Coarsening of (αTi) + (βTi) Microstructure in the Ti–Al–V Alloy at Constant Temperature

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The microstructure evolution of the Ti–6 wt% Al–4 wt% V alloy with increasing annealing time t at constant temperature T = 800 °C is studied. This temperature is in the two-phase region (αTi) + (βTi) of Ti–Al–V ternary phase diagram. The annealing time t varies from 7 to 840 h. The microstructure of the annealed samples is investigated using optical and scanning electron microscopy. The average grain size of (αTi) and (βTi) phases grows approximately proportional to $t^{1/4}$. This indicates that both processes are controlled by the diffusion along grain boundaries (αTi)/(αTi) and (βTi)/(βTi) and/or interphase boundaries (αTi)/(βTi).

1. Introduction

The Ti–6 wt% Al–4 wt% V alloy (called below Ti–6Al–4V, also known as VT6 in Russian nomenclature) and its analogues are widely used in aero-space vehicles,[1] in bio-medical applications,[2] as well as in the automotive and many other industries.[3–5] Various parameters and properties of this alloy like chemical composition and crystal structure of constituent (αTi) and (βTi) phases, the volume fraction of (αTi) and (βTi), their dispersion and morphology, as well as final mechanical properties are determined by thermal and mechanical processing of the alloy.[3,6,7] After thermo-mechanical processing, the microstructure of the alloy is characterized by high stored energy associated with intergranular and interphase boundaries, elastic stresses, and dislocations.[8–10] This means that such structures are rather nonequilibrium and evolve to the equilibrium. So, it is important to know the kinetic parameters of the processes determining the creation or degradation of the quasi-equilibrium state of the microstructure of the alloy, that is, its mechanical characteristics, in order to be able to improve technology of forming and processing of parts from the Ti–6Al–4V alloy.

However, currently, the kinetics of microstructure evolution of the Ti–6Al–4V alloy in the process of isothermal annealing processes is investigated insufficiently. To the best of our knowledge, one detailed study exists on the influence of isothermal annealing in the temperature range of 843–982 °C on the growth kinetics of the (αTi) grains in Ti–6Al–4V.[11] Besides, very recently the study appeared, where the effect of annealings at 700 and 800 °C on the microstructure of selective laser melted Ti–6Al–4V alloy was considered.[12]

In this paper, we study the evolution of microstructure in the Ti–6Al–4V alloy during isothermal annealing at 800 °C (i.e., below the interval studied in ref.[11]) with annealing time *t* between 7 and 840 h. The growth kinetics of (αTi) and (βTi) grains was studied. The long duration of the slowest annealing suggests that the characteristics of the phases of the obtained microstructures are close to the equilibrium.

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2. Results

2.1. The Microstructure of the Alloy before Annealing

Figure 1a shows the initial (i.e., before annealing) microstructure of the Ti–6Al–4V alloy. It contains colonies of alternating lamellae of phases appearing light and dark gray. The size of the colonies is about 100–200 μm. The thickness of the lamellae in the colonies is 1–2 μm. The chemical composition of dark and light gray lamellae is shown in **Table 1**, it corresponds to (αTi) and (βTi) phases, respectively. X-ray diffraction analysis showed that the initial alloy consists of two phases with the h.c.p. and b.c.c. lattices. Their lattice parameters correspond to the crystal structure of (αTi) and (βTi), respectively. This is consistent with the findings from chemical analysis of the phases. The obtained lattice parameters of phases and volume fraction of phases in the initial alloy is presented in **Table 2**.

2.2. The Effect of Annealing Duration on the Microstructure

Micrograph in Figure 1b shows that after 7 h of annealing, the microstructure of the alloy is qualitatively different from the initial one. The colonies of lamellae completely disappeared.

