Material science

DEVELOPMENT AND INVESTIGATION OF NANOCRYSTALLINE AND AMORPHOUS Ti-Zr-Si AND Ti-Zr-Ge ALLOYS

M.MIKABERIDZE, A.GACHECHILADZE, V.GABUNIA, D. RAMAZASHVILI

F. Tavadze Institute of Metallurgy and Material Sciences, Georgia, Tbilisi

Be received 12.03.2018

Abstract. *Corrosion resistant amorphous Ti-55Zr-15Ge and nanocrystalline Ti-23Zr-16Si alloys are received by the fast quenching method. The temperature dependence of internal friction and shear modulus of alloys points that alloying by germanium in comparison with silicon keeps better mechanical characteristics of alloys at high temperature.*
The electron diffraction analysis of alloys after the electrochemical investigations showed that on the surface of alloy samples two phases ZrO_2 and TiO_2 have been revealed after the researches in 10% solutions of NaOH and HCl. The conducted researches give the ground to expect that the behaviour of Ti-55Zr-15Ge and Ti-23Zr-16Si alloys are defined by passivation of titanium in the studied solutions. This effect helps rising the corrosion resistance of alloys.
Alloys are recommended for hardening working surface of medical tools of multiply usage. Application of new alloys will allow improving functional properties and increase quality, reliability and service life of medical tools. Alloys with increased hardness, strength and corrosion resistance are not only suitable for medical tools, but are improvements on currently used materials.

Key words: *nanocrystalline, amorphous, titanium, alloys, corrosion resistance, fast quenching method, structure, physical-mechanical properties.*

Owing to its property strengths, Titanium has becoming a vital material across a number of industry sectors. Chemical process industries rely on outstanding corrosion resistance, consequently making Commercially Pure Titanium strip an ideal material choice. Other demanding applications within Aerospace, such as static and rotating gas turbine engine components, also require a combination of corrosion resistance, low weight and high strength. The ability to withstand some of the most critical and highly stressed conditions has made it ideal for use in civilian and military airframe parts [1-4].

Increased interest on the synthesis of nanocrystalline materials in recent years dates back to the pioneering investigations of H. Gleiter in 1981. He synthesized ultra-fine metallic particles using an inert gas condensation method and consolidated them in situ into small discs under ultra-high vacuum conditions. Since then a number of techniques have been developed in which the starting material is in gaseous state (Inert gas condensation, Sputtering, Plasma processing, Vapor deposition), liquid state (Electrodeposition, Rapid solidification, Pressure-quenching), or solid state (Mechanical alloying, Sliding wear, Spark erosion, Crystallization of amorphous phase). Most of the early results were based on materials produced by gas condensation technique, and porosity was an internal part of the materials. The properties and structures of these materials were interpreted on the basis of a two component mixture--crystalline and interfacial components--whereas they should have been interpreted by taking the porosity into account as well. In fact, reduction in Young's modulus values, increased diffusivities, and in general, variations in mechanical and physical properties have now been ascribed to the presence of porosity in these materials.

Wide-spread use and search for technological application of nanocrystalline materials require the availability of large quantities of well characterized materials with reproducible properties; and this needs to be done economically. Therefore, development of large-size bulk nanocrystalline materials without porosity is an urgent necessity.

Titanium is a standard material for medical devices such as hip joints, bone screws, knee joints, bone plates, dental implants, surgical devices, pacemaker cases and centrifuges due to its total resistance to attack by body fluids, high strength and low modulus. The body readily accepts titanium since it is more biocompatible than stainless steel. Titanium also has higher fatigue strength than many other metals. The unique qualities of titanium prove to be magnetic resonance imaging and computed tomography compatible .

Ultra thin layers of titanium with only a few microns thickness can be added to medical devices to provide marking properties. This process occurs at ambient temperatures and will not negatively affect medical devices. These thin layers of titanium will not change surface geometry of the medical products that are coated.

It is known that a titanium alloy must be subjected to the super plastic forming process at a high process temperature of 850° C. or more and a slow process rate of 10^{-3} /sec or less. However, since the super plastic property is significantly affected by microstructure, a titanium alloy consisting of fine grains can be subjected to the super plastic forming process at a lower process temperature and a quicker process rate. Thereby, as the nano-technology is developed, research into a method for manufacturing a titanium alloy having fine grains has been actively progressed.

On the other hand, a method for manufacturing a material having fine grains includes a powder metallurgy method, a mechanical alloying method, a rapid solidifying method, a recrystallization method, a forging method, a rolling method, and a drawing method. However, it is difficult to manufacture a material having a desired size using these methods, and internal pores may be formed in the material. Since, the size of the recrystallization grain is limited or the cross section is reduced by the increment of the deformation amount. Thus, a large amount of deformation cannot be applied to the material. Accordingly, there is a limit to refining the grain size of the material. Thus, these methods for refining the grain cannot be actually applied.

Recently, rigid-plastic working methods for performing plastic working with separate heat treatment and refining a grain in which pores are not formed have been suggested. The rigid-plastic working methods include a high pressure torsion (HPT) method, an equal channel angular pressing (ECAP) method, and so on. The HPT method shear-deforms a material at a high pressure and can be performed at a rapid rate even at room temperature. However, there is a limit in the size of the material, and the microstructure and the thickness of the material are inhomogeneous.

In case of titanium alloys, however, the process temperature of the titanium alloy is very high and the flow stress thereof is reduced as the deformation amount increases. Thus, extreme cracks may be generated in the surface of the titanium alloy when performing the ECAP method. Accordingly, it is difficult to manufacture a titanium alloy having nano meter-size grains by the ECAP method.Application of nanocrystalline and amorphous titanium alloys is very actual in medicine as for manufacturing of medical instruments including toolkit so for getting implants and coatings [5-11].

