TITANIUM ALLOYS WITH $TI_3(SI, GA)_3$ AND TI_2GA STRENGTHENING

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SUMMARY: The structure and mechanical properties of the Ti-Si-Ga and Ti-Al-Ga alloys (long-time and hot hardness, bending strength and bending diflection) with “in situ” and intermetalic structure over the temperature rang of 20-800^{0}C are presented. The samples were prepared by melting under an pure argon in arc- furnace from commercially available metals. The correlation between structure and mechanical properties is discussed. Mecanical properties of the alloys investigated in this work are given in comparision with properties of the industrial alloy VT-18 (Ti-7Al-11Zr-0.6Mo-1Nb (mass.%)). The investigated alloys are found to possess considerably more high strength at the medium and elevated temperatures than that of the industrial alloy VT-18, but they have a worse ductility at the room temperatures. Thus gallium can be used as effective element for the improving of the Ti alloys mechanical properties.

KEYWORDS: Ti-Ga-Si system, Ti-Ga-Al alloys, liquidus surface, isothermal section, mechanical properties, gallium, silicon, martensitic transformation**.**

INTRODUCTION

Attractive elevated-temperature properties and low density, good oxidation resistance make the titanium aluminides Ti_3Al, TiAl, $TiAl_3$ very interesting for both engine and airframe application, particularly in airspace industry. However, they are extremely brittle near the room temperatures. Alloying of Ti-Al alloys by the elements that retain the attractive high temperature properties whilst improving the low temperature ductility should solve this problem. The influence of isomorphous β-stabilizers of titanium , such as Mo, Nb, Ta, V, W etc. and those which forms eutectoids, such as Cr, Mn, Fe, on the structure and properties of the Ti-Al alloys has been studied by many authors [1,2]. The alloying of titanium with α-stabilizers are almost not investigated. The systems on the Ti-base containing gallium were 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^{0}C) [3], gallium raises the temperature of α ⇔ β

transformation from 882 up to 940^0C [3]. 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 to a significant decreasing 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 1460^0C according to our data. It takes part in the eutectic reaction L⇔ β+ Ti_2Ga [3].

Recently we have investigated structure and some mechanical properties of the eutectic Ti-Ga-Si alloys [12,13]. These alloys are relevant to the group of the natural ('in situ") composites. In such materials the mechanism of strengthening is caused by the rainforcment with refractory phase on the base of the compounds Ti_5Si_3 or Ti_5Si_3 and Ti_2Ga jointly, which are included into a ductile titanium matrix. The alloys have refine eutectic structure due to "in situ" eutectic reactions L ⇔ β + Ti_5Si_3 [3] at 1355^0C [4] and L⇔ β+ Ti_2Ga [3] at 1425 ± 5^0C. Owing to the high thermodynamic stability and high melting temperature the compounds Ti_5Si_3 and Ti_2Ga and the solid solutions on them base can be an effective rainforsment. Such systems as Ti-Al-Si [5-9], Ti-Al-Si-Cr [10], Ti-Al-Si-Zr [11] already have been studied last time. The new heat-proof materials based on them are being developed.

The aim of present study was to carry out the same investigation of the Ti-Ga-Al alloys and to evaluate influence of the different gallium additions on the structure and mechanical behaviour of the eutectic alloys on the Ti-base with silicon and Ti_3Al-base alloys. Mechanical properties of the investigated alloys in present work are given in comparison with conventional alloy VT-18 (Ti-7.Al-11Zr-0.6Mo-1Nb (mass.%)).

EXPERIMENTAL PROCEDURE

The samples were prepared from commercially available metals of high purity (iodide titanium (99.98%), silicon semiconductive monocrystals (99,999%), aluminium (99.995) and gallium (99,99%)) in an arc-furnace with a nonconsumable tungsten electrode on a water-cooled copper hearth under an argon 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 ^{o} C for 70 h under a high purity argon, that is about 100 ^{o} 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 alloys. X-ray studies were carried out with powders of as-cast and annealed samples employing the Debye-Scherrer method by means of URS-2.0 device in a camera with d=57.3mm or DRON-UM diffractometer with monochromic CuKα radiation.