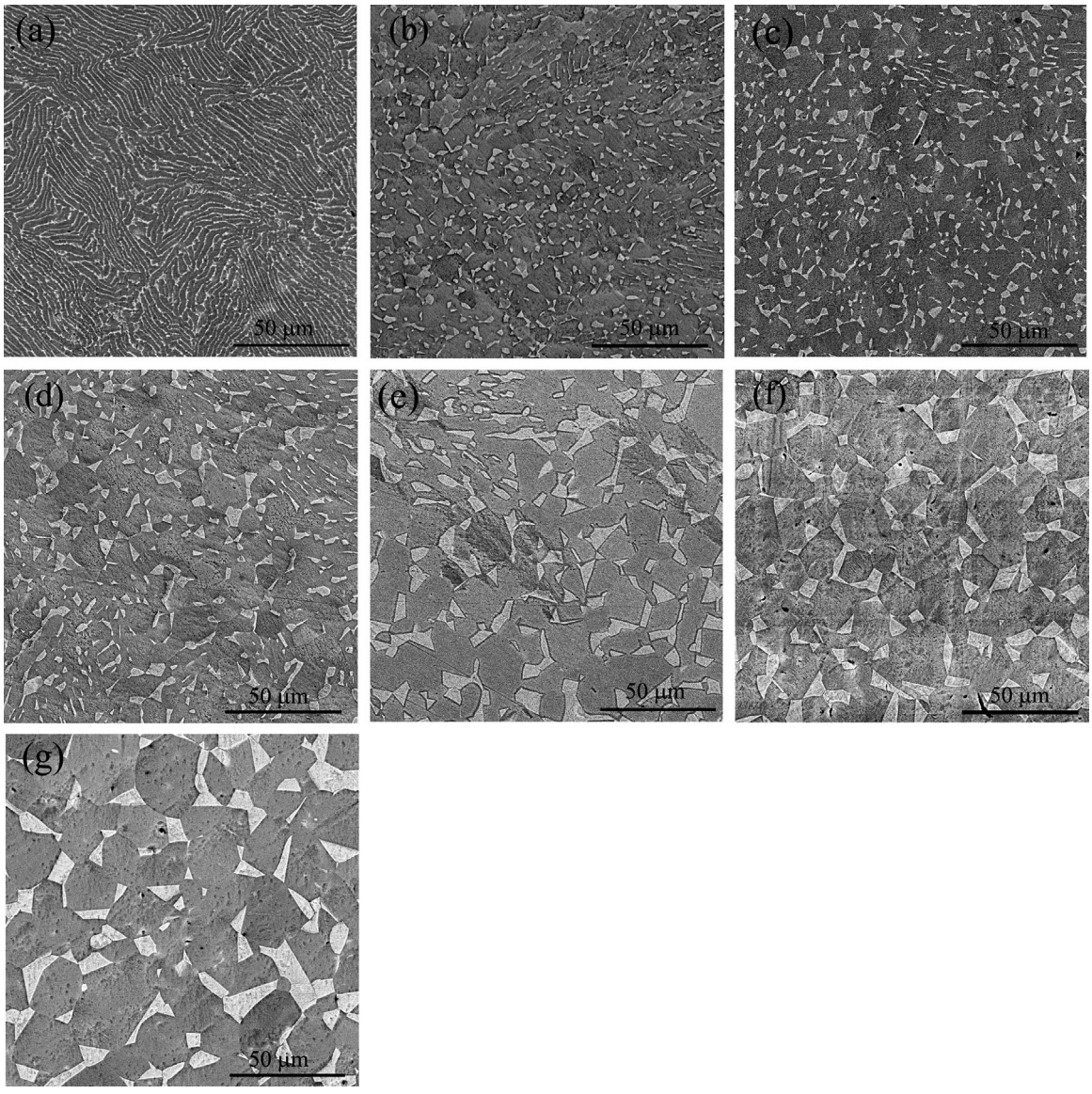

Figure 1. SEM micrograph of Ti–6Al–4V alloy in initial state and after annealing at 800 °C for different times: a) before annealing, b) 7 h, c) 20 h, d) 49 h, e) 144 h, (f) 289 h, (g) 840 h.

