

R. DĄBROWSKI*

INVESTIGATIONS OF $\alpha + \beta \rightarrow \beta$ PHASE TRANSFORMATION IN MONOTONICALLY HEATED Ti6Al7Nb ALLOYBADANIA PRZEMIANY FAZOWEJ $\alpha + \beta \rightarrow \beta$ W STOPIE Ti6Al7Nb PRZY NAGRZEWANIU CIĄGŁYM

This paper presents an evaluation of critical temperatures of $\alpha + \beta \rightarrow \beta$ phase transformation in an Ti6Al7Nb alloy occurring during heating performed by dilatometric and metallographic methods. Also, changes in the alloy microstructure during cooling down from the two-phase ($\alpha + \beta$) and single phase (β) ranges have been analysed. In the microstructure of the alloy quenched from temperature above 1010°C (one-phase range) in water, the very fine, needle-like precipitates (presumably α') were observed as well as abnormal grain growth of the primary β phase. The obtained results may serve for the interpretation of phase transformation occurring in the Ti6Al7Nb alloy during tempering. In future, the kinetics of the phase transformation during tempering will be investigated by original CHT (Continuous-Heating-Transformation) charts, which are commonly applied for iron-base alloys.

Keywords: phase transformations, titanium alloys, hardness, microstructure, dilatometer, dilatometric curve

W artykule metodami dylatometryczną i metalograficzną określono temperatury początku i końca przemiany fazowej $\alpha + \beta \rightarrow \beta$ przy nagrzewaniu stopu Ti6Al7Nb. Dokonano również analizy zmian twardości oraz zmian zachodzących w jego mikrostrukturze przy chłodzeniu z zakresu dwufazowego $\alpha + \beta$ i jednofazowego β . W mikrostrukturze stopu oziębianego w wodzie od temperatury powyżej 1010°C (z zakresu jednofazowego β) obserwuje się drobne, iglaste wydzielenia fazy martenzytycznej (prawdopodobnie α') oraz znaczny rozrost ziaren byłej fazy β . Uzyskane wyniki badań wstępnych stopu Ti6Al7Nb będą podstawą do interpretacji przemian fazowych zachodzących podczas jego odpuszczania. Kinetykę przemian fazowych przy odpuszczaniu zamierza się badać w przyszłości przy pomocy oryginalnych wykresów CTPc° (czas-temperatura-przemiana przy nagrzewaniu ciągłym ze stanu zahartowanego), wprowadzonych już do literatury światowej – jak dotychczas – tylko dla stopów na osnowie żelaza.

1. Introduction

Metallic biomaterials are currently dominating materials applied for implants, mainly in orthopedics, dentistry, heart and intravascular surgery [1÷4]. At the present time majority of implants are made of austenitic Cr-Ni-Mo steels, cast and wrought cobalt alloys, titanium alloys, Ni-Ti shape memory alloys, Nb and Ta alloys as well as alloys based on noble metals like Au, Ag and Pd [2, 4, 5]. Out of the mentioned materials, the titanium alloys have a particular importance in medicine [2÷4]. The properties of these alloys depend on their microstructure resulted from plastic working and heat treatments procedures [5÷11]. One of the most common titanium alloys is the Ti6Al4V alloy which belongs to the so-called first generation of titanium alloys. It found applications in bone surgery and orthopedics for producing hip and knee joints [2÷4]. However, it was found that

endoprosthesis of hip joints made of this alloy are getting loose. Some objections concerned also their mechanical properties. In addition, their chemical composition was not well tolerated by human organisms since the vanadium content caused cytotoxic reactions and neurological disturbances [1÷4]. Therefore a new group of titanium alloys, referred to as the second generation, was developed. The Ti6Al7Nb alloy belongs to this group. Vanadium was substituted by niobium, which is a vital element (well tolerated in large amounts by the human organism) and does not cause inflammatory states and allergenic activities [1÷6].