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 the express method of high-temperature and long-time hardness and scheme of the three-point bend on the air over the temperature interval of 20-800^0C. The samples were annealed at 900^0C for 3h befor testing. 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.

RESULTS

1.1. Structure of Ti-Ga-Si alloys in the Ti-rich region.

The projection of liquidus surface of the Ti-Ga-Si system for the Ti-rich corner is shown in the Fig. 1. The liquidus surface is seen to consist of three surfaces which correspond to the temperatures of the primary crystallization of following phases: Ti-based (β) phase, silicide $Ti_5(Si,Ga)_3$ (z) and Ti_2Ga(χ). Liquidus surfaces mentioned above intersect through three monovariant curves, which meet in the ternary eutectic point E. The positions of the monovariant curves and the point E were determined on the basis of primary crystallization phases data. The alloys solidification completes at the temperature equal to 1405±5°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 to peritectic equilibrium L + z ⇔ χ, which transforms into the equilibrium of the eutectic type close to the point E. The temperature of the L ⇔ β + 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 down to 1405±5°C (point E).

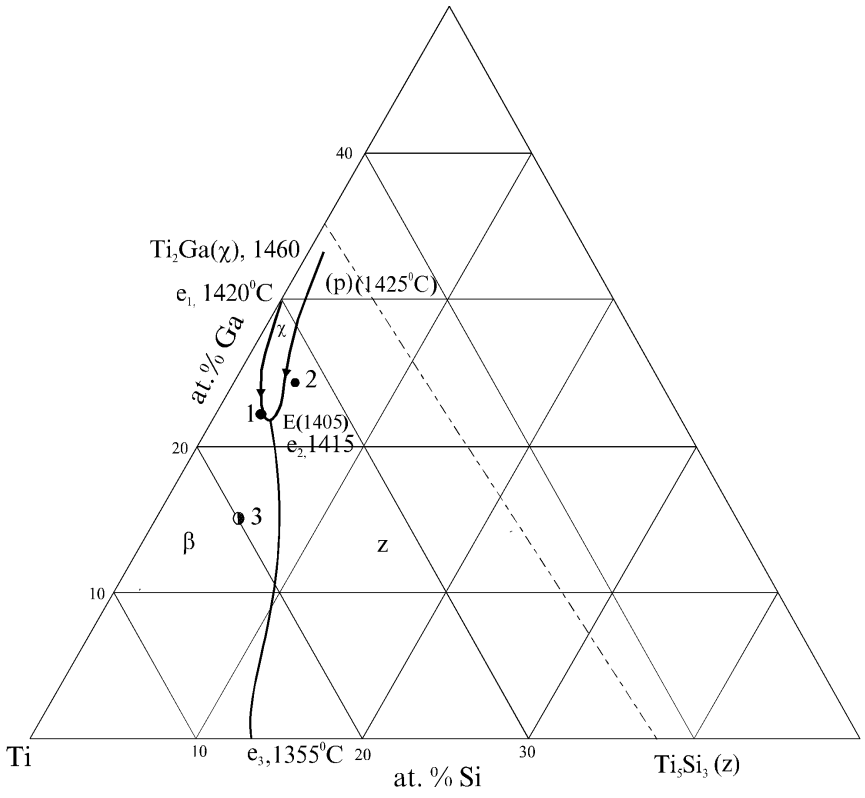


Fig 1: liquidus surface projection of the Ti rich corner of the Ti Si Ga system

The region of the joint crystallization of phases 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 structural constituent of the binary β+z and ternary β+χ+z eutectics is the solid solution $Ti_5(Si,Ga)_3$.

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

Ternary compounds have not been found.

