rich corner is shown in Fig. 1. The liquidus surface is seen to consist of three surfaces which correspond to the temperatures of the primary crystallization of the following phases: Ti-based (β) phase, silicide $Ti_5(Si,Ga)_3$ (z) and Ti_2Ga (χ). Liquidus surfaces mentioned above intersect through the three monovariant curves, which meet in the ternary eutectic point E. The positions of the monovariant curves and the point E were determed on the basis of primary crystallization phases data. The alloys solidification completes at the temperature equal to $1405 \pm 5\,^{\circ}C$. e_1E and e_3e_2E curves correspond to the process of joint eutectic crystallization of β with χ and β with z respectively, and pE curve-peritectic $L + z \Leftrightarrow \chi$, which passes into the equilibrium of the eutectic type close to the point E.

It should be noticed that Ti_2Ga melts congruently in the binary Ti-Ga system [9], but in the ternary Ti-Ga-Si system it takes part in the peritectic reaction $L + z \Leftrightarrow \chi$. The width of the Ti_2Ga primary crystallization surface does not exceed 2 at %.

The curves eE and e_3e_2E correspond to a composition of liquids taking part in the monovariant eutectic reactions $L \Leftrightarrow \beta + \chi$ and $L \Leftrightarrow \beta + z$. Owing to these processes the as-cast alloys have refined eutectic structure. With increasing of the silicon content the temperature of the $L \Leftrightarrow \beta + \chi$ reaction decreases from 1420 °C in the binary Ti-Ga system down to $1405 \pm 5\,^{\circ}C$ in the ternary, the temperature of the $L \Leftrightarrow \beta + z$ reaction at first rises with increasing of Ga content from 1355 °C in the Ti-Si system up to ~1415 °C (e_2) and then decreases to $1405 \pm 5\,^{\circ}C$ (point E).

The region of the joint phases crystallization based on Ti- and Ti_5Si_3 is the most extended. The solubility of Ga in the silicide is considerable (up to 24 at %), so the refractory phase which is a constituent in the binary $\beta + z$ and ternary $\beta + \chi + z$ eutectics is the solid solution $Ti_5(Si,Ga)_3$.

TABLE I Structure of the eutectic Ti-Ga-Si alloys in the Ti-rich corner

Alloy no.	Composition of alloys	Phase composition	Structural constituents
1	Ti-3Si-22Ga (at %)	$\beta(\alpha) + \chi + z$	$e_1 + E$
2	Ti-4,6Si-22,7Ga (at %)	$\beta(\alpha) + \chi + z$	$z + E$
3	Ti-5Si-15Ga (at %)	$\beta(\alpha) + z$	$\beta(\alpha) + e_2$
BT-18	Ti-7,6Al-11Zr-0,6Mo-1Nb (mass %)	$\beta(\alpha)$	$\beta(\alpha)$

β is Ti-based phase, which transforms to $\alpha(\alpha')$ during cooling; z is the solid solution based on the compound Ti_5Si_3, $(Ti_5(Si,Ga)_3)$; χ is Ti_2Ga; e_1 is eutectic $\beta + Ti_2Ga$; e_2 is eutectic $\beta + Ti_5(Si,Ga)_3$; and E is ternary eutectic $\beta + Ti_5(Si,Ga)_3 + Ti_2Ga$.

It is to be noted that Ti-based (β) phase of bcc W-type structure was never observed in this study due to $\beta \Leftrightarrow \alpha$ solid-state transformation during cooling, therefore the X-ray patterns contained the reflections of the $\alpha(\alpha')$ phase of cph Mg-type structure.

Ternary compounds have not been found. The alloys of three compositions (Table I) containing a considerable volume fraction of eutectic matrix according to the Ti-Ga-Si phase diagram [10] were chosen for the investigation of the mechanical properties. It was shown, that alloys of region shown as grey in Fig. 1, have long-time hot hardness which is 2–3 times more than that known industrial alloy VT-18 (Ti-7.Al-11Zr-0.6Mo-1Nb (mass %)) at medium and elevated temperatures (200–800 °C) [11]. The high level of high-temperature resistance of these alloys can be explained the strengthening exerted by the dispersive participles of the refractory compounds Ti_2Ga and $Ti_5(Si,Ga)_3$, additionally to similar solid-solution influence, and the transition from single-phase $\beta(\alpha)$ to two-phase composite structure $\beta(\alpha) + z$ or $\beta(\alpha) + \chi$.