The objective of the present work was the development of new high corrosion resistant nanocrystalline and amorphous Ti-Zr-Si and Ti-Zr-Ge alloys (received by the fast quenching method) with increased strength and hardness by investigating phase equilibrium and structural transformations, physical-mechanical properties and corrosion resistance as well as giving recommendations for their application for some medical tools and coatings. There are no data in the literature on the behavior of ternary titanium alloys based on Ti-Zr. The influence of alloying elements such as silicon and germanium on the corrosion, physical, and mechanical properties is not investigated; there are scarce data about phase equilibrium in titanium rich multi component alloys.

The amorphous and nanocrystalline types of Ti-55Zr-15Ge and Ti-23Zr-16Si alloys are obtained by a fast quenching method. The x-ray analysis was made on the diffractometer Dron-2,0 on a copper radiation with a nickel filter. Alloys in fast-quenched condition, and also after annealing at 250-350^{0}C have identical diffractograms with a halo phase in the field of corners 2θ =38-39^0, that specifies their amorphous condition. Conversion from amorphous into crystal condition at 500^{0}C begins after 0.5 h and 1 h, for alloys Ti-Zr-Ge and Ti-Zr-Si accordingly. Crystallization of alloy Ti-Zr-Ge begins with extractions of original crystals of titanium and then zirconium germanides Ti_5Ge_3, Zr_5Ge_3 and after that α -phase based on titanium. During crystallization of amorphous Ti-Zr-Si alloy chemical compounds of (Ti, Zr) $_5Si_3$ type and then α -phase based on the titanium are formed. The temperature of crystallization of Ti-Zr-Ge alloy is 570^{0}C, while Ti-Zr-Si alloy has -620^0 C according to the diffraction - thermal analysis. By broadening lines of the obtained x-ray photographs it is possible to estimate the average grain size, which was calculated according to Debbie-Sheerer formula.Obtained results are given in table 1 and Fig. 1, 2.

Table 1

Alloys	Phases	Grain size, nm
Ti-55Zr-15Ge	amorphous	< 3
Ti-23Zr-16Si	$\beta+\alpha''+Ti_2Si_3$	≈100

Study of microstructure with contact and free surface of tapes has been performed. Micro structural research was carried out on a "Neophot-2" microscope at 320-600 increase.Micro structural research of alloys showed that the free surface of tapes is marked by homogeneity without crystal inclusions (Figures 3 and 4).

Study of mechanical properties and micro hardness showed that before starting of crystallization they are crisped, while their micro hardness increases with the rising of annealing temperature, especially for amorphous Ti-55Zr-15Ge alloy constitutes 600-700-kg/mm^2.Grain sizes and morphology extracted during annealing at 500^{0}C was studied on the transmission electron microscope IEM-1000 by the analysis of light-hollow and dark-hollow pictures.

Characteristic structure of Ti-Zr-Si alloy after annealing is presented on Fig.5,a. On a background of an amorphous matrix crystal extractions are clearly seen which are mainly of a spherical form. Poly dispersity of extracted grains takes place. The maximal size of extractions makes 1000Å. The annealing at 500^o during 2h brings to the increase of a part of a crystal phase - sillicide of (Ti, Zr) $_5Si_3$ type in the structure of the alloy. Thus, it has been established, that the alloy after annealing at 500^o about 1 hour has the structure consisting of an amorphous matrix with poly dispersive fine-crystalline extractions of sillicides (Ti, Zr) $_5Si_3$.Ti-23Zr-16Si alloy has a nanocrystalline structure and it is the meta stable. Alloy' structure is characterized by non stationary crystal state, which influences on its physical, mechanical properties and corrosion resistance. High corrosion resistance of this alloy is explained by formation of a homogeneous passive film on the surface without any defects. High speed of formation of a passive film defines corrosion resistance of the alloy. Introduction of silicon into Ti-Zr system defines formation titanium silicides in alloys. On account of a great difference in electro-negativity of titanium and silicon high-melting-point and stable titanium silicides with different kind of chemical bond are formed; hence they have different physical and chemical properties.In the presence of a high content of silicon in this system Ti and Zr silicides ($TiSi_3$, $TiSi_2$, Ti_3Si_5, Ti_5Si_3 and Zr_5Si_3) are formed. Microstructure of nanocrystalline Ti-Zr-Si alloy taken by an electron microscope is given in figure 5. There is a dark field pictures and micro diffractions from silicides – $(Ti, Zr)_5Si_3$.

Titanium silicides have high heat resistance, high temperature strength and corrosion resistance against oxidation. Process of spinning of Ti-Zr-Si alloy helps to enrich surface film of the alloy with titanium silicides. The formed passive film opposes diffusion of oxygen in the metal; it plays a part of a “barrier film” and it causes high corrosion resistance. From the other way out, silicon is a strong strengthener for titanium; it increases its heat resistance and high temperature strength. When increasing silicon content over 2%, strength increases linearly, but with less intensity; at the same time plastic properties reduce. Formation of titanium silicides in the form of dispersoids gives possibility to realize the mechanism of dispersion strengthening. Thus, strengthening of titanium by silicon in the saturation concentration and precipitations of dispersive inclusion of silicides increases physical and mechanical properties of Ti-23Zr-16Si alloy.

Nonelastic properties of alloys Ti-23Zr-16Si and Ti-55Zr-15Ce have been studied by a method of registration of logarithmic decrement of attenuation turn vibrations of swing pendulum. Temperature spectrum of internal friction and a square frequency were measured in temperature intervals from a room temperature to 600^0C. All measurements have been performed in vacuum, the heating speed was 2^0 c/min, a vibration deformation ~ $5 \cdot 10^{-6}$, frequency of curve vibrations, 3,7Hz.