The alloys of three compositions (Tabl. 1) containing a considerable volume fraction of eutectic matrix according to the Ti-Ga-Si phase diagram were chosen for the investigation of the mechanical properties.

The composition of the alloy $N^0$1 (75Ti-22Ga-3Si (at.%)) lies on the monovariant curve e_1E close to 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. 2, a), 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 structure of the alloy $N^0$2 (72.7Ti-22.7Ga-4.6Si (at.%)) consist from small primary $Ti_5(Si,Ga)_3$ grains included into fine ternary eutectic (2, b).

Alloy $N^0$3 (80Ti-15Ga-5Si (at.%)) is situated in the two-phase region β(α)+ z (Fig. 2, c). The structure constituents of this alloy are primary grains of β Ti-based phase and the binary eutectic β(α) + z (Fig. 2, c). The evidences of the β⇔ α(α‘) transformation, which takes place during cooling are visible in the β grains.

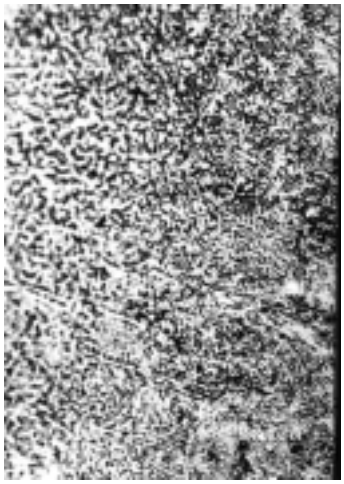


Fig 2a

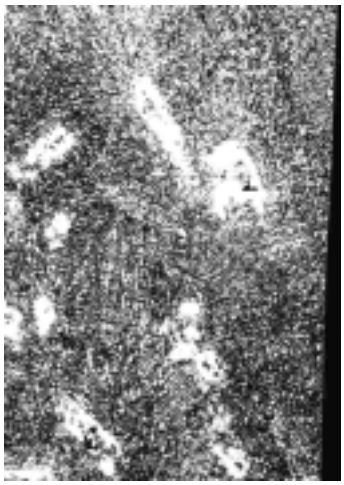


Fig 2b

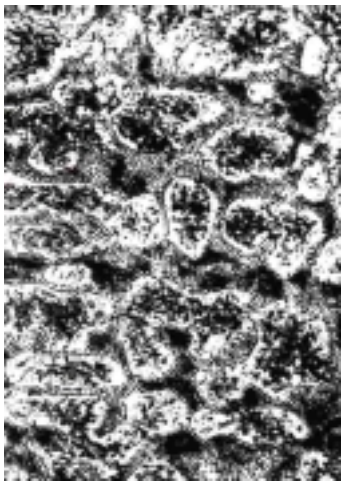


Fig 2c

1.2 Mechanical properties of the Ti-Ga-Si alloys.

1.2.1. Lond-time hardness.

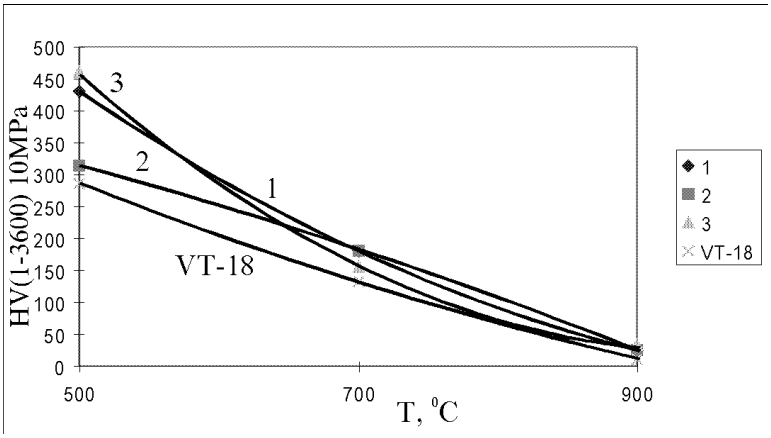


Fig 7 : Long time hardness of the Ti-Ga-Si Alloy