The Ti6Al7Nb alloy belongs to the two-phase ($\alpha + \beta$) alloys group $\alpha + \beta$. This makes possible shaping its optimal mechanical properties like ultimate and fatigue strength, crack nucleation and propagation resistance by means of a heat treatment. The development of the optimal heat treatment requires the knowledge of the phase

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF METALS ENGINEERING AND INDUSTRIAL COMPUTER SCIENCE, 30-059 KRAKOW, 30 MICKIEWICZA AV., POLAND

transformation kinetics occurring in this alloy at continuous cooling or at heating from the as-quenched state [12÷17].

The paper presents preliminary results of the investigation of the Ti6Al7Nb alloy. In particular, the microstructure and analysis of critical temperatures at heating from the as-delivered condition hardness changes as well as microstructure changes at cooling from the two-phase $\alpha+\beta$ and single-phase β range were examined. The results will be used for the interpretation of phase transformations occurring at continuous cooling and at alloy tempering from the as-quenched state. Currently, the investigation of the phase transformation kinetics at continuous heating from the as-quenched state is commonly used in ferrous alloys by means of the Continuous – Heating – Transformation diagrams (CHT) [18]. These diagrams show the possibility of the regulation of the progress of successive (intermediate) transformations at tempering and thus influence the final alloy properties, including their hardness and fracture resistance. It is expected that the determination of final mechanical properties by means of regulating the progress of successive transformations occurring during heating from the as-quenched state is possible also in the Ti6Al7Nb alloy. It is believed, that the detailed analysis of the phase transformation kinetics along with the evolution of microstructure and resulting mechanical properties of the Ti6Al7Nb alloy will enable more complete control of these properties and thus satisfy more and more demanding requirements for metallic biomaterials.

2. Research material

Investigations were performed on the two-phase martensitic Ti6Al7Nb alloy. The detailed chemical composition of the alloy according to the ISO 5832-11 as well as the ladle analysis are given in Table 1.

TABLE 1
Chemical composition of the Ti6Al7Nb alloy

Chemical composition, [wt. %]						
–	Al	Nb	Fe	C	H	O
ISO 5832-11 specification	5.5÷6.5	6.5÷7.5	Max 0.25	Max 0.08	Max 0.009	Max 0.2
Analysis	5.80	6.50	0.037	0.017	0.001	0.14

The material was delivered in a form of a bar 8 mm in diameter and 1000 mm in length. It was subjected by manufacturer to the hot working in the two-phase $\alpha + \beta$ range followed by air-cooling.

3. Experimental procedure

Samples of dimensions $\varnothing 8 \times 10$ mm were heated up to temperatures from the range $800 \div 1150^\circ\text{C}$ and annealed for 60 minutes and then water quenched. After the heat treatment the samples were mounted in duracryl and mechanically ground on the magnetic grinder with the borazon grinding wheel. Then, they were ground on abrasive papers with gradually decreasing abrasive grains. The ground samples were polished in SiC suspension. Subsequently the samples were etched in two steps:

- 6% HF – for a few seconds,
- solution consisting of 2 ml HF+ 2 ml HNO₃+ 96 ml H₂O – for a few seconds.

Microscopic examinations were performed on the light microscope AXIOVERT 200MAT of the ZEISS Company.

Hardness was measured by the Vickers apparatus, type HPO 250 at the load of 10 kG. Three hardness measurements, from which the arithmetic mean was calculated, were carried out on each sample.

Temperatures of phase transformations occurring during heating of the Ti6Al7Nb alloy were measured by the dilatometric method using an L78 R.I.T.A. dilatometer of the German LINSEIS Company. Sample elongations resulting from the temperature changes were recorded digitally. Samples with dimensions of $\varnothing 3 \times 10$ mm were heated from room temperature to 1070°C at the rate $180^\circ\text{C}/\text{hour}$. The heating curve was differentiated $\Delta(\Delta L/L_o)/\Delta T=f(T)$. This makes possible to determine precisely the start and finish temperatures of the phase transformations.