After annealing and subsequent quenching in water, the microstructure of the alloy consisted of light and dark gray grains that accurately replaced the grains (βTi) and (αTi) formed during annealing at 800 °C before quenching. This is confirmed by the fact that the average chemical composition of light and dark gray grains corresponds to the composition (βTi) and (αTi) at 800 °C in accordance with the Ti–V–Al phase diagram. After quenching, the grains of former (αTi) and (βTi) became heterophase as a result of decomposition of the (αTi) and (βTi) solid solutions. A new microstructure manifests itself as a two-phase polycrystal composed of more or less equiaxial (αTi) and (βTi) grains. Grain size of (βTi) is significantly lower than the grain size of (αTi). Upon further annealing, the character of the microstructure does not change. The increase in the duration of annealing leads to increase in grain size of (αTi) and (βTi) phases. The grain growth, of course, is accompanied by a decrease in grain number per unit volume (or per unit cross-sectional area). This is clearly seen when comparing Figure 1b–g. We determined the average grain size of (αTi) and (βTi), $\overline{d_\alpha}$ and $\overline{d_\beta}$, after each annealing. The measurements were carried out using a random cross-sections method.[13] Each value $\overline{d_\alpha}$ and $\overline{d_\beta}$ was determined on the basis of 200–300 measurements. The results of the measurements are presented in **Table 3**. Also, we determined the volume fraction of (αTi) and (βTi) phases formed during the anneal at 800 °C using random cross-sections method. It is equal to $(82 \pm 2)\%$ and $(18 \pm 2)\%$, respectively. Besides, the volume fraction of (αTi) and (βTi) phases formed during quenching was also determined by XRD (Table 2). These values markedly differ from those determined by image analysis. It is due to the decomposition of the former (αTi) and (βTi) solid solutions during cooling of the

Table 1. The content of Al, V, and Ti in (αTi) and (βTi) phases in the Ti–6Al–4V alloy in the initial state and after annealing for various durations at 800°Ñ followed by quenching[a].

	Al [wt%]		V [wt%]		Ti [wt%]	
t [h]	(αTi)	(βTi)	(αTi)	(βTi)	(αTi)	(βTi)
0	6.8	4.6	2.0	8.6	91.2	86.8
7	6.7	5.0	3.0	9.1	90.3	85.9
20	6.8	4.6	2.7	9.1	90.5	86.3
49	6.8	4.6	2.9	9.5	90.3	85.9
144	6.3	4.6	2.7	8.6	90.9	86.7
289	6.6	4.5	2.6	9.2	90.8	86.3
840	6.6	4.4	2.4	9.4	91.0	86.2

[a] The chemical composition of the phases of the alloy was determined with an accuracy of 0.25 wt% Al, 0.95 wt% Ti, and 0.45 wt% V.

Table 2. The lattice parameters and volume fraction of (αTi) and (βTi) phases in the Ti–6Al–4V alloy in the initial state and after annealing at 800 °C for 144 and 840 h followed by quenching[a].

	(αTi) h.c.p.			(αTi) b.c.c.	
t [h]	$\grave{a}$ [nm]	$\tilde{n}$ [nm]	Fraction [%]	$\grave{a}$ [nm]	Fraction [%]
0	0.2930	0.4673	95	0.3222	5
144	0.2923	0.4668	96.5	0.3220	3.5
840	0.2923	0.4668	96.3	0.3219	3.7

[a] The lattice parameters of the phases were determined with an accuracy of ±0.0002 nm, and the volume fraction of the phases with an accuracy of about 1%.

alloy. Table 1 shows the concentrations of aluminum, vanadium and titanium in (αTi) and (βTi) phases measured after annealing of different durations and subsequent quenching.

2.3. Kinetics of Coarsening of the Alloy Structure

Let us suggest that the initial size of the (αTi) and (βTi) grains is small and the incubation period is short. Then for analysis of the growth kinetics of the average grain size in (αTi) and (βTi) one can use the expression $\overline{d} \approx Kt^{1/n}$, where K is the kinetic coefficient, t is the annealing time and n is the parameter, which is determined by the mechanism controlling the kinetics of coarsening. **Figure 2**a shows in double logarithmic coordinates the average grain size in (αTi) and (βTi), $\overline{d_\alpha}$ and $\overline{d_\beta}$, depending on the annealing time. The behavior of both dependencies is well approximated by straight lines for growth of (αTi) and (βTi) grains with slopes equal to $1/n_\alpha = 0.22 \pm 0.02$ ($n_\alpha = 4.6 \pm 0.4$) and $1/n_\beta = 0.26 \pm 0.02$ ($n_\beta = 3.8 \pm 0.4$), respectively. From the kinetic dependencies of the growth of (αTi) and (βTi) grains one can determine the kinetic coefficients $K_\alpha = 0.59^{+0.14}_{0.11}\,\mu m^n\ s^{-1}$ and $K_\beta = 0.11^{+0.03}_{0.02}\,\mu m^n\ s^{-1}$, respectively. **Figure 3** shows the dependence of the ratio $\overline{d_\alpha}/\overline{d_\beta}$ on the annealing time. The dotted line shows the average value of the ratio $\overline{d_\alpha}/\overline{d_\beta}$ which is equal to 3.1 ± 0.3.