The results of the Ti-Ga-Si alloys testing by long-time hardness method are presented in Fig.3 [10]. It was shown [10], that alloys of region shown as grey in the Fig. 1 have long-time hardness which is 2-3 times more than known commercial alloy VT-18 (Ti-7.Al-11Zr-0.6Mo-1Nb (mass.%)) at medium and elevated temperatures (200-800^{0}C). The high level of high-temperature strength of these alloys can be due to strengthening exerted by the dispersive particles of the refractory compounds Ti_2Ga and $Ti_5(Si,Ga)_3$, additionally to similar solid-solution influence, and the conversion from single-phase $\beta(\alpha)$ to two-phase composite structure $\beta(\alpha)$ + z or $\beta(\alpha)$ + χ.

1.2. 2. The bending strength and the bending deflection.

Fig. 4 shows the bending strength and bending deflection curves [11].The strength test was conducted by three point bend scheme method. The highest strength is seen to be possessed by the alloy N^{0}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). The rather good strength properties of this alloy can be explained by finely dispersed structure of the strengthening phases $Ti_5(Si,Ga)_3$ and Ti_2Ga (mainly Ti_2Ga).

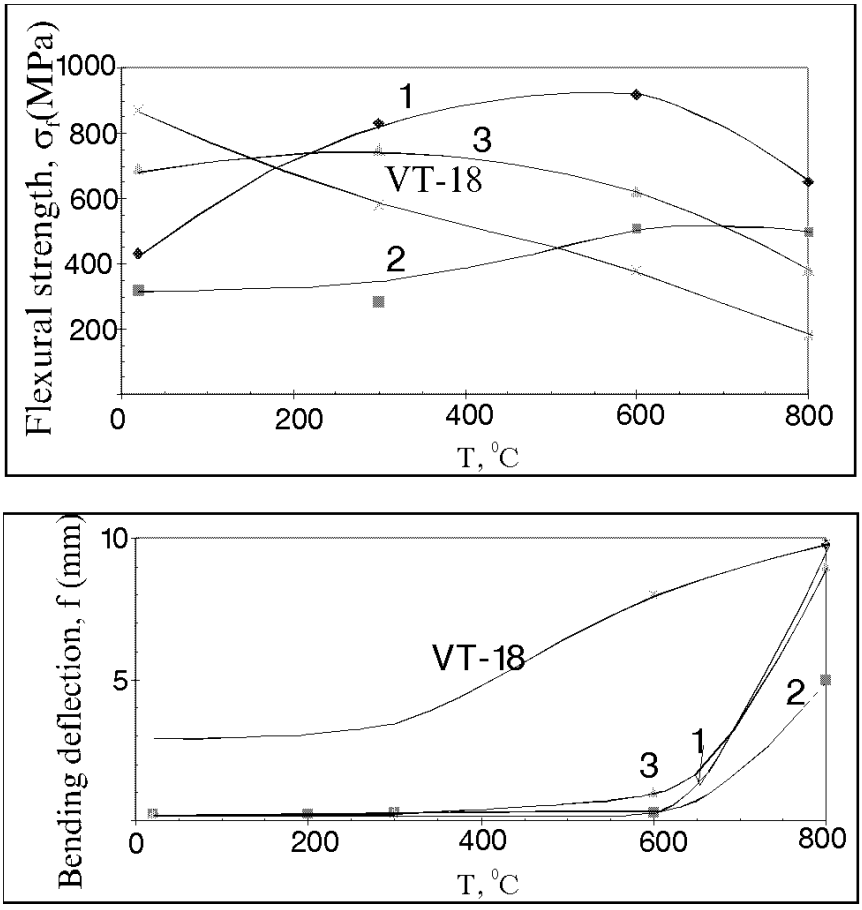


fig 4 – Flexural strength and bending deflection if the Ti-Ga-Si alloys

The appearance of the primary grains $Ti_5(Si,Ga)_3$ in the structure of the alloy N^{0}2 leads to the sharp decreasing of its strength and rising of brittleness. The particles of the brittle silicide are stress concentrators at deformation and, as a rule, promote a decrease of the strength and especially ductility properties.

