

Titanium alloys for implants in medicine

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Abstract

This study is focused on the influence of alloying elements such as Al, V, Nb, Fe, Mo, and Ta on the microstructure and properties of titanium based alloys. The TiAlV, TiAlNb, TiAlFe, TiMo, and TiTa alloys with various concentrations of alloying elements were prepared by arc melting. Molybdenum and niobium do not harden Ti alloys. In opposite to these two elements, Fe hardens Ti alloys, mostly, and creates particles of FeTi intermetallic phase. A slow cooling leads to a local redistribution of alloying elements and a rapid increase in local chemical inhomogeneity. Experiments of bio-behaviour have shown unsuitability of alloys with Fe for implants in medicine.

Key words: titanium alloys, heat treatment, microstructure, chemical composition, hardness, biocompatibility

1. Introduction

In recent time, the production and usage of Ti based alloys for structural applications spread very quickly. Ti based alloys and intermetallics are also perspective materials for the human medicine applications because of their mechanical behaviour, low specific weight, good corrosion resistance and high level of biocompatibility [1–4]. However, some specific requirements are posed on metals for medical applications. In the case of Ti alloys, a suitable choice of alloying elements has to be taken into account to keep required level of biocompatibility. Metals such as tantalum, niobium, zirconium and in some cases molybdenum meet these requirements [5] and can be added up to high concentrations. For another metals, the level of alloying is limited, because a high concentration can lead to their release from the alloy to the organic tissue, which can cause adverse reaction of the organism.

Nowadays, pure Ti or especially TiAl6V4 alloys are used for implants. The reason is a limited range of available products from commercial Ti alloys. On one hand, there are a number of other alloys intended for medical applications in according to their chem-

ical composition, corrosion resistance and mechanical behaviour. On the other hand, a range of available semi-finished products achievable in small volumes is limited to Ti3Al2.5V alloy and often used TiAl6V4 alloys with purity 4N. Generally, all other alloys are produced by prestigious companies on a special demand of customers, but minimum quantity is limited by parameter of industrial furnaces. In addition, the post-solidification treatments of cast or forged ingots must be clearly specified. Assuming small material requirements for implants, these alloys are unavailable for majority of producers of biomedical implants.

Some alloys have already an excellent corrosion resistance and good results of biocompatibility tests [6, 7]. The first of all, β alloys, seem to be very perspective due to their good cold- and hot-working properties. According to this knowledge, a number of new $\alpha + \beta$ or β alloys with good working properties for implants in medicine have been developed [8, 9]. In some alloys, titanium as the base metal is partially replaced with a zirconium [10].

The aim of this study is to evaluate influence of alloying elements such as Al, V, Nb, Fe, Mo, and Ta on the microstructure and properties of Ti based alloys developed for implants in medicine.

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Table 1. Chemical composition of studied alloys

Alloy type	Alloying element	Concentration of alloying elements (wt.%)						
TiAlFe	Al	5.15	5.30	5.38	5.11	5.00		
	Fe	1.10	2.69	4.22	7.38	10.18		
TiAlNb	Al	6.11	5.91	5.85	5.93	5.90		
	Nb	2.42	4.84	7.16	8.36	10.45	31.81	
TiAlV	Al	6.56	6.70	6.59	6.85			
	V	1.75	3.71	5.63	7.85			
TiMo	Mo	5.16	9.96	15.12	19.78	24.90	29.41	34.49
TiTa	Ta	5.39	10.28	14.80	19.70	24.39	28.95	33.81

2. Materials and experimental methods

Studied Ti-based alloys were prepared in an arc furnace Leybold-Heraeus L2004 under low pressure (300–400 mbar) of a pure He atmosphere using a tungsten electrode. The chemical composition after melting and casting is shown in Table 1.

Binary TiTa and TiMo alloys were alloyed up to high concentrations. According to applications in medicine implants, these binary systems are the base of modern $\alpha + \beta$ or β alloys. Furthermore, the ternary systems present the base of earlier developed structural alloys, which were used or recommended later for implant production.

The alloys were studied at four basic conditions – as-cast and annealed at 650°C/15 min/air cooling, 850°C/10 min/furnace cooling, and 950°C/10 min/furnace cooling. The first two conditions represent a fast cooling down from a high temperature (annealing at 650°C led to elimination of internal stresses in fast cooled castings). The last two ones should satisfy the requirements for diffusion controlled homogenization process to achieve an equilibrium state.

The samples for metallographic observations were ground with SiC papers and mechanically polished. The etching was performed using a mixture of 5 ml HF, 20 ml HNO₃ and 75 ml H₂O. Structural analysis was performed by a light scanning electron microscopy, including the energy dispersion X-ray microanalysis. The hardness was measured using Vickers hardness method with a load of 98.0865 N (HV 10). Some specimens were also prepared for testing in a biological environment.

