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Malinov, S., Markovsky, P., Sha, W., & Guo, Z. (2001). Resistivity study and computer modelling of the isothermal transformation kinetics of Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo-0.08Si alloys. *Journal of Alloys and Compounds*, 314(1-2)(1-2), 181-192. [https://doi.org/10.1016/S0925-8388\(00\)01227-5](https://doi.org/10.1016/S0925-8388(00)01227-5)

Published in:
Journal of Alloys and Compounds

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Resistivity study and computer modelling of the isothermal transformation kinetics of Ti–6Al–4V and Ti–6Al–2Sn–4Zr–2Mo–0.08Si alloys

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Received 26 June 2000; accepted 7 September 2000

Abstract

A resistivity technique is used to study the kinetics of $\beta \Rightarrow \alpha + \beta$ transformation for Ti–6Al–4V and Ti–6Al–2Sn–4Zr–2Mo–0.08Si alloys at isothermal conditions. The kinetics are modeled in the framework of the Johnson–Mehl–Avrami (JMA) theory. The JMA kinetic parameters for different temperatures and conditions of the above transformation are derived. A good agreement between the calculated and the experimental kinetics is demonstrated. Two different mechanisms of α -phase formation depending on the temperature of isothermal exposure are proposed. The calculation of the thermodynamic equilibria showed good agreement with the experimental data for the Ti–6Al–4V alloy and disagreement for the Ti–6Al–2Sn–4Zr–2Mo–0.08Si alloy. Based on the resistivity results, time–temperature–transformation diagrams for both alloys are designed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Metals; Ti alloys; Phase transformation; Modelling; Kinetics; Resistivity

1. Introduction

Titanium and titanium alloys are currently finding increasingly widespread use in many industries due to their desirable combination of properties. Notable among these are their low densities, which give very attractive strength-to-weight ratios, high temperature capability and almost total immunity to corrosion in many environments. Although the titanium materials are still considered as expensive materials, for many applications the cost of titanium alloys can be justified on the basis of their desirable properties.

The mechanical properties of titanium alloys are very sensitive to the microstructure. It is well known that the final microstructure depends highly on the processing route and the heat and/or thermo-mechanical treatment. It is, therefore, very important to know the thermodynamics and kinetics of the phase transformation taking place under different conditions. The thermodynamics of the phase equilibria in titanium alloys is generally well-studied and known [1]. Most of the binary and ternary titanium phase

equilibrium diagrams are available [2–5]. However, at present there is no comprehensive knowledge on the kinetics of the phase transformations in the variety of the titanium alloys in different time–temperature regimes. There is limited but far from enough work on the study of the kinetics of phase transformations in titanium alloys [6,7].

In this paper we aim to model the kinetics of the $\beta \Rightarrow \alpha + \beta$ phase transformation in Ti–6Al–4V and Ti–6Al–2Sn–4Zr–2Mo–0.08Si alloys under isothermal conditions. An electrical resistivity technique is used to study the course of the transformation. The kinetics are traced within the theoretical frame of the Johnson–Mehl–Avrami (JMA) theory.

2. Experimental procedure

Two of the most widely used ($\alpha + \beta$) and near- α commercial titanium alloys were studied, namely Ti–6Al–4V (Ti 6-4) and Ti–6Al–2Sn–4Zr–2Mo–0.08Si (Ti 6-2-4-2). The chemistry of the alloys was as follows:

- (i) Ti–6-4–Al=6.20 wt.%, V=5.0 wt.%, Fe and other heavy impurities ≤ 0.1 wt.% each, O=1350 ppm;
- (ii) Ti–6-2-4-2–Sn=1.93 wt.%, Mo=1.95 wt.%, Zr=

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3.97 wt.%, C<0.01 wt.%, Fe=0.07 wt.%, Si=0.11 wt.%, Al=6.13 wt.%, O=650 ppm, N=20 ppm, H=45 ppm.