Microhardness of particular phases in as-delivered and in as-quenched conditions was measured on the Hanemann apparatus at the load of 10 G.

The chemical composition of particular phases in the as-delivered condition was established by means of the electron microprobe (X-ray microanalyser). This method allows to determine the chemical composition in the selected pre-polished microsections of a diameter approximately 1 μm . After the sample placement in the chamber and obtaining the vacuum the place for analysis was selected by means of a built-in light microscope. The analysis was performed by the Energy Dispersive Spectroscopy (EDS) technique.

4. Results and discussion

The dilatometric curve of heating the Ti6Al7Nb alloy at the rate of $3^\circ\text{C}/\text{min}$ up to 1070°C , $\Delta L/L_o = f(T)$, is shown in Fig. 1. This curve was differentiated in order to precise determine phase transformations temperatures during heating from as-delivered condition.

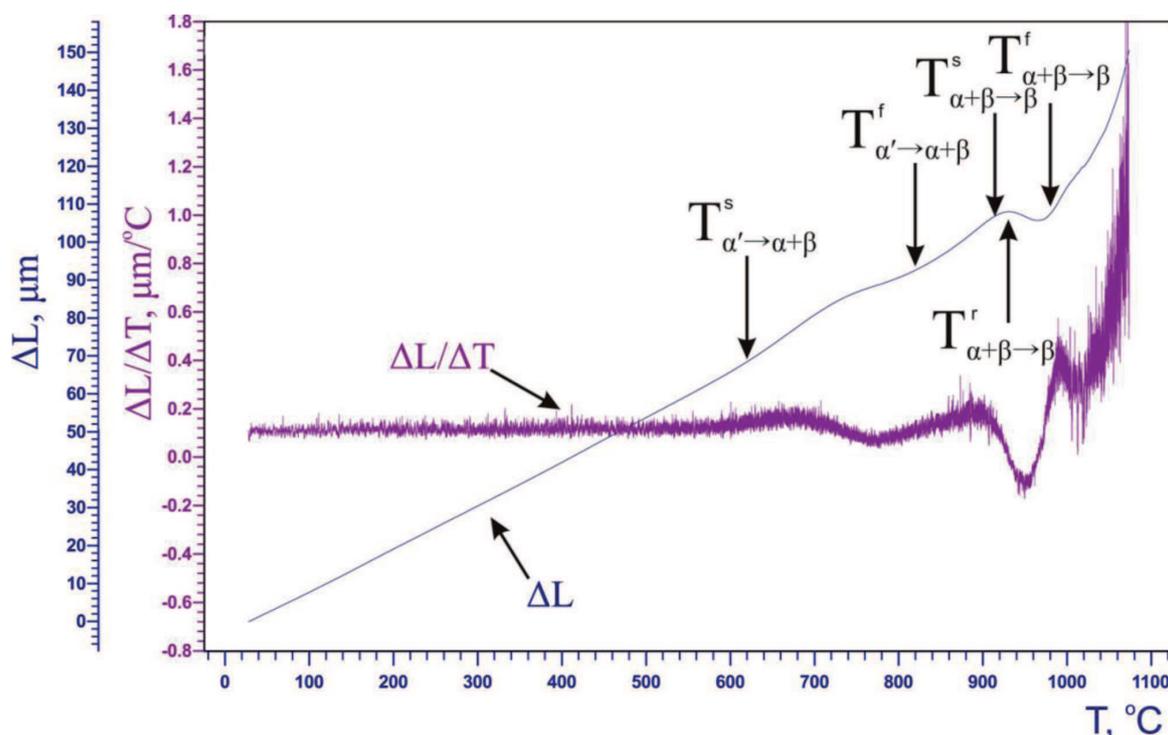


Fig. 1. The dilatometric curve $\Delta L/L_o = f(T)$ of heating the Ti6Al7Nb alloy to 1070°C at the rate of 3°C/min, differentiate curve $\Delta(\Delta L/L_o)/\Delta T = f(T)$ and marking the critical temperatures