3. Results

3.1. Microstructure and hardness

Vickers hardness of TiTa alloys slowly increases with increasing tantalum concentration (Fig. 1). A

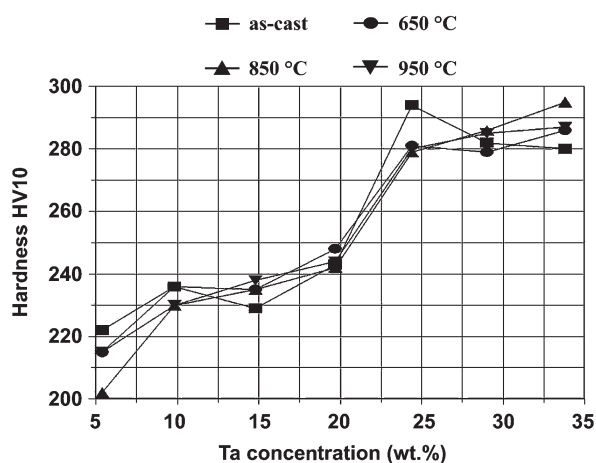


Fig. 1. Relation between hardness and tantalum concentration.

rapid increase in hardness has been determined at Ta concentration of 25 wt.%. On the other hand, annealing has practically negligible effect on the hardness. This type of binary alloys is biocompatible at a good level and is useable as simple workable $\alpha + \beta$ alloy. In the case of a higher concentration of Ta, volume fraction of α phase can be controlled by cooling rate. That means that it is possible to change cold-working properties by changing the cooling rates. The structural analysis of this alloy after fast cooling has shown a microstructure composed of α phase and martensitic α' phase (Fig. 2). Increase of the content of tantalum to 10 wt.% results in microstructure containing α' plates in β phase matrix, as seen in Fig. 3. Very slow cooling forms a two-phase $\alpha + \beta$ structure in this alloy. In the case of the highest concentration of 25 wt.% Ta, the microstructure is formed by the β phase hardened with α particles (Fig. 4).

Alloying with molybdenum did not influence the hardness of as-cast, as well as heat treated alloys (see Fig. 5). Behaviour of the binary alloys is affected by the stabilization of the β phase with Mo. Except of al-

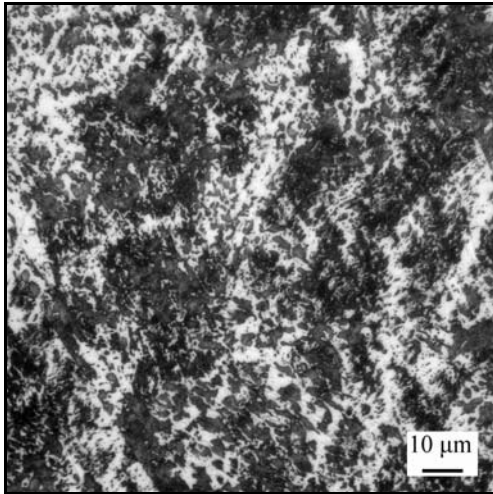


Fig. 2. Microstructure of Ti5Ta alloy, 650°C/15 min.

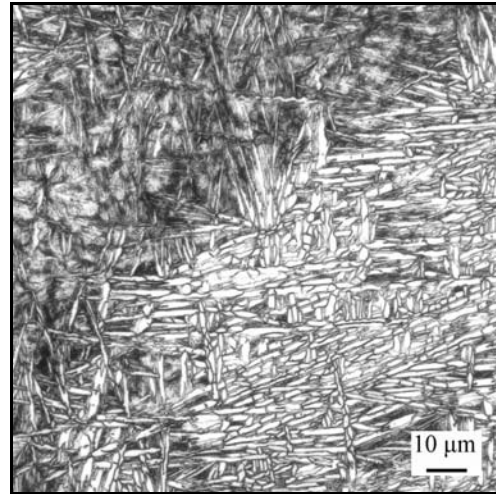


Fig. 4. Microstructure of Ti25Ta alloy, 850°C/10 min.

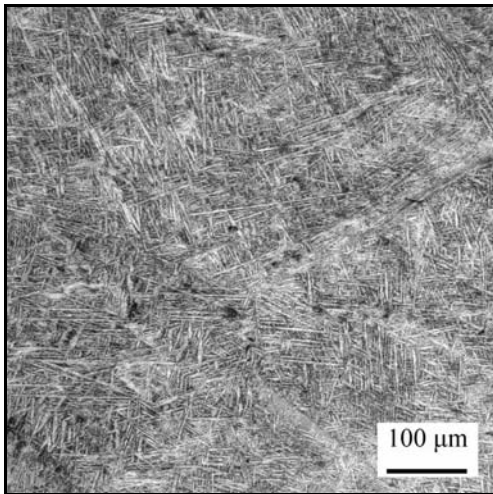


Fig. 3. Microstructure of Ti10Ta alloy, 650°C/15 min.

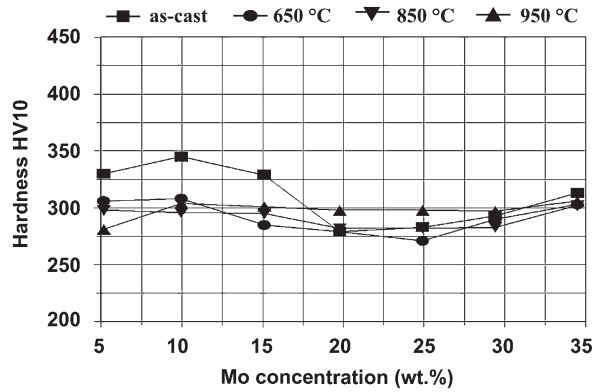


Fig. 5. Relation between hardness and molybdenum concentration.

loys with 5 or 10 wt.% of molybdenum, the structure has β matrix with segregated particles of α phase (see Fig. 6). As-cast alloys with 5 or 10 wt.% of molybdenum are in a meta-stable state that causes a higher level of measured hardness.