Alloy $N^0$3 possesses the most favourable combination of strength and ductility. Its structure is presented by the primary Ti-based phase(β) and eutectic β(α) + 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 $N^0$1 (~70 vol.%) and the gallide-silicide in the alloy $N^0$2 (>70 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 leads to its strengthening. Moreover the increase of the β⇔α(α‘) transformation temperature provides the additional rise of the high-temperature strength. 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 in the Ti-Si systemto ~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. At that the melting point of the silicide decreases from 2130 (for Ti_5Si_3) down to ~1400^{0}C in the three-phase alloys $N^0$1 and $N^0$2, but in the two-phase alloy $N^0$3 this phase is enough refractory (~1800^{0}C). Therefore its presence in the alloy $N^0$3 is more favourable in comparison with the silicide (T_{melt}=~1400^{0}C) and the gallide (T_{melt}=1460^{0}C) in the alloys $N^0$1 and $N^0$2.

Eutectic β(α)+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^{0}C. Alloying by gallium decreases the content of silicon in the eutectic down to ~7 at.%Si in the alloy $N^0$3 and almost down to 3 at.% in the ternary eutectic in the alloys $N^0$1 and $N^0$2 which is favorable for ductile properties. Simultaneously the temperature of the eutectic reaction rises. The maximum temperature of the eutectic reaction, ~1415^{0}C, is observed for the alloys, which are on the tie-line, corresponding to the pseudobinary eutectic reaction L⇔β(α)+z. Alloy $N^0$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 $N^0$3 the most favourable conditions for the occurrence of the highest mechanical properties at the elevated temperatures are realised.

Alloy $N^0$1 with mainly Ti_2Ga strengthening at the temperatures above 800^{0}C besides 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 temperatures. Mechanical properties improvement of the alloys investigated in present work in comparison with VT-18 is the result of the dispersional strengthening by the refractory particles of the secondary phases - Ti_2Ga and $Ti_5(Si, Ga)_3$.

2.1. Structure of Ti-Ga-Al alloys in the Ti-rich region.

The isothermal section of the Ti-Ga-Al system at 1350^{0}C in the Ti-rich region is shown in Fig.5.

Table 2 shows phase compositions and the temperature of the phase transformations of the investigated alloys. The existence of the broad homogeneity region of the cristallization on the (βTi)-base is found. The β-phase with bcc W-type structure transforms in to the α(α‘)-Ti phase of Mg-type structure or α_2 of Ni_3Sn-type structure due to β Δ α(α_2) solid-state

martensitic transformation at low temperature. In the alloy TiAlGa1 with rather high gallium contens the Ti_2Ga precipitates from the (βTi) at cooling too peritectoidaly and Widmanstätten structure is formed. Morphology of the former β phase is very unique, becaus it is similar to eutectic (Fig.6 a, b). Such morphology conserves after annealing at 1350^0C for 70h. Alloy TiAlGa2 with small gallium adding has typical martensite of titanium.