The following factors have been observed on the spectrum of internal friction and on a share modulus of the Ti-23Zr-16Si alloy (Figures 6 and 7.). Slight decreasing of share modulus in the interval of temperatures from a room to 250^0C and hence slight increase of internal friction. This process is defined by increasing of diffusion activity of defects. Internal friction starts increasing from 250^0C, when reaching 300^0 an area of ~50^0C width is observed. The activation energy of this process is calculated by Vert-Marx formula: H=1,26 EV/atom; Frequency factor $\tau_0 = 10^{-14}sec^{-1}$.

Proceed from a structural state of the alloy (presence of intermediate metastable δ and α phases and dispersive precipitation of silicides) we can suppose that in this temperature interval interaction process of intermediate phases with dispersive chemical compounds become active. Thus, silicon which is introduced into Ti-Zr system in the quantity transcending the saturation concentration is segregated into dispersive precipitation of titanium and zirconium silicides. Interaction of dispersive precipitation of silicides with the interface of intermediate phases realizes dispersive strengthening bringing to increasing of mechanical properties of Ti-23Zr-16Si alloy.

The temperature dependence of internal friction and shear modulus of amorphous Ti-55Zr-15Ce alloy are given on the figures 8 and 9.On the temperature dependence spectrum of internal friction and shear modulus the following features are shown: In the 300-350^{0}C temperature interval the maximum of attenuation with the intensity $Q_m = 5 \cdot 10^{-4}$ is observed. Activation parameters of this process, calculated by the Verta-Marx formula are: H = 1,54 EV/atom $\tau_0 \approx 10^{-13}$, sec^{-1}. Introduction of germanium into the system Ti-Zr causes the formation of chemical compounds Ti_5Ge_3 and TiGe; titanium and zirconium have formed row of solid solutions too. The presence of germanides of titanium and zirconium and also the solid solution in the system Ti-Zr determines simultaneously the solutional and dispersion mechanism of titanium strengthening. The metallochemical properties of germanium and titanium are much nearer than properties of silicon and titanium in the system Ti-Zr-Si, that predetermines the high degree of strengthening of lattice during the addition of germanium into this system. This effect is observed on the temperature dependence of the share modulus. The high values of the share modulus of alloy Ti-55Zr-15Ce remain at higher temperatures in comparison with the alloy Ti-23Zr-16Si.

Electrochemical investigations of nanocrystalline Ti-23Zr-16Si alloy have been carried out in 10% solutions of sodium chloride, hydrochloric acid and sodium hydroxide. Potentiodynamic curves E-lgi are given on Figure 2.10. As the analysis of curves shows, this alloy is characterized with self passivation in sodium hydroxide solution; passive field at current density 0,8 $\mu A/sm^2$ during the 0,3V – 0,8V voltage interval. In the solutions of NaCl and HCl passivation takes place at lower current density – 0,9 $\mu A/sm^2$ (NaCl) and at ~ - 1,5 $\mu A/sm^2$ (HCl) but passive fields are comparatively narrow.

Corrosion current and rate was defined graphically, according to method proposed by us previously, and calculated. Results are given in table 2.2.Corrosion rate of this alloy in solution of sodium hydroxide is two orders higher than in NaCl and HCl solutions. Apparently it is caused by segregation corrosion resistant compounds $(Ti, Zr)_N Si_m$ on the surface of alloy.