Behaviour of ternary TiAlMe alloys depends on alloying additions. Focusing on hardness behaviour, the lowest values occur in the as-cast alloys with niobium as well as after annealing (see Figs. 7 and 8). Considering microstructure shown in these two figures, increasing concentration of Nb has no effect on hardness values. Unlike, an increasing concentration of V causes an increasing hardness of alloys, but annealing at 850 and 950°C leads to its decrease. Finally, Ti alloys are the most hardened by alloying with iron. While slow cooling decreases hardness of Ti alloys with Fe, this process has almost no effect

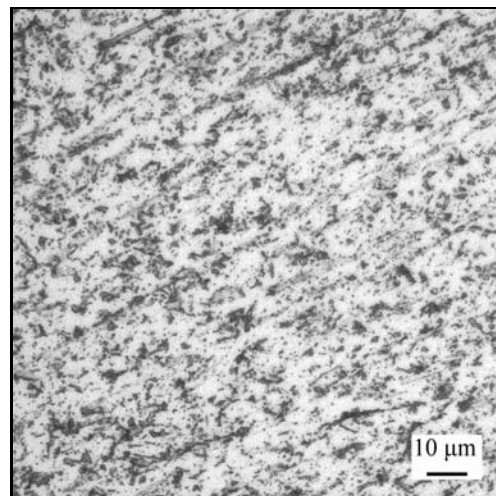


Fig. 6. Microstructure of Ti25Mo alloy, 850°C/10 min.

on the other TiAlMe alloys. Considering the hardness dependence on a concentration, the as-cast al-

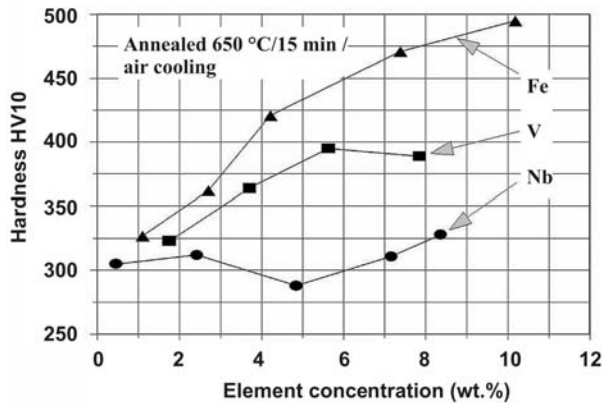


Fig. 7. Relation between hardness and Fe, V and Nb concentration.

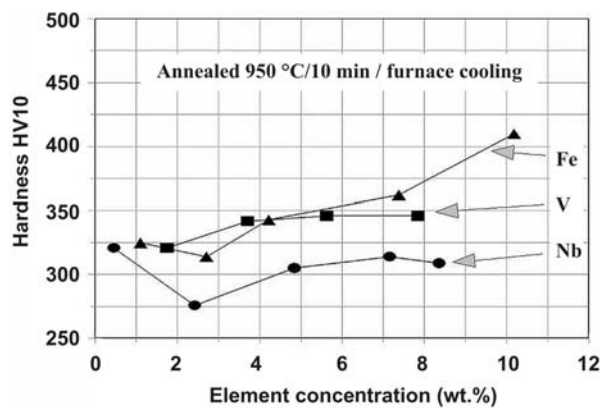


Fig. 8. Relation between hardness and Fe, V and Nb concentration.

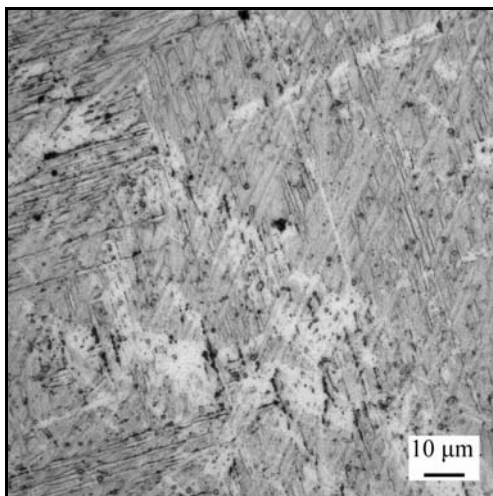


Fig. 9. Microstructure of Ti5Al1Fe alloy, as-cast alloy.

loys show similar behaviour as alloys after annealing at 650 °C.