Table 3. Average values of (αTi) grain size ($<d_\alpha>$) and (βTi) grain size ($<d_\beta>$) after annealing of Ti–6Al–4V alloy at 800 °C.

t [h]	$<d_\alpha>$ [μm]	$<d_\beta>$ [μm]
7	5.6 ± 0.2	1.6 ± 0.1
20	6.5 ± 0.2	1.9 ± 0.1
49	8.4 ± 0.3	2.5 ± 0.2
144	10.2 ± 0.4	3.9 ± 0.3
289	11.8 ± 0.5	4.2 ± 0.3
840	19.3 ± 0.7	5.5 ± 0.3

3. Discussion

It was shown that the microstructure of Ti–6Al–4V alloy after annealing at 800 °C is a polycrystal composed of (αTi) and (βTi) grains. In this case, the chemical equilibrium between (αTi) and (βTi) phases limits the possibility of moving the (αTi)/(βTi) interphase boundaries. In addition, the triple junctions must remain in mechanical equilibrium. The deviation from this mechanical equilibrium induces the force leading to the migration of boundaries. Therefore, the processes of coarsening of the grains of both phases are strongly connected with each other and have collective character. At least, the changes caused by each displacement of the grain or phase boundaries must include a significant surrounding area, which is much bigger than the characteristic grain size. In this case, the characteristic lengths of the diffusion pathways are much larger than the size of the grains.[14] According to the experimental studies[15,16] and numerical simulations,[17–19] the obtained value $n \approx 4$ corresponds to the grain growth in (αTi) and (βTi), which is controlled by diffusion along grain and/or interphase boundaries. Note that similar result was obtained theoretically in ref.[20–22] for the case of coarsening of an ensemble of inclusions at grain boundaries, which can be realized if the volume fraction of second phase is low. However, the results [20–22] are not applicable for describing the grain growth kinetics in the two-phase polycrystal where the amount of both phases is comparable. It is because they describe the kinetics of coarsening in an ensemble of inclusions at grain boundaries.

In our case, the growth processes of (αTi) and (βTi) grains are connected with each other and occur simultaneously. Therefore, the kinetics of one of them contributes to the kinetics of the other. It is because the grain growth in each of two phases leads to an increase in the average length of diffusion paths while simultaneously reducing the total number of these paths. Therefore, the above-obtained kinetic coefficients K_α and K_β should only be considered as effective. Unfortunately, currently there are no relations connecting the kinetic coefficients of grains growth in a two-phase polycrystal with the parameters of the elements of its microstructure. Note also that the weak dependence of the grain size ratio $\overline{d_\alpha}/\overline{d_\beta}$ on the annealing time (Figure 3) characterizes the preservation of self-similarity of the microstructure of two-phase polycrystal with the grain growth during annealing. A weak dependence of $\overline{d_\alpha}/\overline{d_\beta}$ on t also means that the asymptotic regime is achieved in our experiments.

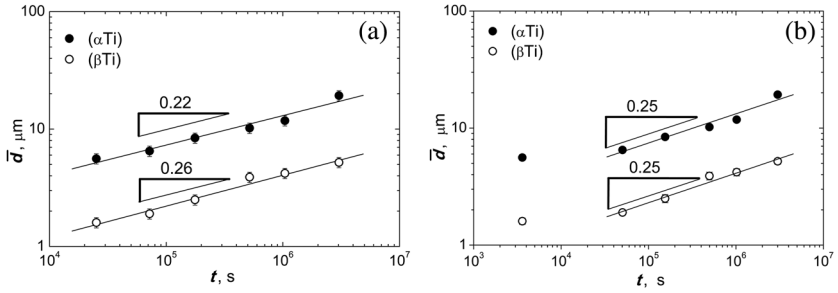

Figure 2. The dependence of average grain size in (αTi) and (βTi) phases on the annealing time. (a) Incubation period is absent (b) Incubation period is 6 h.

It corresponds to the law of growth of (αTi) and (βTi) grains controlled by the diffusion along grain boundaries and/or interphase boundaries ($n = 4$).