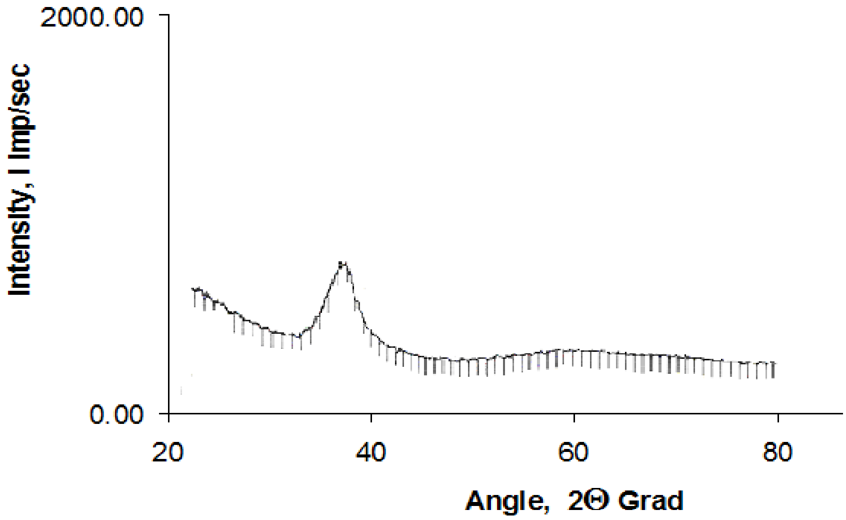


Fig. 1. X-ray diagram of Ti-55Zr-15Ge alloy

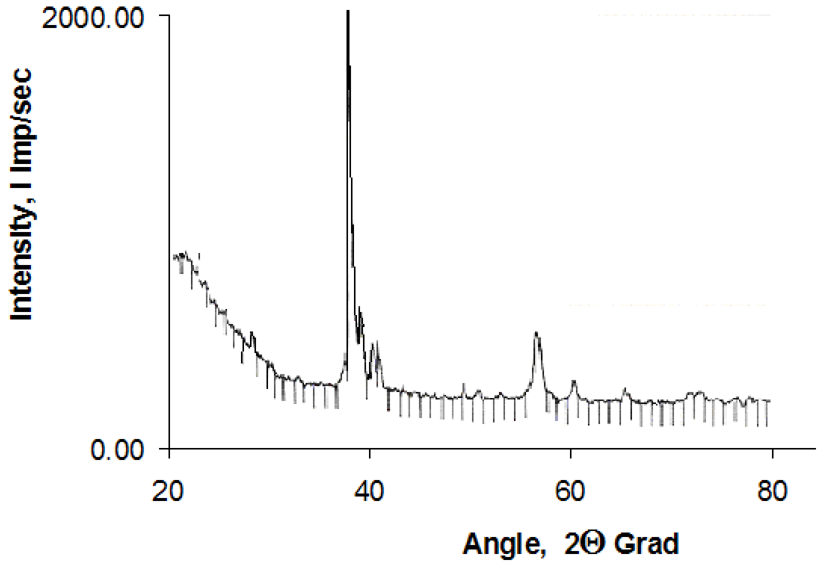
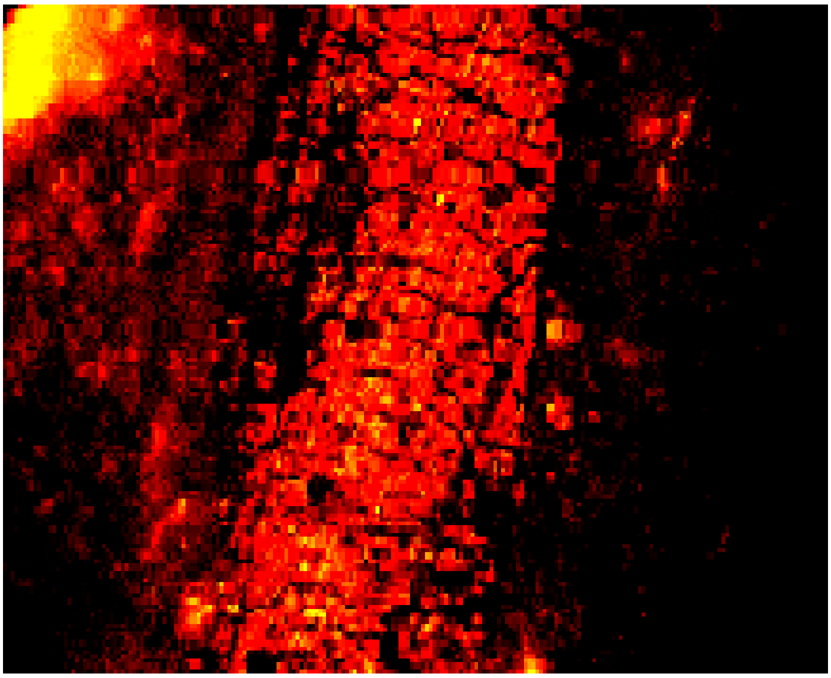
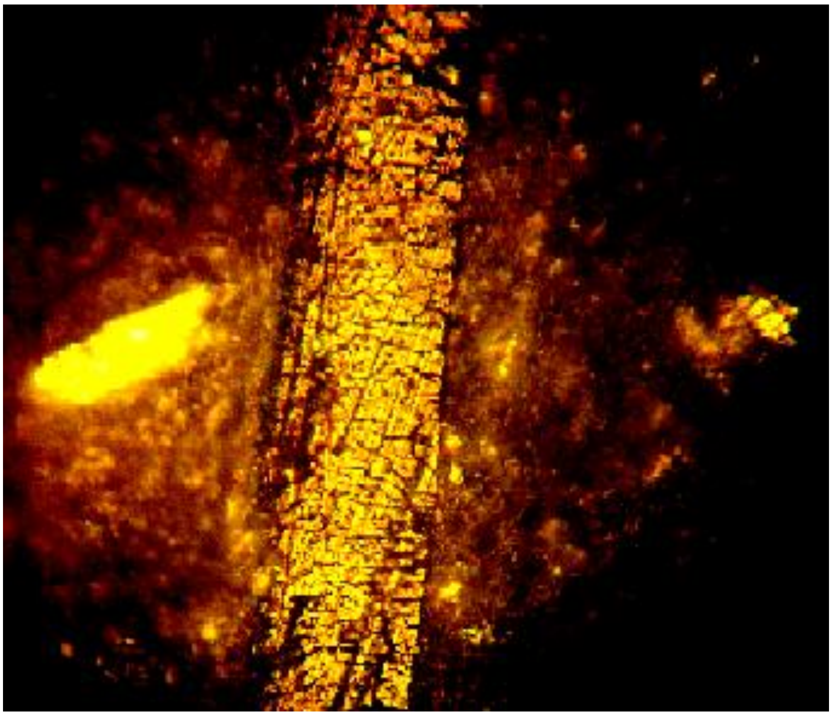