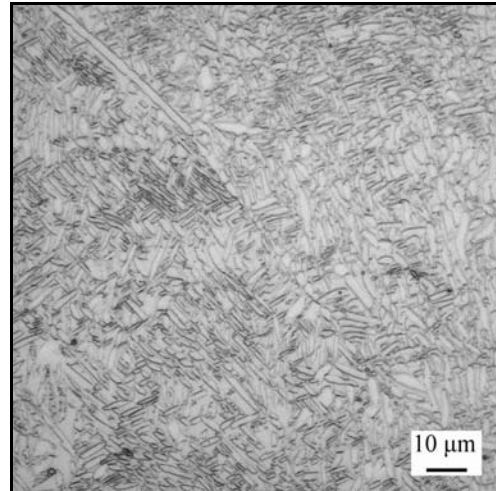


Fig. 10. Microstructure of Ti5Al8Fe alloy, 850 °C/10 min.

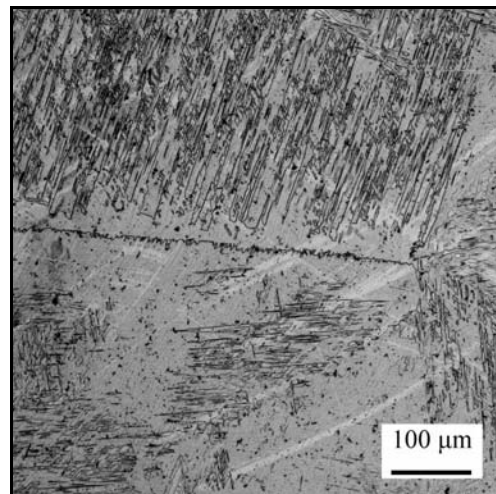


Fig. 11. Microstructure of Ti6Al2V alloy, 650 °C/15 min.

Microstructure of alloy with 1wt.% of Fe is formed by very thin long plates of α' phase (Fig. 9). Volume fraction of β phase increases with an increase of concentration of iron in alloy. Annealing at 850 and 950 °C followed by slow cooling effects morphology of α' phase. Long thin plates transform to short wide ones (Fig. 10). Since iron is insoluble in solid Ti, it precipitates in a form of fine globular FeTi particles. Therefore, increasing concentration of Fe causes precipitation hardening of the alloy.

During laboratory processing of vanadium charged alloys, concentration of vanadium increased step-by-step up to 8 wt.%. Figures 11 and 12 refer to an alloy with 1.75 and 7.85 wt.% of V, respectively. The microstructure of Ti6Al2V alloy is formed by α phase, including acicular martensitic α' phase and fine globular β phase (Fig. 11). Effect of annealing is evident

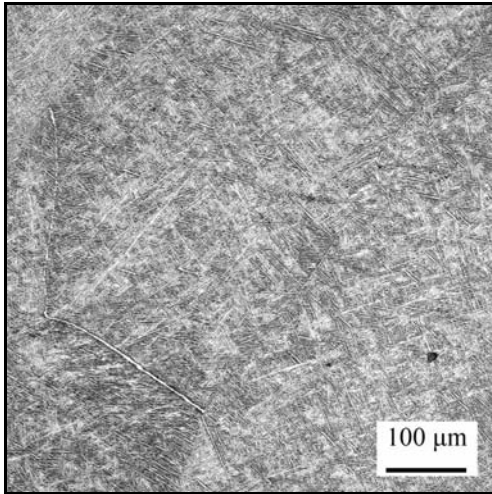


Fig. 12. Microstructure of Ti6Al8V alloy, 850°C/15 min.

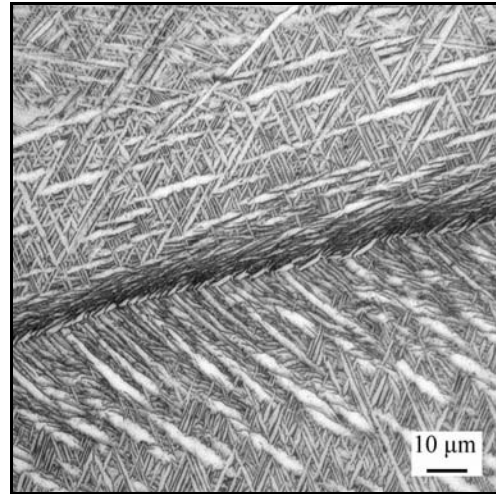


Fig. 14. Microstructure of Ti6Al7Nb alloy, as-cast alloy.

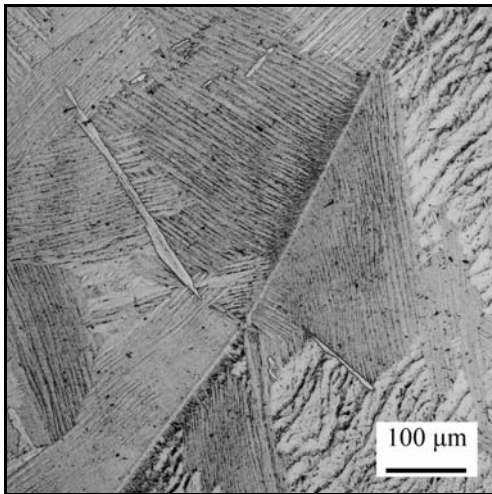


Fig. 13. Microstructure of Ti6Al1Nb alloy, as-cast alloy.

only at temperatures of 850 and 950°C, when a volume fraction of α' phase has decreased. By contrast, the microstructure of Ti6Al8V alloy is formed mainly by α' phase (Fig. 12). Increase of martensitic phase with increasing of V concentration probably causes a mild hardening of alloy.