Because the material, prior to the experiment, was hot worked in the two-phase range (just below the temperature of the transformation $\alpha + \beta \rightarrow \beta$) and subsequently air-cooled, the microstructure was composed primarily of $\alpha + \beta$ phases. However, small amounts of the martensitic α' phase was also found. The presence of this phase is associated with a relatively high hardenability of this alloy. It is expected that during air-cooling followed the hot working the local martensitic transformation $\beta \rightarrow \alpha'$ may occur. Examinations performed on a similar two-phase Ti6Al3Mo alloy [8, 13, 14] confirm such a phase transformation.

Two stages on the heating curve can be distinguished. In the first stage only the sample elongation - related to its thermal expansion - occurs. At a temperature of approximately 600°C a small positive dilatation effect is observed. It is likely related to the $\alpha' \rightarrow \alpha + \beta$ transformation. The temperature when this transformation starts is marked as $T_{\alpha' \rightarrow \alpha + \beta}^s$ while the temperature when it finishes as $T_{\alpha' \rightarrow \alpha + \beta}^f$. The latter temperature was estimated at 830°C. The other stage of the heating curve consists of a 'slow' and an 'intensive' part. At temperature of 910°C, marked as $T_{\alpha + \beta \rightarrow \beta}^s$, the beginning of the sample shrinkage is noticeable. It is likely related to the nucleation of the a new β phase (start of the transformation: $\alpha + \beta \rightarrow \beta$). This transformation proceeds to the temperature $T_{\alpha + \beta \rightarrow \beta}^f$. The point of inflection, marked as $T_{\alpha + \beta \rightarrow \beta}^r$, determines the start of the 'real' transformation

and is characterised by a significant sample volume decrease relevant to the change of the close packed hexagonal crystal structure into the cubic body centered one. The temperature in this point was estimated at 930°C. Within the temperature range between T^s and T^r , alloying elements diffuse into β phase areas. This brings about the decrease of their content in the primary $\alpha + \beta$ phases and the retardation of the transformation $\alpha + \beta \rightarrow \beta$. The temperature of the transformation finish (T^f) was estimated at 980°C. A further sample elongation - above this temperature - is related solely to its thermal expansion.

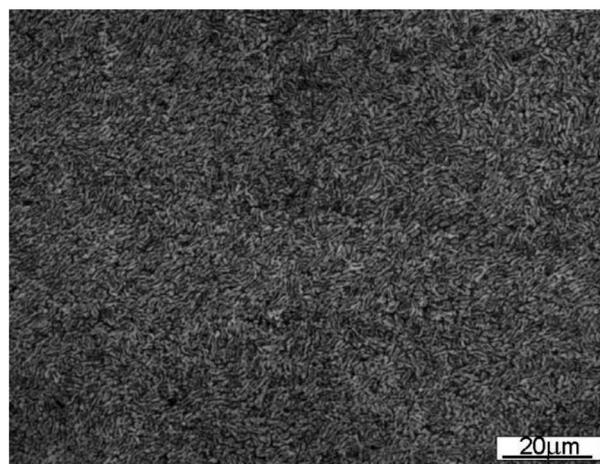


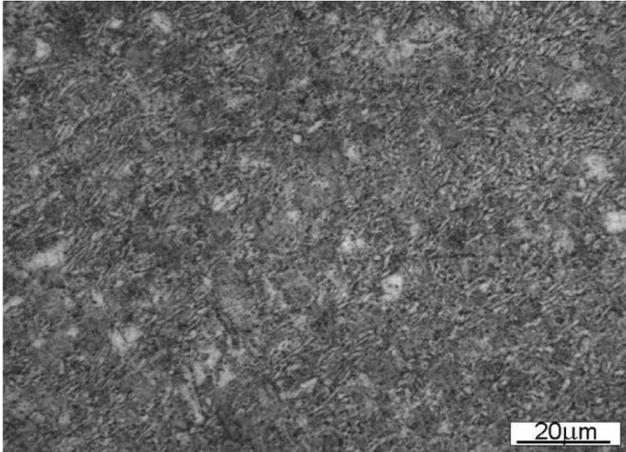
Fig. 2. The Ti6Al7Nb alloy microstructure in as-delivered condition

The Ti6Al7Nb alloy microstructure in as-delivered condition is presented in Fig. 2.