Fig. 2. X-ray diagram of Ti235Zr-16Si alloy

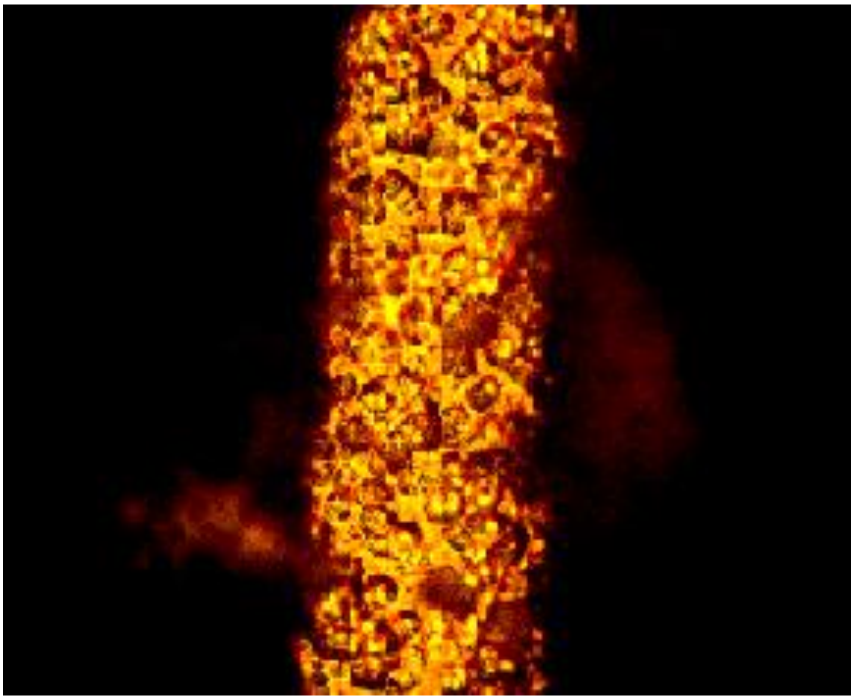


X 1000

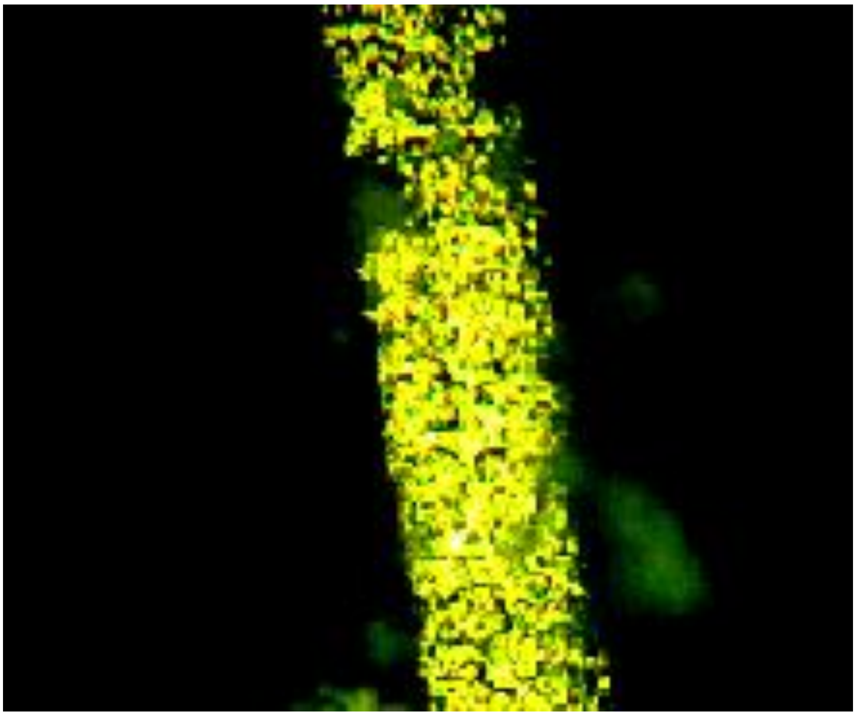


X 400

Fig. 3. Microstructure of the nanocrystalline alloy Ti-23Zr-16Si

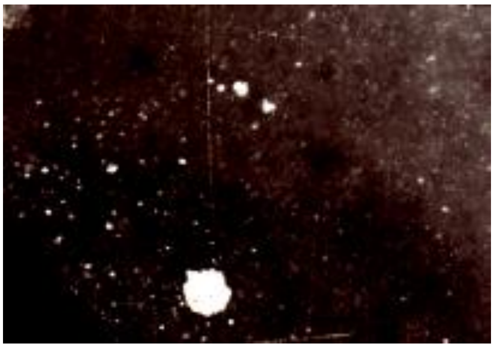


X 1000

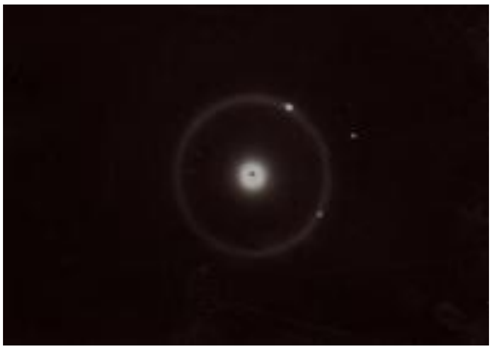


X 400

Fig. 4. Microstructure of the amorphous alloy Ti-55Zr-15Ge



a



b

c

X 25000

Fig. 5. Microstructure of Ti-23Zr-16Si alloy:
a – dark field picture;
b, c – microdiffraction;
c – microdiffraction from the silicides $(Ti,Zr)_5Si_3$