In contrast to this study, it has been shown in ref.[11] that the growth of (αTi) particles in the Ti–6Al–4V alloy during isothermal annealing in the temperature range of 843–982 °C took place under the law with $n = 3$. The microstructures images of the alloys after annealing[11] indicate that they, like in our case, represent the two-phase polycrystals. These images also indicate the simultaneous growth of (αTi) and (βTi) grains. Numerical modeling of the growth of grains in two-phase polycrystal shows that the growth law with $n = 3$ corresponds to a process of coarsening of grains, controlled by the bulk diffusion.[14,17–19] The authors of ref.[11] came to the same conclusion and they used the modified theory of Lifshitz–Slezov–Wagner (LSW) for the quantitative analysis of the obtained results. However, the LSW theory describes the kinetics of coarsening of second-phase particles included in the bulk of the matrix phase. Therefore, the LSW theory is not directly applicable for the analysis of grain growth in two-phase polycrystal. In order to explain the difference between n values in our study and in ref.,[11] we suggested that it might be related to the different initial microstructure of the alloy: lamellar structure in our work and two-phase polycrystalline structure in ref. [11]. In our case, the transition from lamellar structure to the two-phase polycrystalline structure could take a considerable period of time, which could affect the obtained value of n, whereas in ref. [11] the transition period was absent. In ref.,[11] it was found that at all temperatures after annealing for various durations, the microstructure of the alloy remained self-similar. To check this assumption, we reconstructed the kinetic dependence of the growth of (αTi) and (βTi) grains assuming the presence of 6-hour incubation period, and found that at $t > 20$ h both dependencies are described by $n = 4$ (see Figure 2b).

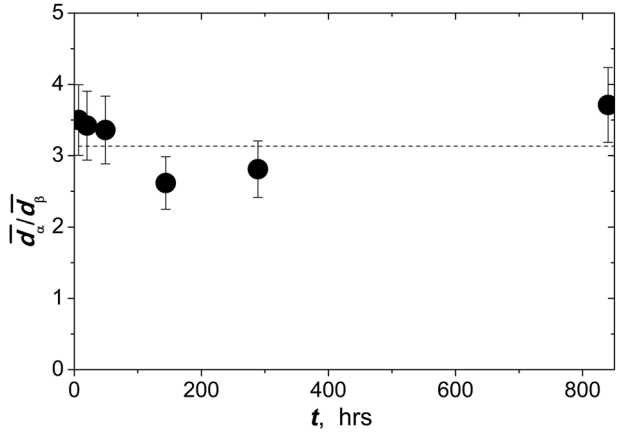

Figure 3. The dependence of the ratio of the average grain size in (αTi) and (βTi) phases, $\overline{d_\alpha}/\overline{d_\beta}$, on the annealing time. The dotted line shows the average value of the ratio $\overline{d_\alpha}/\overline{d_\beta}$ equal to 3.1 ± 0.3.

The difference of the grain growth laws obtained in our study and in ref. [11] can also be related to lower temperature in our study. Lowering the temperature may result in a change of control mechanism of grain growth from bulk diffusion to the diffusion along grain and/or interphase boundaries. With decreasing temperature the ratio of grain boundary and bulk diffusion coefficients increases from 10^3 to 10^5 and more.[23] This fact may lead to the dominance of grain boundary diffusion at lower temperature. Some indications of a change in the controlling mechanism could be found in ref.[16] In this work the $1/n$ value in the grain growth law increased with increasing annealing temperature from 0.28 to 0.32 in the Ti–Mn alloys and from 0.24 to 0.29 in the Ti–V alloys.[16]

Indeed, the data[24] (see Figure 5 and Figure 8) show that the volume fraction of (βTi) phase in the Ti–6Al–4V alloy remains unchanged by heating from room temperature to about 800 °C with speed of 30 K s^{-1}. This is probably due to the low rate of volume diffusion at these temperatures; leading to the conservation of the chemical composition of the phases and, consequently, volume fractions of phases in the alloy between 25 and 800 °C. Therefore, we can assume that in our case (at 800 °C) the kinetics of the process of coarsening is determined by the contribution of the diffusion along the interphase and/or grain boundaries.