Furthermore, five ternary alloys with a niobium concentration increased by step-by-step up to 10 wt.% and 6 wt.% of aluminium were prepared by laboratory melting. The as-cast as well as annealed alloys with the lowest concentration of Nb have a martensitic microstructure with very thin and long plates, as seen in Fig. 13. An increasing concentration of Nb causes coarsening of martensitic plates and an increase of volume fraction of non-transformed β phase (Fig. 14). Annealing has no significant effect on the microstructure.

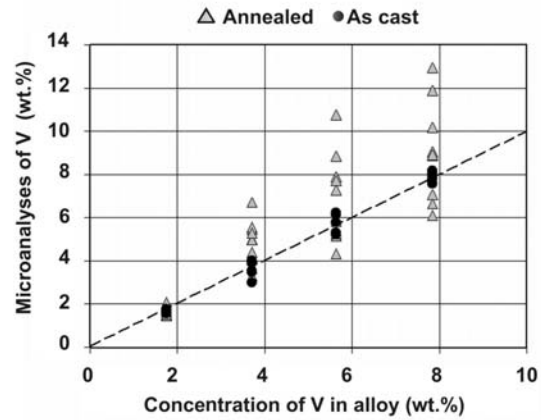


Fig. 15. Influence of annealing on concentration homogeneity of TiAlV alloy.

For the use in human medicine, a chemical homogeneity plays very important role. Therefore, chemical composition of all alloys has been studied after cooling at fast and very slow cooling rates. Scanning electron microscope with the energy dispersion X-ray microanalysis was used for measurements of chemical composition.

Different heat treatment conditions significantly influence the distribution of alloying elements. Considering microanalyses, the fast cooled alloys have only small differences in their chemical composition as seen in Figs. 15 and 16 (black symbols) unlike the slow cooled ones, which have chemical elements more redistributed in separated phases. Therefore, the samples show large variations in local concentration of V and Ta, as seen in Figs. 15 and 16 (shadow symbols). Linear regression lines represent no dispersion in V or Ta concentration in the alloys.

Table 2. Results of biocompatibility tests

Alloy	Sign.	Test no. 1	Test no. 2	Test no. 3	Results
Ti6Al2V	1VZ	40	not	not	biocompatible
Ti6Al4V	2VZ	45	not	not	biocompatible
Ti6Al6V	3VZ	36	not	not	biocompatible
Ti6Al8V	4VZ	39	not	not	biocompatible
Ti6Al2Nb	1NZ	37	not significant	not	biocompatible
Ti6Al4Nb	2NZ	40	not significant	not	biocompatible
Ti6Al6Nb	3NZ	42	not significant	not	biocompatible
Ti6Al8Nb	4NZ	46	not significant	not	biocompatible
Ti6Al10Nb	5NZ	53	not significant	not	biocompatible
Ti5Al1Fe	1FZ	23	yes	inhibition	intolerant
Ti5Al2,5Fe	2FZ	19	yes	inhibition	intolerant
Ti5Al4Fe	3FZ	15	yes	inhibition	intolerant
Ti5Al6Fe	4FZ	12	yes	inhibition	intolerant
Ti5Al8Fe	5FZ	12	yes	inhibition	intolerant
Ti5Ta	1MZ	86	not	not	biocompatible
Ti10Ta	2MZ	80	not	not	biocompatible
Ti15Ta	3MZ	65	not	not	biocompatible
Ti20Ta	4MZ	53	not	not	biocompatible
Ti25Ta	5MZ	50	not	not	biocompatible
Ti5Mo	P1	86	not	not	biocompatible
Ti10Mo	P2	75	not	not	biocompatible
Ti15Mo	P3	95	not	not	biocompatible
Ti20Mo	P4	67	not	not	biocompatible
Ti25Mo	P5	70	not	not	biocompatible
Ti30Mo	P6	55	not	not	biocompatible
Ti35Mo	P7	92	not	not	biocompatible

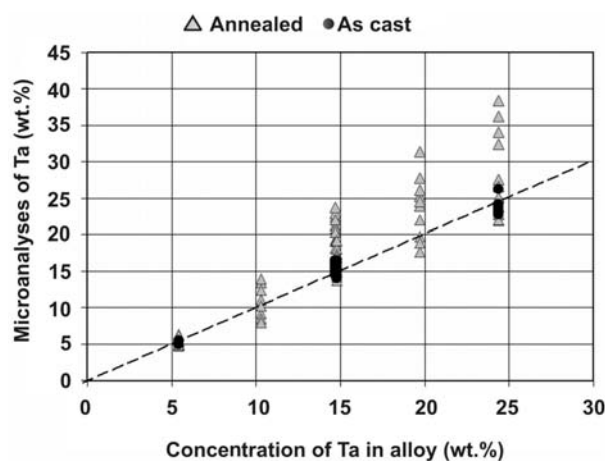


Fig. 16. Influence of annealing on concentration homogeneity of TiTa alloy.