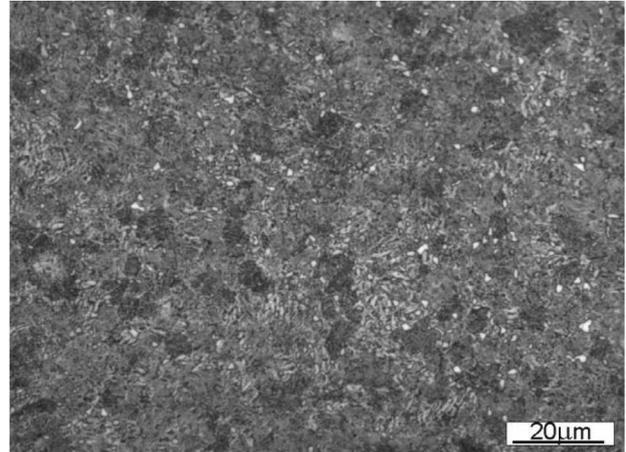
This is a highly dispersed microstructure, in which bright areas – α phase – and darker ones – β phase – can be distinguished. The hardness of this alloy was 304 HV10. The precipitates of the martensitic phase of the α' – type were not recognized, although the character of transformations during heating of this alloy (as men-

tioned earlier) could indicate the possibility of its local occurrence.

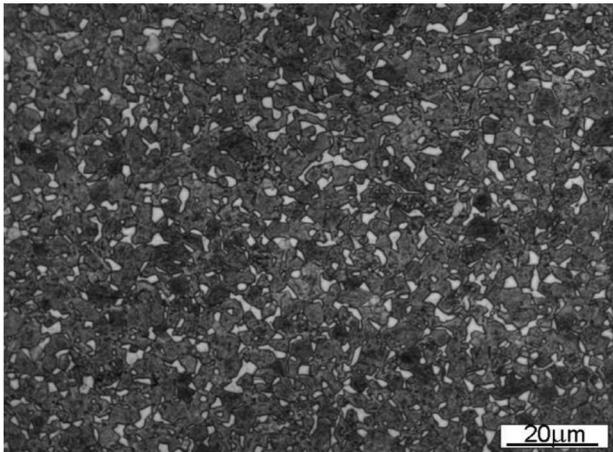
Changes in the microstructure of the Ti6Al7Nb alloy after heating to a temperature from the range: 800÷1150°C, annealing for 60 minutes and cooling in water, are presented in Fig. 3.