The difference in temperature also leads to a change in the equilibrium volume fractions of the phases in the alloy, which can also affect the kinetics of grain growth. As shown in ref.,[17] if the volume fraction of one of two phases is about 10–30%, the $1/n$ value describing its growth is close to 0.25. If the volume fraction of this phase increases up to 70–90%, the $1/n$ describing its growth approaches 1/3. This means that if the length of diffusion paths in the other phase increases then increases also the contribution of diffusion along the grain boundaries. Note that in ref.,[17] the same diffusion kinetics in both phases is assumed. In ref.,[25] the grain growth in the mixture of two phases has been simulated. It has been shown that the growth mode with $n = 4$ appears when the bulk diffusion in both phases is frozen, or otherwise, if the bulk diffusion is frozen in one of the phases and is slow in the other phase.[25] These works indicate that the change of the diffusion mechanism can be influenced by the decrease of the (βTi) volume fraction in the alloy. In our case, the (βTi) volume fraction at 800 °C is 18%. It is much less than at 843 °C (29%). It is well known that the growth rate of (αTi) phase during the cooling of the Ti–6Al–4V alloy is determined by the vanadium diffusion through (βTi).[26] This

means that, most probably, the lower diffusion supply of vanadium through (βTi) at 800 °C contributes to the change of the grain growth mechanism.

Note that in most experimental and numerical modeling works on the grain growth in two-phase polycrystals the grain coarsening controlled by the interfacial and/or grain boundary diffusion was not observed. In case of experimental studies it is most probably due to the high temperatures of the experiments. In this case, the difference between coefficients of bulk and grain boundary diffusion is relatively small. In case of numeric simulations it also may be associated with high temperatures. High temperature is necessary to obtain noticeable changes in the system within a limited calculation time. Other reason could be the small size of studied systems where volume diffusion obviously dominates. In the numerical modeling (in the framework of used models) it is also difficult to quantify correctly the contribution of the intergranular and interphase diffusion in the grain growth in two-phase polycrystal. The only way would be to insert "by hands" in the model the corresponding parameters (like coefficients of grain boundary and interphase diffusion, surface tension, and/or thickness of intergranular and interphase boundaries). In several studies, the contribution of diffusion along the grain boundaries is generally ignored, see for example.[14] We also would like to underline that the supeplasticity appears in the Ti–6Al–4V alloy with submicro- or nanograins at temperature between 600 and 700 °C.[8–10] This fact also can be due to the change of the diffusion-controlling mechanism because the decrease of grain size should decrease the temperature of the transition from processes controlled by the bulk diffusion to the ones controlled by the diffusion along grain or interphase boundaries.

4. Conclusions

The study of the grain growth kinetics and evolution of the microstructure of (αTi) and (βTi) phases in the Ti–6Al–4V alloy during annealing at 800 °C demonstrated that the initial lamellar structure quickly transformed into mixture of nearly equiaxed (αTi) and (βTi) grains. Subsequent changes with increasing annealing time t are associated with the growth of (αTi) and (βTi) grains. In particular, the (βTi)/(βTi) grain boundaries appeared during coarsening of the microstructure. The average size of growing (αTi) and (βTi) grains is roughly proportional to $t^{1/4}$. This indicates that both processes are controlled by diffusion along grain and/or interphase boundaries.

5. Experimental Section

The study was conducted on the Ti–6Al–4V alloy supplied in the form of an as-cast 25-mm diameter bar. The 5 mm thick slices were cut from the bar using an electric-spark machine. The damaged surface layer was mechanically removed from the slices. Then the samples were sealed in quartz ampoules (residual pressure of 4×10^{-4} Pa) and annealed at 800 °C, that is, in the two-phase (αTi) + (βTi) region of ternary Ti–Al–V phase diagram.[27] The duration of annealing was 7, 20, 49, 144, 289 and 840 h. The temperature of annealing was controlled with an accuracy of 1 °C. After annealing, the samples were subsequently quenched in water. For the detection and subsequent analysis of the microstructure the samples were mechanically ground, polished and etched in 1% HF aqueous solution. Observation of microstructure of the samples was performed using optical microscope (LM) Neophot-32. Measurements for quantitative analysis of the microstructure of the samples were also carried out on the BSE microstructure images obtained with a scanning electron microscope (SEM) Tescan Vega TS 5130 MM. To determine the chemical composition of the phases the energy dispersive X-ray spectrometer LINK (Oxford Instruments) was used. Chemical analysis showed that the alloy studied had a composition (89.83 ± 0.07) wt% Ti, (6.21 ± 0.05) wt% Al, (3.92 ±0.06) wt% V and (0.04 ± 0.02) wt% Fe. The phase composition of the samples and lattice parameters of the phases in the alloy were determined using X-ray diffractometer (XRD) Siemens D-500 with Cu-$K_{\alpha 1}$ radiation.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

coarsening, diffusion, grain size, titanium alloys

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