3.2. Tests of biocompatibility

The main attention of the research was focused on methods used to evaluate material biocompatibility. These methods should identify those materials that are anyway intolerant at the cellular level or inhibit the propagation of cells, even kill them.

We have chosen three basic tests supposing they can qualitatively express the suitability of a mate-

rial for medical applications. These three tests examine the behaviour of cells to adhere to the material, cellular tolerance of the material, and the clastogenic effects that could mean a mutagenic activity of the material. The tested cells are of heteroploid cell line, human origin, respectively lymphocytes of human peripheral blood. All the tests were performed with fast cooling cast alloys.

3.2.1. Tests of cell adhesion to material

An inert standard and materials samples, hot-air-sterilized, were placed on a culture plate and covered by cell suspension. After 48-hour propagation, the samples were taken up and evaluated in incident light in off-axis illumination mode to get the number of cells (per area unit). This number was compared with a number obtained on an inert standard. The results (percentage values) are shown in column "Test no. 1" in Table 2. The highest values belong to TiTa alloys, whereas values of TiAlV and TiAlNb alloys balance at the lowest level of suitability. Finally, the values obtained of TiFe alloys are extremely low. An example of a metal covered by cell suspension is shown in Fig. 17.

3.2.2. Cell tolerance tests of material

Hot-air-sterilized material samples were placed on

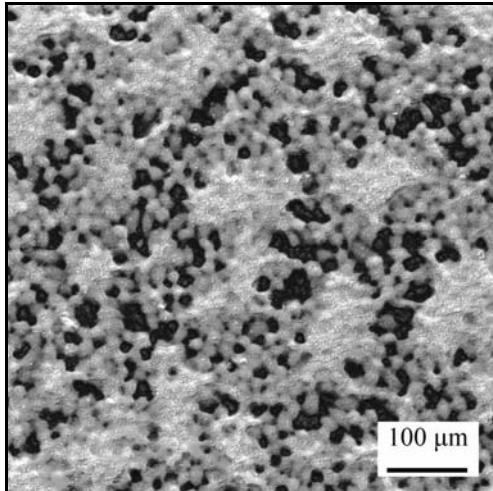


Fig. 17. Metal covered by cell suspension.

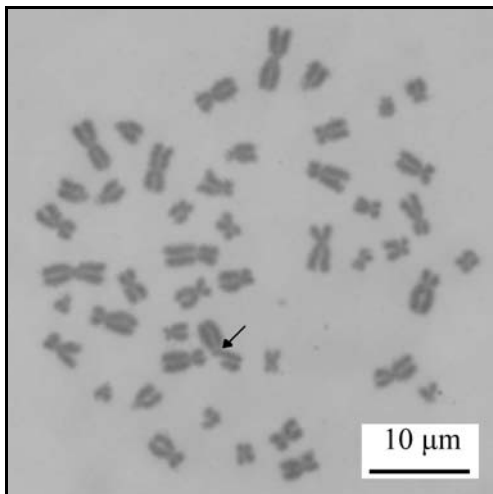


Fig. 18. Example of chromosome break.

culture plate, always three small sample rollers on one culture plate. Thus, we have achieved the same number of results like by triple repeating of the test. The role of evaluation criterion was played by a gap between a sample and dilated cells after five-day cultivation. The results are shown in a column “Test no. 2” of Table 2, where the words “yes, not”, or “not significant” reflect a visibility of the gap. The existence of gap itself indicates the cell intolerance of the alloy. That means the alloy is not suitable for use in implants medicine. It is the case of all Ti alloys with Fe.

3.2.3. Induction tests of chromosome aberrations

Lymphocytes of peripheral blood were cultivated at the same time as material samples. After 72-hour

cultivation, the preparations of dividing cells mitoses were prepared ordinarily [13]. The test consists in the observation and analysis of chromosome aberrations in mitoses (clastogenicity). 25 metaphases were measured on each sample. The results are shown in a column “Test no. 3” in Table 2, where the words “not”, or “inhibition” reflect a detection of a higher frequency of chromosome breaks (means 2 % of aberrant mitoses). The word “inhibition” means, that the dividing cells in the preparations were not found, i.e. the cell dividing was inhibited. An example of a chromosome break is shown in Fig. 18.

The last column of Table 2 describes whether the alloy is considered as biocompatible.

4. Discussion

Titanium creates alloys very similar to stainless steels with comparable strength and toughness behaviour. These alloys have a higher corrosion resistance and about 40 % lower specific weight. Like iron, titanium exists in two allotropic modifications, a high-temperature β phase with BCC crystal lattice and a low-temperature α phase with HCP crystal lattice. According to miscibility with the Ti modifications, we can divide all alloying elements into three groups. The first group includes elements stabilizing α phase, therefore, produced alloys are called α alloys. These alloys are formed by only solid solution of α phase, or β phase scantily occurs. Aluminium belongs to the first group of elements. A combination with other elements enables to influence α phase composition of the alloy at ambient temperature. The second group of elements, such as Cr, Fe, Mn, Co, and Ni, forms $\alpha + \beta$ alloys. Here, particles of α phase transformed in long thin plates during fast cooling. This structure is usually called martensitic and inscribed as α' , α'' or ω' according to the type of alloy, concentration, and crystallography. Like in steels, this morphology involves a high strength, too. Despite fast cooling, slow cooling causes a two-phase structure formed by equiaxial grains, wide plates, or needles, often evoking a cast structure. Finally, the third group represents elements stabilizing β phase, in which they are well soluble and create a solid solution up to high concentrations. Significant elements of this group are molybdenum, tantalum, niobium, and vanadium.