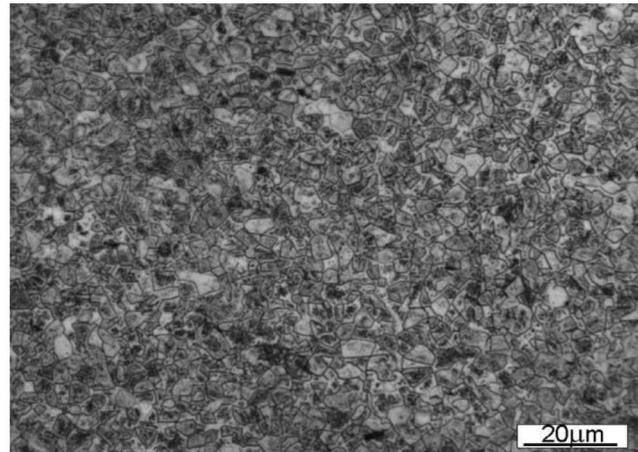
a) T=800°C



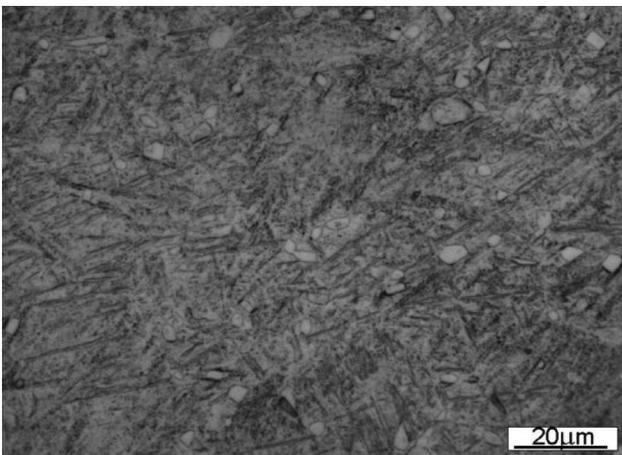
b) T=850°C



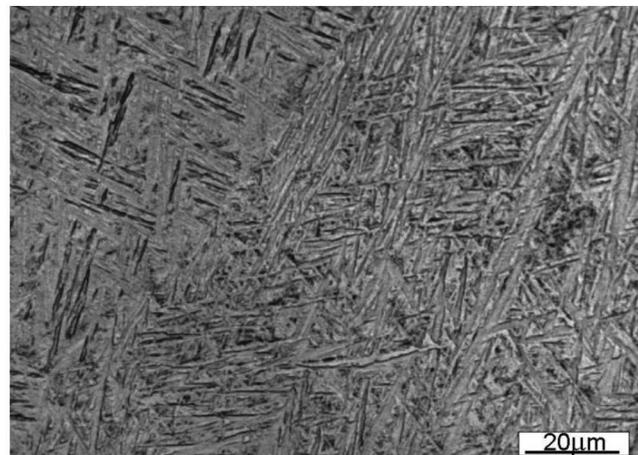
c) T=900°C



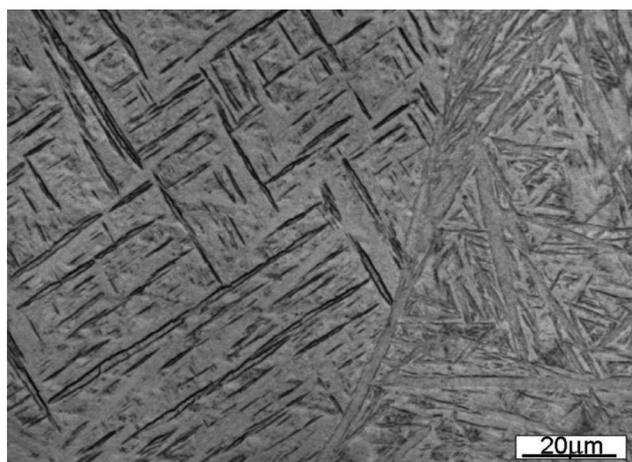
d) T=950°C



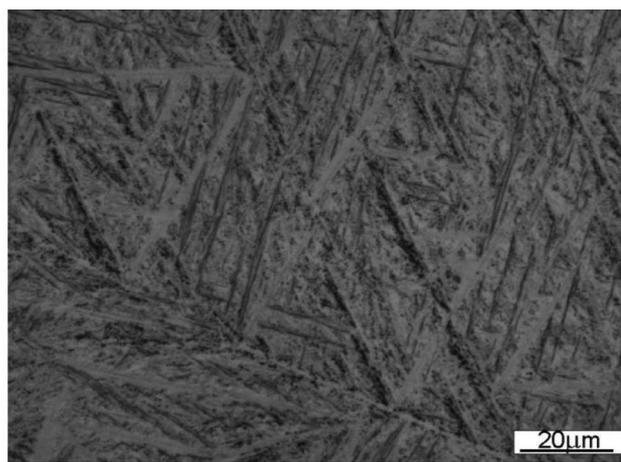
e) T=1000°C



f) T=1010°C



g) T=1020°C



h) T=1150°C

Fig. 3. Changes in the microstructure of the Ti6Al7Nb alloy after heating to a temperature from the range: 800÷1150°C, annealing for 60 minutes and cooling in water