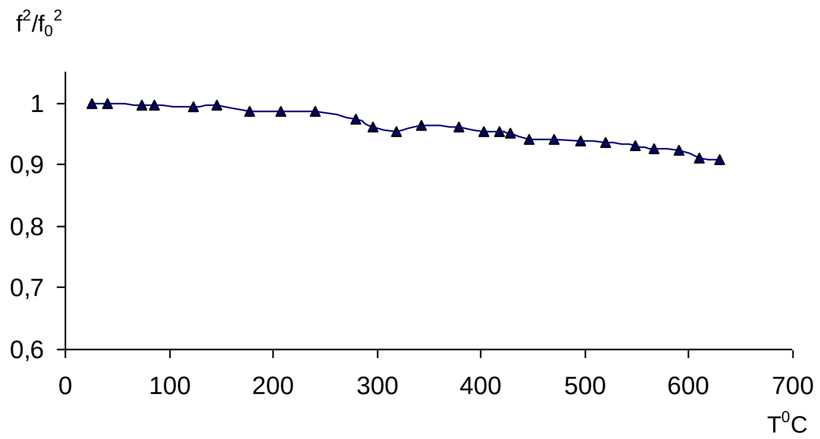


Fig. 6. Share modulus of Ti-23Zr-16Si alloy

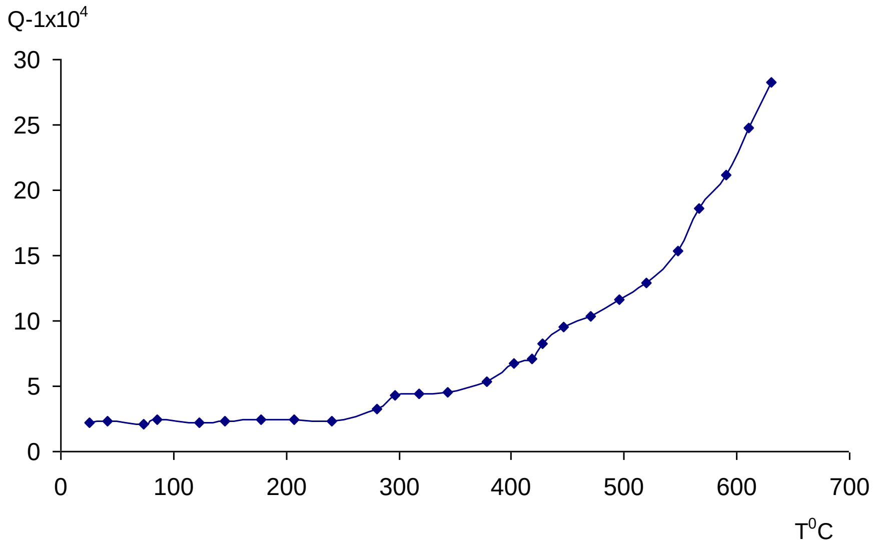


Fig. 7. Internal friction of Ti-23Zr-16Si alloy

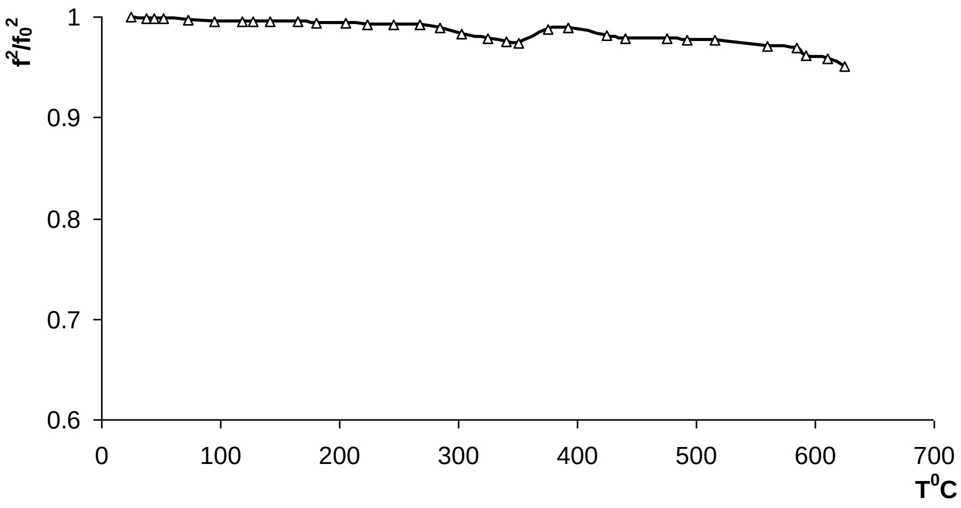


Fig.8. Share modulus of Ti - 55%Zr - 15%Ge

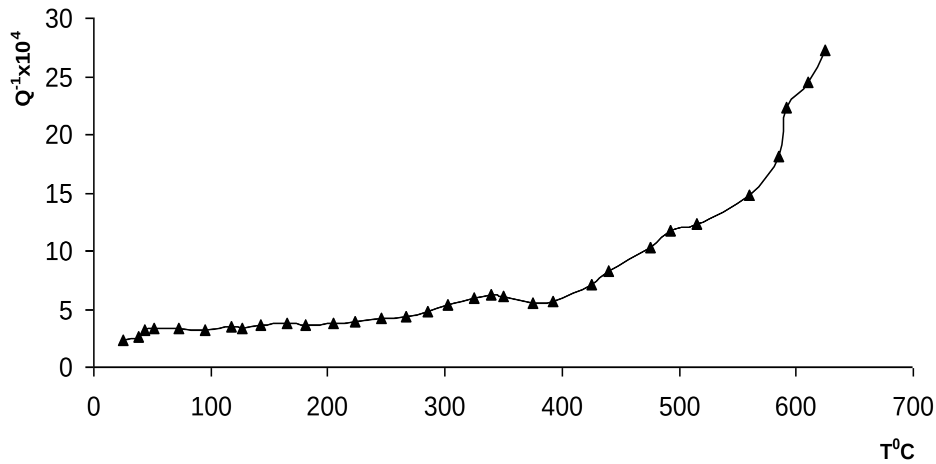


Fig.9. Internal Friction of Ti - 55%Zr - 15%Ge

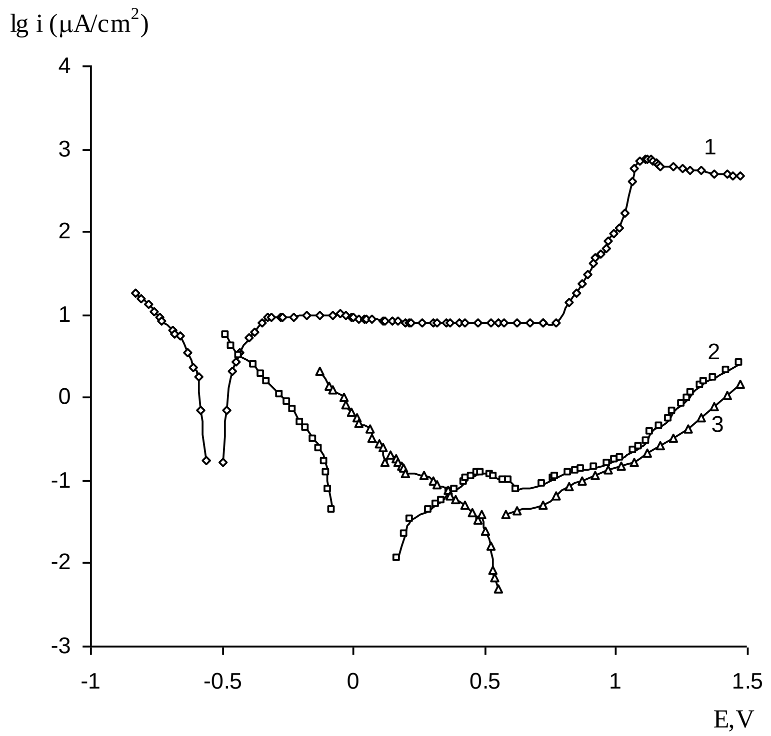


Fig.10. Potentiodynamic curves of Ti-23Zr-16Si alloy in 10% solutions:
1. NaOH; 2. NaCl; 3. HCl

Stationary potentials (E, V), corrosion currents (i_{cor}, μA/sm^2) and corrosion rate (K, g/m^{2}hr) of Ti-23Zr-16Si alloy in 10% solutions: NaCl, HCl and NaOH

Table 2

Solutions	**E, V**	**i, μA/sm^2**	**K, g/m^{2}hr**
NaCl	0,03	0,0040	0,00002
HCl	0,07	0,0067	0,00004
NaOH	-0,52	0,1670	0,0010

Electrochemical investigations of amorphous Ti-55Zr-15Ge alloy were conducted in the 10% solutions of hydrochloric acid, sodium chloride and sodium hydroxide. In 10% HCl alloy's instability was revealed. As a result of dissolution the stationary potential is not established (it skips within the limits – 0,007- +0,004V). The corrosion centers are conceived in the cathodic area of which regenerate themselves into the transparent (through) ulcers. A sample by the weight of 0,0042 g. was dissolved completely in 24 hours without an external current. Decrease of concentration of acid up to 1% somehow increases the potential of corrosion and within 100 minutes remains equal +0,08V. The pittings are formed on the anode part of curve at the E=0,02 V. In the acidulous solution of sodium chloride (pH=3) electrode potential is equal to +0,05 V. Pittings appear already at the potential +0,9V.