Studied TiTa and TiMo systems create the base of alloys developed for implants medicine in recent time [8–10, 13]. The lack of information on the necessary pre-clinic testing and clinic verification of new alloys represents insufficiency of these mentioned works. The analysis of certificated medical applications [14, 15] and commercial offer of implants has shown that the discussed systems were not pre-clinic tested and verified, in most case, and the works ended at the stage

Table 3. Average concentration of added metals and extreme concentrations in microvolume measurements by the energy dispersion X-ray microanalysis

Added element	Alloy conditions	Chemical composition	Concentration (wt.%)				
Fe	–	average	1.10	2.69	4.22	7.38	10.18
	cast alloy	maximum	1.21	–	4.84	7.90	10.26
		minimum	0.80	–	3.81	6.10	7.34
	950°C/10 min/furnace cooling	maximum	3.56	8.11	10.93	13.65	24.11
minimum		0.71	1.85	3.36	5.05	7.34	
Mo	–	average	5.16	9.96	15.12	24.90	34.49
	cast alloy	maximum	5.43	11.00	15.32	27.60	35.70
		minimum	4.95	9.30	14.82	23.00	32.00
	950°C/10 min/furnace cooling	maximum	9.20	17.10	26.90	28.10	37.80
minimum		4.30	8.30	12.50	21.10	30.72	
Nb	–	average	2.42	4.84	7.16	10.45	31.81
	cast alloy	maximum	–	4.90	7.70	10.64	35.80
		minimum	–	4.52	6.60	10.10	29.20
	950°C/10 min/furnace cooling	maximum	3.80	7.50	11.10	16.30	49.50
minimum		2.15	4.45	6.50	9.30	28.30	
Ta	–	average	5.39	10.28	14.80	19.70	24.39
	cast alloy	maximum	5.43	–	16.55	–	26.19
		minimum	4.91	–	14.03	–	22.74
	950°C/10 min/furnace cooling	maximum	6.26	13.40	18.05	31.33	38.40
minimum		4.82	7.90	14.27	17.60	21.88	
V	–	average	1.75	3.71	5.63	7.85	
	cast alloy	maximum	1.78	4.01	6.24	8.19	
		minimum	1.55	3.00	5.20	7.56	
	950°C/10 min/furnace cooling	maximum	2.07	5.55	10.75	11.88	
minimum		1.54	4.12	4.33	6.10		

of materials research. That presents a difficulty in applying the alloys in clinical medicine.

Tantalum, niobium and especially molybdenum stabilize β phase and create with titanium no intermetallic phases. Thus, these alloys can be precipitation hardened with particles of α phase. Alloys with 12 wt.% of Mo and 25 wt.% of Ta are called β alloys and have good cold-working properties. Their structures are formed by β phase matrix with particles of α phase or plates of metastable α' phase, but they depend on the history of forming and heat treatment. Only a little influence of an element concentration and a heat treatment on mechanical properties is characteristic for these alloys. It is caused by similar mechanical properties of α and β phases considering high concentrations of alloying elements [16]. Even, our work

has confirmed this conclusion during the microhardness measurement of precipitated phases of Ti25Ta and Ti15Mo alloys after annealing at 650 and 850°C. The obtained values of microhardness differ no more than by 35 HVM.

The three studied ternary systems represent alloys applied or referred to apply in human medicine. One of the studied ternary alloys is the oldest and most spread Ti alloy known as TiAl6V4. Aluminium in this alloy stabilizes α phase and provides good strength properties at higher temperatures as well [11, 17, 18]. Conversely, vanadium closes the field of α phase and slightly hardens the alloy by increasing volume fraction of martensitic α' phase [12].

Niobium has similar behaviour to tantalum and its influence on properties of Ti alloys is very similar,

too. Comparing tantalum, the influence of niobium concentration and a heat treatment on the hardness of alloy is small. As an example of Ti alloy with niobium, we should mention alloy TiAl6Nb7, known in technical practice and referred as a substitute for alloy TiAl6V4 to avoid prospective toxic effects of vanadium [5, 7].

Ti alloys are significantly hardened with alloying by iron, which solubility is very limited in Ti based solid solution. Therefore, iron creates intermetallic FeTi phase precipitating in the form of fine globular particles. Their size influences the mechanical behaviour of the alloy. Therefore, the slow cooling causes a precipitation of coarse particles of FeTi phase and thereby, the lower values of the hardness.

In term of alloy biocompatibility, a distribution of alloying elements is very important. Most of elements stabilizing β phase are only partially soluble in α phase that leads, during a slow cooling, to the precipitation of α phase depleted of those elements and enrichment of β phase. Hence, there are structural areas of different elements concentrations. Microanalyses of the chemical composition have shown an influence of cooling rate on increasing local chemical inhomogeneity. In some cases, the values of concentration deviation reach more than 50 %, respectively 150 % in case of alloys with Fe (Table 3).