According to the phase diagram (see Fig. 1) and structure study of the samples No. 1, No. 2 and No. 3 the partials sections at 22.5 at % Ga and 15 at % Ga were constructed (Fig. 2a and b). For the explanation of the alloys structure it can be supposed with some approximation that the alloys No. 1 and No. 2 with 22 and 22.7 at % Ga respectively lie in the plane of the section which is shown in Fig. 2a. The alloy No. 3 with 15 at % Ga is in the plane of section shown in Fig. 2b.

The composition of the alloy No. 1 (75Ti-22Ga-3Si (at %)) lies on the monovariant curve e_1E close to the point E (Fig. 1), so its structure is presented by mixture of binary and ternary eutectics. Since the content of $Ti_5(Si,Ga)_3$ silicide in the ternary eutectic E is rather small and eutectic structure is extremely refined (Fig. 3a), we did not observe it in the as-cast alloys either by X-ray diffraction or by MSA methods, but it appears well in the annealed alloy. The crystallization of the alloy No. 2 (72.7Ti-22.7Ga-4.6Si (at %)) starts with precipitation of the primary $Ti_5(Si,Ga)_3$ grains (Fig. 3b) which as the temperature decreases have to interact with the liquid phase and due to this reaction Ti_2Ga phase should be formed. However, the peritectic reaction $L + z \Leftrightarrow \chi$, which occurs at the narrow temperature interval (between 1425 and 1405 °C) has no time to complete during the rapid cooling on the hearth of the arc furnace. Therefore, the structure of the alloy No. 2 is presented only with the small primary silicide grains in the ternary eutectic.

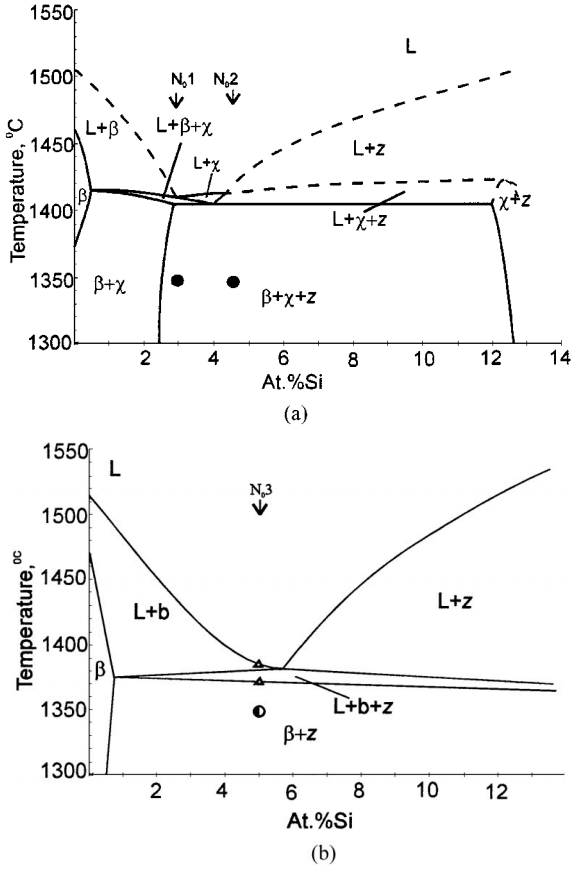

Figure 2 Section of the Ti-Ga-Si system at 22.5 at % Ga (a) and at 15 at % Ga (b); (◑): two-phase; (●): three-phase.

Alloy No. 3 (80Ti-15Ga-5Si (at %)) is in the two-phase region $\beta(\alpha)+z$ (Fig. 3c). The structure constituents of this alloy are primary grains of β Ti-based phase and the binary eutectic $\beta(\alpha)+z$ (Fig. 3c). The evidences of the $\beta \Leftrightarrow \alpha(\alpha')$ transformation, which takes place at cooling, are visible in the β grains.

3.2. Mechanical properties of the alloys

The results of the strength investigations of the alloys by means of testing by three point bend scheme are shown in Fig. 4. The highest strength is seen to be possessed the alloy No. 1. As was shown above, this alloy exhibits the high-refined eutectic structure formed by $\beta(\alpha)$, $Ti_5(Si,Ga)_3$ and Ti_2Ga phases (Table I). The rather good strength properties of this alloy can be explained by high-dispersive structure of the strengthening phases $Ti_5(Si,Ga)_3$ and Ti_2Ga (mainly Ti_2Ga).