In the temperature range: 800÷900°C (Figs. 3a÷c) the microstructure is clearly fine-grained. Bright grains of the α phase and darker areas of the β phase are clearly recognized. Bright grains in Fig. 3c are the most probably precipitates of a new phase originated due to the alloy heating directly after the plastic deformation. They can result from the α' phase recrystallisation or the α phase coalescence. At higher temperatures the growth of this phase is observed. Starting from 950°C (Fig. 3d), well defined morphology changes of the precipitated phases occur. Large, nearly equiaxed grains of the bright α phase and darker areas, being probably the transformed β phase – are visible. At 1000°C (Fig. 3e) the volume fraction of the α phase is very small (not numerous bright precipitates). This phase transformed upon heating into the β phase and then, during cooling, this β phase transformed into the α' phase. Distinct acicular referred to as the titanium martensite (probably α') are seen. This martensite was formed due to the diffusionless martensitic transformation: $\beta \rightarrow \alpha'$. Between temperatures 1010°C (Fig. 3f) and 1150°C (Fig. 3h) only the martensitic phase of the α' -type was revealed in the microstructure. Starting from the temperature of 1010°C a substantial growth of the primary β phase grains is observed. After quenching a coarse-acicular titanium martensite α' forming the characteristic Widmannstätten pattern is present in the microstructure.

The results of hardness measurements after heating the Ti6Al7Nb alloy to 800÷1150°C, holding it for 60 minutes and water-quenching are presented in Table 2.

The macroscopic hardness of the Ti6Al7Nb alloy annealed in the temperature range 800÷1150°C and then water-quenched oscillates from 277 to 393 HV10. Within the range 800÷900°C (before the phase transformation: $\alpha + \beta \rightarrow \beta$) the hardness is nearly constant (approx-

imately 277 HV). The increase in hardness observed from 950°C is most likely related to the increase in volume fraction of the martensitic α' phase. When the temperature increases the microhardness of this phase also increases. At 1050°C it is equal to 357 μ HV5, while at 1150°C – 406 μ HV5. Generally, it should be emphasized that martensitic type phases in the titanium based alloys do not exhibit high values of hardness contrary to the martensitic phases in the ferrous based alloys. This is because the ferrous alloys (are supersaturated interstitial solutions while titanium alloys are usually substitutional ones [8]).

TABLE 2

The results of hardness measurements after heating the Ti6Al7Nb alloy to 800÷1150°C, holding it for 60 minutes and water-cooling

Annealing temperature, °C	HV 10			HV10 _{med.}
800	274	283	274	277
850	279	272	279	277
900	279	276	276	277
950	312	304	306	307
1000	336	317	314	322
1010	330	330	333	331
1020	342	345	348	345
1050	363	348	342	351
1100	375	370	380	375
1150	401	390	390	393

The results of the chemical microanalysis of the Ti6Al7Nb alloy (basic alloying elements content in α

and β phases) together with the results obtained for a Ti6Al4V alloy (Refs. [15, 16]) are collected in Table 3.

TABLE 3
The results of the chemical composition microanalysis of the Ti6Al4V (acc. to [15, 16]) and Ti6Al7Nb alloys

	Ti6Al4V, acc. to [15, 16]		Ti6Al7Nb	
	Al (%)	V (%)	Al (%)	Nb (%)
α phase	7.35±0.02	1.27±0.02	9.24±0.02	1.85±0.03
β phase	4.30±0.02	10.74±0.03	5.37±0.03	13.51±0.04

The data from Table 3 indicate the significantly higher solubility of vanadium and niobium in the β phase. The elements constitute the stabilizers of this phase. On the other hand, the aluminium content in the α phase is higher than in the β phase. As such, aluminium is considered as the α phase stabiliser. It is confirmed in other studies on titanium alloys, e.g. Refs. [5, 6, 8, 9, 11, 13÷15].