The potentiadynamic curves of amorphous alloy Ti-55Zr-15Ge in 10% solution of NaCl are given on figure 11. Established electrode potential is equal to – 0,015 V. On the anodic curve the area of self – passivation is observed within the limits of – 0,1 – 1,0 V. In this area calculated corrosion rate of alloy composes $0,0008 \cdot 10^{-6}$ g/m^2h. Corrosion rate, calculated graphically on crossing of the Tafel's sections of anodic and cathodic curves does not exceed $8,94 \cdot 10^{-6} g/m^2h$. Presence of chlorine ions promotes initiation of pittings. Potential +0,07 V is a breakdown potential. Visual control of alloy after testing showed the presence of two shallow pittings. Reduction of the concentration NaCl up to 5% promotes insignificant increasing of stationary potential up to +0,08 V, but doesn't influence on character of corrosion processes. In this case a breakdown potential also corresponds to value +0,07 V.

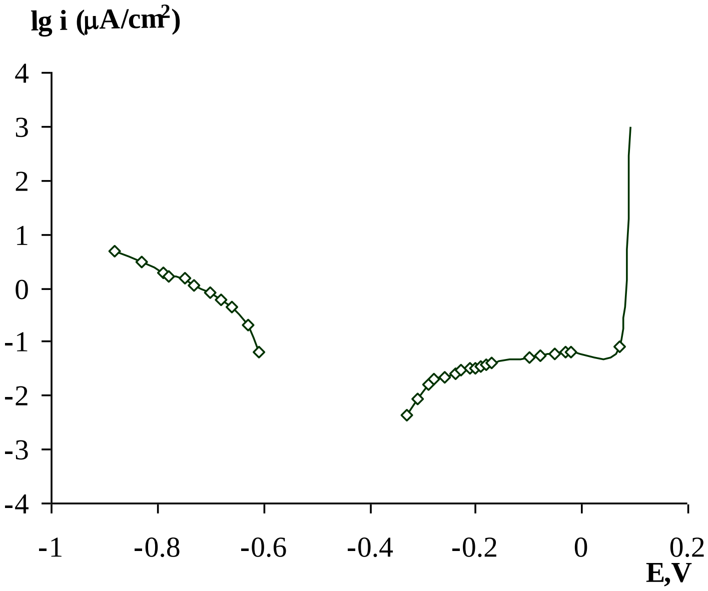


Fig.11. Potentiodynamic curve of amorphous Ti-55Zr-15Ge alloy in 10% NaCl solution

In 10% NaOH solution the stationary potential of alloy is equal to– 0,28 V. On the anodic curve the feebly marked area of active dissolution and passivation is observed (Fig.12.). Corrosion rate, determined graphically is near to zero. In passive area average of corrosion rate is also minimal. After the potential +0,73 V begins the transpassivation and then an area of secondary passivation takes place.

The electron diffraction analysis of alloys after the electrochemical investigations has been carried out. On the surface of alloy samples two phases ZrO_2 and TiO_2 (rutile) have been revealed after the researches in 10% solutions of NaOH and HCl. The conducted researches give the ground to expect that the behaviour of Ti-55Zr-15Ge and Ti-23Zr-16Si alloys are defined by passivation of titanium in the studied solutions.