The appearance of the primary grains $Ti_5(Si,Ga)_3$ in the structure of the alloy No. 2 the sharp decreasing of its strength and rising of brittleness. The particles of the brittle silicide are concentrators of stress at deformation and, as a rule, promote a decrease of the strength and especially ductility properties.

Alloy No. 3 possesses the most favourable combination of strength and ductility. Its structure is presented by the primary Ti-based (β) phase and eutectic $\beta(\alpha)+z$ which has the composition close to the composition of the pseudobinary eutectic e_2. According to our estimation the content of the silicide $Ti_5(Si,Ga)_3$ in this alloy is near 15 vol %. This is considerably less than the content of the gallide phase Ti_2Ga in the alloy No. 1

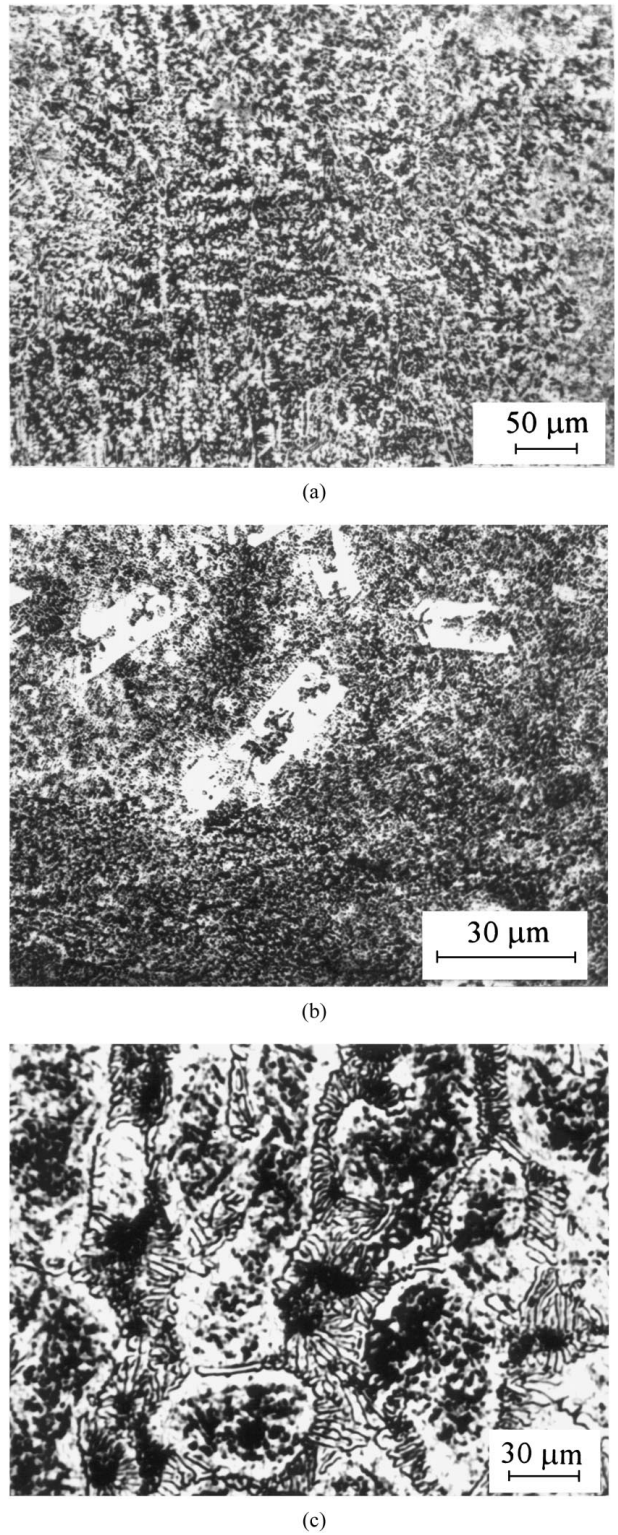

Figure 3 Microstructure of the as-cast Ti-Ga-Si alloys: (a) Ti-22Ga-3Si (b); (1) Ti-22.7Ga-4.6Si (2); (c) Ti-15Ga-5Si(3).

(~40 vol %) and the gallide-silicide in the alloy No. 2 (>40 vol %), that provides its acceptable ductility.