5. Conclusions

1. The alloy in as-delivered condition exhibits a fine-grained two-phase microstructure with α and β phases differed in microhardness (266 and 312 μHV5 – respectively).

2. During heating two stages were distinguished in the dilatometric curve. In the first stage probably the transformation $\alpha' \rightarrow \alpha + \beta$ occurs, while in the other one the specific transformation $\alpha + \beta \rightarrow \beta$. The finish temperature of this transformation determined dilatometrically was estimated at 980°C, while determined metallographically at 1010°C.

3. The microstructure of samples water-quenched from above 1010°C contains acicular precipitates of a martensitic phase (probably α') resulted from the diffusionless transformation $\beta \rightarrow \alpha'$. Above this temperature a significant growth of the primary β phase grains occurs.

4. The solubility of fundamental alloying elements (aluminium and niobium) in individual phases is considerably different. The niobium solubility in the β phase is approximately 7 times higher than in the α phase.

REFERENCES

- [1] J. Marciniak, Biomateriały, Wyd. Pol. Śląska, Gliwice 2002.
- [2] M. Niinomi, Materials for biomedical devices, Wood Head Publishing Limited 2010.
- [3] H.J. Rack, J.I. Qazi, Titanium alloys for biomedical applications. Mat. Sci. Eng. **C26**, 1269-1277 (2006).
- [4] J. Marciniak, Metallic Biomaterials – directions and development forecast, 19th International Scientific and Technical Conference, Kontech, Advanced Forming Technologies and Nanostructured Materials, 103-124 (2012).
- [5] S. Skrzypek, K. Przybyłowicz, Inżynieria metali i ich stopów, AGH, Kraków 2012.
- [6] C. Layens, M. Peters (red.), Titanium alloys: fundamentals and applications, Wiley-VCH 2003.
- [7] ASM Committee on titanium alloys: Heat treatment of titanium and titanium alloys, Metals Handbook, 9th edition **4**, 763-774 (1981).
- [8] A. Bylica, J. Sieniawski, Tytan i jego stopy, PWN, Warszawa 1985.
- [9] V.A. Joshi, Titanium Alloys: An atlas of surfaces and fracture features 7-13 (2006).
- [10] D.R. Askeland, Titanium alloys. The Science and Engineering of Materials, PWS-Kent, Publishing Company 231-236 (1984).
- [11] U. Zwicker, Titan und Titanlegierungen, Berlin – Heidelberg – New York: SPRINGER – Verl 1974.
- [12] T. Ahmed, H.J. Rack, Phase transformations during cooling in $\alpha + \beta$ titanium alloys, Mat. Sci. Eng. **A243**, 206-211 (1988).
- [13] M.K. McQuillan, Phase transformations in titanium and its alloys, Imperial Metal Industries, Metallurgical Reviews 1963.
- [14] H.H. Weigand, Zur Umwandlung von $\alpha + \beta$ Titanlegierungen mit Aluminium, Metallkunde **54**, 1, 43-49 (1963).
- [15] R. Dąbrowski, Analysis of the critical temperatures, hardness and microstructure changes of Ti6Al4V alloy during cooling from two-phase $\alpha + \beta$ and one-phase β range, Ores and Non-Ferrous Metals **10**, 708-716 (2010).
- [16] R. Dąbrowski, The kinetics of phase transformations during continuous cooling of the Ti6Al4V alloy from the single-phase β range, Archives of Metallurgy and Materials **56**, 3, 703-707 (2011).
- [17] R. Dąbrowski, The kinetics of phase transformations during continuous cooling of Ti6Al4V alloy from the diphas $\alpha + \beta$ range, Archives of Metallurgy and Materials **56**, 2, 217-221 (2011).
- [18] J. Pacyna, Metaloznawstwo pękania stali narzędziowych, Metalurgia i Odlewnictwo, 120 (1988).