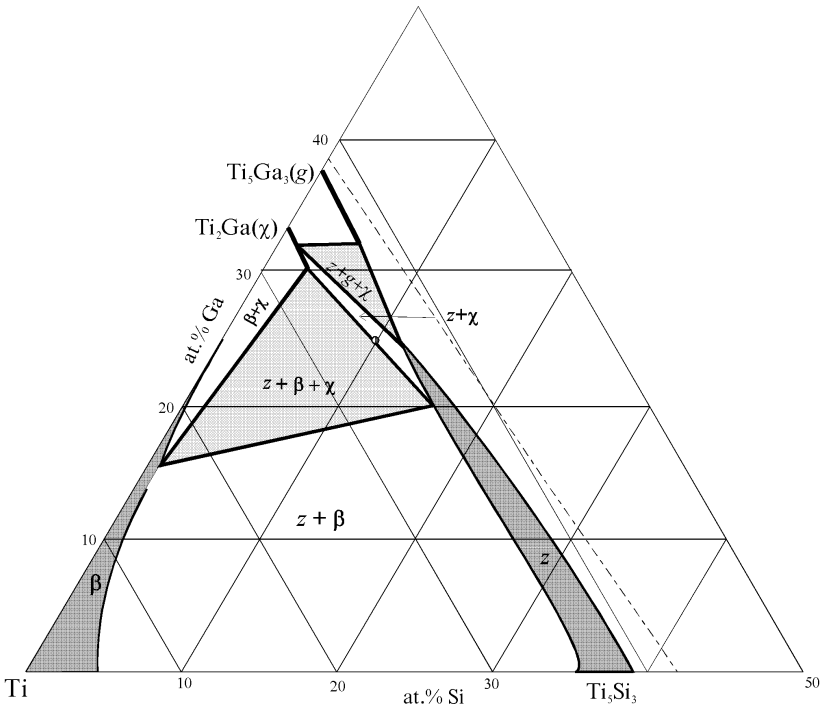
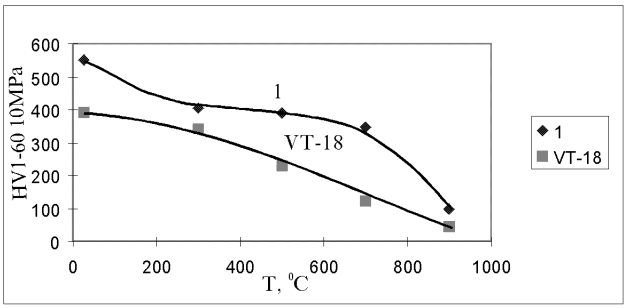


Fig 5 : Isothermal Section of the Ti Si Ga system at 1350°C [4]

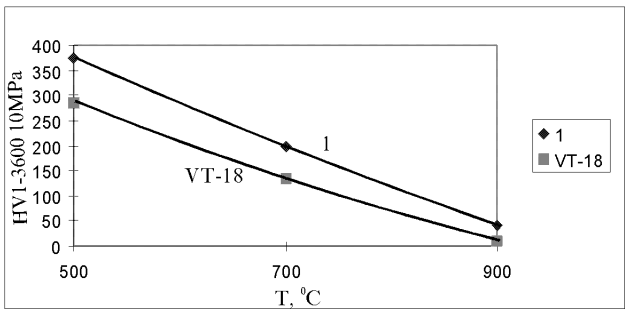
2.2. Mechanical properties.

2.2.1. Hot and long-time hardness.

Fig.7 shows hot and long-time hardness-temperature curves of the TiAlGa1 alloy. This alloy exibits a good hardness at medium and high temperatures.



a



b

Fig 8 – Long time and hot hardnessof the Ti Ga Si Alloy

2.2.2. Bending strength and bending diflection.

As one can see from Fig. 8, Ti-Al-Ga alloys exibit a good strength (σ_f) over temperature rang of 200-800^{0}C. What is interesting, the bending stength rises with increasing of temperature. This is result is not clear until.