Mechanical properties of the Ti-Ga-Si alloys in the Ti-rich area are formed under the influence of both dispersional and solid solution strengthening mechanisms. The solution of gallium in the titanium phase results in strengthening. Moreover the increase of the $\beta \Leftrightarrow \alpha(\alpha')$ transformation temperature provides the additional rise of the high-temperature resistance. The decrease of the silicon content in the metallic phase with solution of gallium in it (from 4.7 at % Si at the eutectic temperature

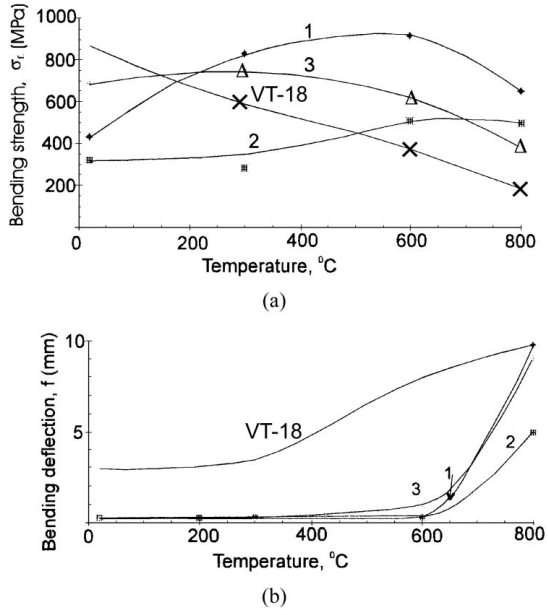

Figure 4 Temperature dependence of the mechanical properties for as-cast Ti-Ga-Si alloys: (a) bending strength; (b) bending deflection.

in the Ti-Si system up to ∼1 at % Si at Ga content more than 15 at %) is also favourable.

Solution of gallium in the silicide $Ti_5(Si,Ga)_3$ occurs through the substitution of the silicon atoms by gallium ones. Besides the melting point of the silicide decreases from 2130 °C (for Ti_5Si_3) down to ∼1400 °C in the three phase alloys No. 1 and No. 2, but in the two-phase alloy No. 3 this phase is enough refractory (∼1800 °C). Therefore, its presence in the alloy No. 3 is more favourable in comparison with the silicide ($T_{melt} = \sim 1400$ °C) and the gallide ($T_{melt} = 1460$ °C) in the alloys No. 1 and No. 2.

Eutectic $\beta(\alpha) + Ti_5Si_3$ in the Ti-Si system, which is the base for the development of the composite materials, obtained by the directional solidification, contains 13.5 at % Si and melts at 1355 °C. Alloying with gallium decreases with content of silicon in the eutectic down to ∼7 at % Si in the alloy No. 3 and almost down to 3 at % in the ternary eutectic in the alloys No. 1 and No. 2. Simultaneously the temperature of the eutectic reaction rises. The maximum temperature of the eutectic reaction, ∼1415 °C, is observed for the alloys, which are on the tie-line, corresponding to the pseudobinary eutectic reaction $L \Leftrightarrow \beta(\alpha) + z$. Alloy No. 3 is close to this tie-line, and the composition of the eutectic mixture in it is close to the composition of the pseudobinary eutectic with maximum melting temperature.

On the base of all facts considered above one can conclude that in the alloy No. 3 the most favourable conditions for the occurrence of the highest mechanical properties at the elevated temperatures are realised.

Alloy No. 1 with mainly Ti_2Ga strengthening at the temperatures above 800 °C along with good high-temperature strength revealed good ductility too.

Thus, the investigated alloys are found to possess considerably more high strength at the elevated temperatures than that of the commercial alloy VT-18, but the first alloys have a worse ductility at the room temperature. Mechanical properties improvement of the alloys investigated in present work in comparison with VT-18 is the result of the reinforcements with the refractory particles of the secondary phases—Ti_2Ga and $Ti_5(Si,Ga)_3$.

4. Conclusion

1. According to the phase diagram [11] and structure studies of the alloys the partial sections which the compositions of alloys investigated are in were constructed.

2. The bending strength and the bending deflection are determined over the temperature interval of 20–800 °C.

3. The correlation between structure and mechanical properties is considered. The most favourable combination of strength and ductility is found for the alloy with $Ti_5(Si,Ga)_3$ strengthening (No. 3). The mechanical properties of this alloy are formed under influence of both solid solution and dispersional mechanisms of strengthening.

4. The alloys with mainly Ti_2Ga strengthening have good strength and ductility at the elevated temperatures too. But they possess rather high brittleness at the medium and room temperatures. This fact can be explained by the large content of the gallide phase (∼40 vol %).

5. Thus gallium can be used as effective element to improve the Ti alloys mechanical properties, in particular Ti-Si alloys.

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