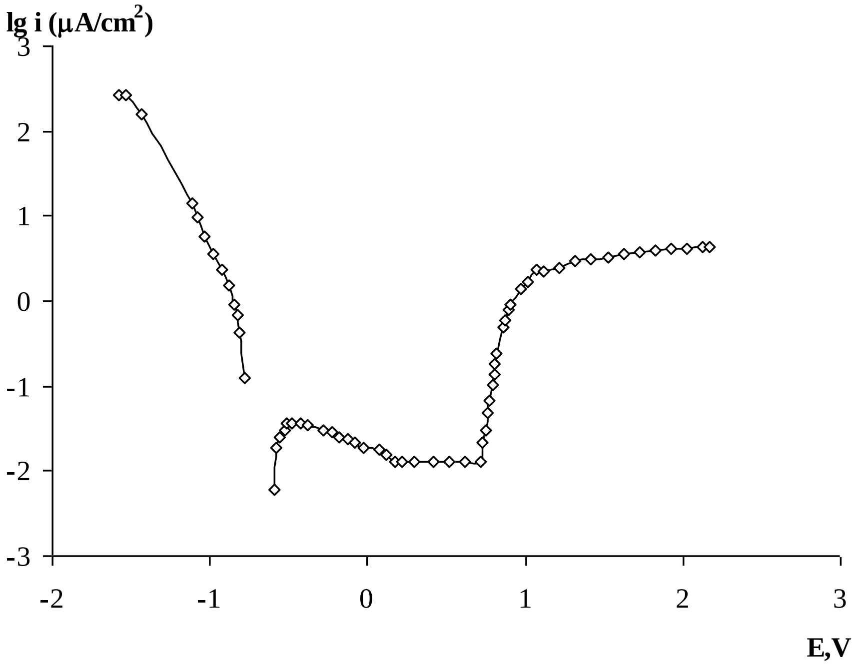


Fig.12. Potentiodynamic curve of amorphous Ti-55Zr-15Ge alloy in 10% NaOH solution

Conclusions

Amorphous and nanocrystalline Ti-Zr-Si and Ti-Zr-Ge alloys are received by the fast quenching method. The temperature dependence of internal friction and shear modulus of alloys points that alloying by germanium in comparison with silicon keeps better mechanical characteristics of alloys at high temperature.

The electron diffraction analysis of alloys after the electrochemical investigations showed that on the surface of alloy samples two phases ZrO_2 and TiO_2 have been revealed after the researches in 10% solutions of NaOH and HCl. The conducted researches give the ground to expect that the behaviour of Ti-55Zr-15Ge and Ti-23Zr-16Si alloys are defined by passivation of titanium in the studied solutions. This effect helps rising the corrosion resistance of alloys.

Amorphous and nanocrystalline Ti-Zr-Si and Ti-Zr-Ge alloys are recommended for hardening working surface of medical tools and implants of multiply usage. Application of new alloys will allow improving functional properties and increase quality, reliability, service life of medical tools and implants.

Alloys with increased hardness, strength and corrosion resistance are not only suitable for medical tools, but are improvements on currently used materials.

R E F E R E N C E S

1. H. Sibum. Titanium and titanium alloys - from raw material to semi-finished products. Advanced Engineering Materials.# 5(6) (2003). 393.
2. K. Wang. The use of titanium for medical applications in the USA. Materials Science and Engineering. A 213. (1996). 134.
3. H.J. Rack and J.I. Qazi. Titanium alloys for biomedical applications. Materials Science and Engineering. C 26. (2006). 1269.
4. J.G. Ferrero. Candidate materials for high-strength fastener applications in both the aerospace and automotive industries// Journal of Materials Engineering and Performance. # 14. (2005). 691.
5. C.Leyens, R.Braun, M.Fröhlich and P.Eh.Hovsepian. Recent progress in the coating protection of gamma titanium-aluminides// Journal of the Minerals, Metals and materials and Materials Society. Vol. 58. Number 1/January, 2006.
6. John D.K. Rivard, Craig A.Blue, David C.Harper, Jim O.Kiggans, Paul A. The thermomechanical processing of titanium and Ti-6Al-4V thin gage sheet and plate//Journal JOM Journal of the Minerals, Metals and Materials Society. Vol. 57. Number 11/ November, 2005.
7. H.J.Rack and Javaid Qazi. Advanced titanium alloys and processes for minimally invasive surgery// JOM Journal of the Minerals, Metals and Materials Society. Vol. 57, Number 11/ November, 2005.
8. Don Larsen and Greg Colvin. Journal Article. Vacuum-Die casting titanium for aerospace and commercial components. JOM Journal of the Minerals, Metals and Materials Society. Vol. 51. Number 6/ June, 1999.
9. O.M.Ivasishin, P.E.Markovskym, Yu.V.Matviychuk and S.L.Sematin. Precipitation and recrystallization behavior of beta titanium alloys during continuous heat treatment//Journal Metallurgical and Materials Transactions A. Vol. 34. Number 1/ January, 2003.
10. J.Solid State Sciences Vol.8. Issue 6. June 2006. p.685-691.
11. Adriana Bigi, Elisa Boanini, Barbara Bracci, Alessandro Facchini, Silvia Panzavolta, Francesco Segatti and Luigina Sturba. Nanocrystalline hydroxyapatite coatings on titanium: a new fast biomimetic method Surface and coatings Technology. Vol.186. Issue 3. 2004. p.346-352.

MANANA MIKABERIDZE, Academic Doctor
(+995 32) 2300535; Mob.: +995 599 723577

E-mail: mananamikaberidze@yahoo.com