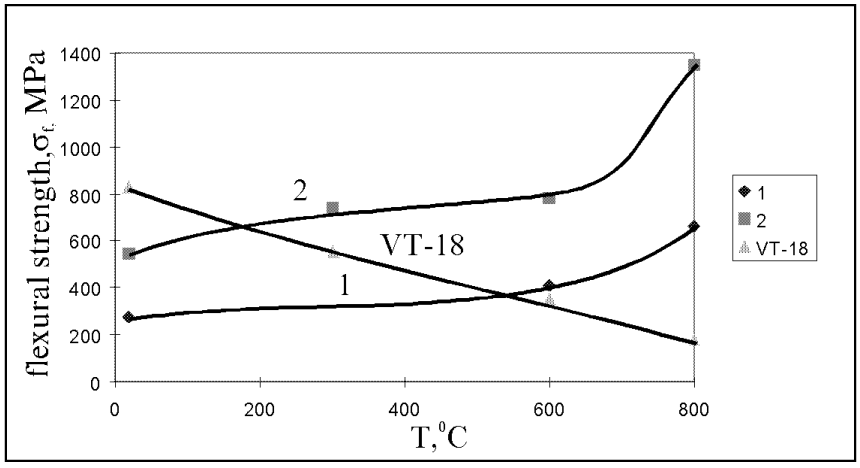


Fig. 8 Flexural strength of the Ti-Si-Ga Alloys – TiGaAl1 and Ti GaAl2

Bending diflection (f) of the both alloys is about 1.2 mm at 600^{0}C. This is worse than that for VT-18, but not bad.

The mechanical properties of Ti-Al-Ga alloys in the β region are formed under influence of the both dispersional and solid solution factors. The solution of gallium in the titanium and Ti_3Al phases leads to them strengthening. Precipitation of the dactile and reinforce T_2Ga compound from β during cooling provides unique dispersive structure and complementary strengthening. Moreover the increasing of the βΔα(α‘) transformation

temperature from 880 to 925^{0}C provides the additional rising of the high-temperature resistance.

Conclusions.

1. The investigated alloys are found to possess considerably more high strength at the elevated temperatures than that of the industrial alloy VT-18, but the such alloys have a worse ductility at the room temperatures.

2. The correlation between structure and mechanical properties is considered.

Thus gallium can be used as effective element to improve the mechanical properties of Ti alloys, in particular alloys on the Ti-Si and Ti_3Al base.

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Fig 6A

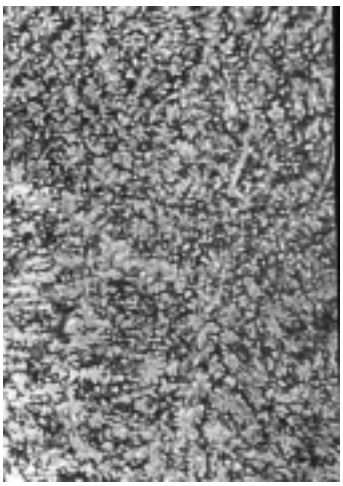

Fig 6B

Table 1: Structure of the eutectic Ti-Ga-Si alloys in the Ti-rich corner.

Alloy [1]	Composition of alloys	Temperature of the transformation, ^{0}C T_s T_{melt}		Phase composition	Structure constituents
1	Ti-3Si-22Ga(at.%)	1405±5	1440	β(α)+χ+z	e_1+Å
2	Ti-4,6Si-22,7Ga(at.%)	1405±5	-	β(α)+χ+z	z+E
3	Ti-5Si-15Ga(at.%)	1410±5	1445	β(α)+z	β(α)+e_2
BT-18	Ti-7,6Al-11Zr-0,6Mo-1Nb (mass. %)			β(α)	β(α)

β- Ti-based phase, transformed in α(α′) at cooling;
z - solid solution on the Ti_5Si_3 compound base (Ti_5 (Si, Ga)$_3$);
χ - Ti_2Ga;
e_1 - eutectic β+Ti_2Ga;
e_2 - eutectic β+Ti_5(Si, Ga)$_3$;
E - ternary eutectic β+Ti_5(Si, Ga)$_3$+Ti_2Ga.

Table 2: Structure of the Ti-Al-Ga alloys in the Ti-rich corner.

Alloy [1]	Temperature of the transformation, ^{0}C T_s T_{melt}		Phase composition
TiAlGa1	1465±5	1530	β
TiAlGa2	1545±5	1590	β

β- Ti-based phase, transformed in α(α′, α_2) and Ti_2Ga precipitates at cooling