Considering the measured concentration by microanalysis, influenced by surroundings, the real variance could be much bigger. However, all for now obtained results of microanalysis measurement are summarized in Table 3, which contains minimal and maximal values of concentration of fast and slow cooled samples. As can be seen from this table, the concentration of alloying elements has no significant effect on the variance of deviations.

The deviations of Nb, Ta and V concentrations are similar. In this case, no enriched intermetallic phase is formed, conversely, the redistribution of elements concentrations proceeds between β phase and α , respectively α' phase. Unlike these elements, iron creates an intermetallic FeTi phase containing 50 at.% of Fe. In this case, the deviation exceeds the double value of average concentration, which is unfriendly in biocompatible point of view because of very probable releasing of Fe ions into surrounding tissue followed with a possible averse reaction of the organism.

5. Conclusions

The paper summarizes results of effect of alloying elements such as Fe, Nb, Mo, Ta, and V on the titanium alloy structure and hardness. The recent study leads to following conclusions:

– Molybdenum and niobium do not harden Ti alloys. In opposite to these two elements, Fe significantly hardens Ti alloys and creates particles of an in-

termetallic FeTi phase. A change of cooling rate influences the morphology of metastable phases, or dispersing FeTi particles.

– In the case of $\beta \rightarrow \alpha$ transformation, the influence of a cooling rate on alloy (with Mo, Nb, Ta) hardness is small, whereas a slow cooling slightly decreases a value of hardness of alloys with vanadium, and rapidly of alloys with iron.

– Slow cooling leads to a local redistribution and a rapid increase in local chemical inhomogeneity that is very unfriendly from biomedicine point of view. The high concentrations of alloying elements may cause a release of metal to an ambient environment and, in this way, cause an intolerance of organic tissue.

– Following research of bio-behaviour of these alloys has already resulted in unsuitability of alloys with Fe for implants in medicine.

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References

- [1] LEYENS, C.—PETERS, M.: Titanium and Titanium Alloys – Fundamentals and Applications. Weinheim, Wiley-VCH Verlag GmbH & Co. KGaA 2005.
- [2] LAPIN, J.—GABALCOVÁ, Z.—BAJANA, O.—DALOZ, D.: Kovove Mater., 44, 2006, p. 297.
- [3] LAPIN, J., Kovove Mater., 43, 2005, p. 81.
- [4] LAPIN, J.: Kovove Mater., 44, 2006, p. 57.
- [5] Handbook of Materials for Medical Devices. Ed.: Davis, J. R. Materials Park, OH 44073-02, ASM International, 2003, p. 21.
- [6] Metals and Biomaterials. Eds.: Helsen, J. A., Breme, H. J. West Sussex PO19, England, John Wiley and Sons 1998, p. 101.
- [7] Handbook of Biomaterial Properties. Eds.: Blach, J., Hastings, G. London, Chapman and Hall 1998, p. 179.
- [8] LIN, J. H. CH.—JU, CH. P.—HO, W. F.: Biocompatible Low Modulus Titanium Alloy for Medical Implant. United States Patent No.: US 6,409,852 B1, Ju. 25, 2002.
- [9] DAVIDSON, J. A.: Titanium Molybdenum Hafnium Alloy. United States Patent No.: US 6,200,685 B1, Mar. 13, 2001.
- [10] ZHANG, T.—SATO, K.—KUROSAKA, K.—OGATA, Y.—WANG, X.—KANEKO, T.—KASORI, Y.: Ti Zr Type Alloy and Medical Appliance Formed Thereof. United States Patent No.: US 6,767,418, B1. Jul. 27, 2004.
- [11] SMITH, B.: Advanced Materials Processes, 161, 2003, p. 41.
- [12] BOYER, R.—WELSCH, G.—COOLINGS, E. V.: Material Properties Handbook – Titanium Alloys.

- Eds.: Wheaton, N. D., Woodruff, J., Weintraub, T. Metals Park, OH, ASM Internat. 2004, p. 34.
- [13] HENCH, L. L.: Biomaterials: a Forecast for the Future. *Biomaterials*, 19, 1998, p. 1419.
- [14] JANOTA, M.: Schvalování stomatologických nástrojů v ČR. In: *Evropské normy ve stomatologii*. Praha, Česká společnost pro zdravotnickou techniku, Český normalizační institut 1997, p. 13.
- [15] JIRKŮ, J.: Používání dentálních a chirurgických nástrojů vzhledem k evropským normám. In: *Evropské normy ve stomatologii*. Praha, Česká společnost pro zdravotnickou techniku, Český normalizační institut 1997, p. 9.
- [16] NIINAMI, M.: Science and Technology of Advanced Materials, 4, 2003, p. 445.
- [17] HUNGERFORD, D. A.: *Stain. Technol.*, 40, 1965, p. 333.
- [18] LAPIN, J.—PELACHOVÁ, T.: *Kovove Mater.*, 42, 2004, p. 143.