Both alloys were provided by Timet. The Ti 6-4 alloy was rolled with a reduction degree not less than 60% at temperatures in the $\alpha+\beta$ field. Thereafter, recrystallization annealing at 800°C for 2 h was employed. The Ti 6-2-4-2 alloy was processed from an ingot at a temperature above the β -transition and then successively α/β rolled to the final thickness.

The resistivity experiments were performed on a specially developed installation. In all experiments direct resistance heating with industry frequency electric current was employed. This allowed both the heating/cooling rates and the temperatures to be varied within wide ranges. Moreover, this method of heating allowed the heating/cooling procedure to be united with 'in situ' measurement of the relative change of the electrical resistivity. In order to avoid sample oxidation, the experiments were performed in a protective chamber in a flow of dried argon. During the cooling processes, high flow argon was used to speed up the cooling.

Specimens with dimensions of 60×3×1.5 mm were cut and used in the experimental study. The resistivity experiments were performed using the following time-temperature cycle: heating up to a β homogenisation field (1100°C for Ti 6-4 and 1200°C for Ti 6-2-4-2) using a heating rate of 5°C/s; isothermally holding at these temperatures for 5 min; rapid cooling ($\sim 300^\circ\text{C/s}$) to the chosen holding temperature within the $\alpha+\beta$ field and then isothermally holding at this temperature. Electrical resistivity measurements were performed during the isothermal exposure to trace the course of $\beta \Rightarrow \alpha + \beta$ transformation. The measure-

ments were performed at different constant temperatures namely 950, 920, 900, 870, 850, 800 and 750°C for the Ti 6-4 alloy and 930, 900, 850, 800, 750 and 735°C for the Ti 6-2-4-2 alloy. All the above temperatures were in the ranges between the β -transition and M_s temperatures for the corresponding alloy. For each temperature, three separate measurements were conducted on three samples and the results were averaged. The results were reproducible. The difference between the measurements performed on different samples at the same conditions was within $\pm 3\%$ error range.

A light microscopy (LM) study of the initial and final samples and samples quenched from intermediate stages was used to establish the correlation between the relative resistance effect and the amount of the precipitated α -phase. Image analysis was performed using different available software. After isothermal exposure all specimens were quenched at a cooling rate of about 300°C/s. A LM study was performed to check the final microstructure, peculiarities of the α -phase morphology formed and their volume fractions.

3. Results

3.1. Resistivity study

Following the experimental procedure curves $\Delta R/R_0$ ¹ versus time for different temperatures of isothermal exposure were recorded (Fig. 1). It is clear from the obtained data that the resistometric signal increased when the

¹ $\Delta R/R_0$ is the relative increase of the resistivity during isothermal exposure at the corresponding temperature.

Fig. 1. Resistivity measurement results at different temperatures of isothermal exposure for Ti-6Al-4V (a) and Ti-6Al-2Sn-4Zr-2Mo-0.08Si (b) alloys.

temperature was lower. This may be associated with the growth of the α -fraction. It is also possible that the change of the composition of the α - and β -phases (for example the enrichment of the β -phase with vanadium) will have an influence on the resistivity effect. In order to avoid this influence and to separate the above two effects we created calibration curves. The results from the LM study of samples quenched from different temperatures and after different times were used to create the calibration curves of the relative resistance ($\Delta R/R_0$) versus the amount of α -phase (%) for each alloy. It must be pointed out here that for both titanium alloys linear relations between $\Delta R/R_0$ and the amount of α were found and used. The linear relation was well proved and very clear when the degree of transformation varied between 10 and 90%. The relative error of the calibration curve within this range was $\pm 6\%$. For the very early stages ($<10\%$ degree of transformation) as well as for the final stages ($>90\%$ degree of transformation) some deviations from the linear relation and higher errors were possible.

Using aforementioned calibration relations the experimental curves were recalculated to give the amount of α -phase versus time (Fig. 2). As a result of the above procedure the curves in Fig. 2 traced the kinetics of the $\beta \Rightarrow \alpha + \beta$ transformation for the Ti 6-4 and Ti 6-2-4-2 alloys at the temperatures given. It is obvious that at different temperatures of isothermal exposure different final amounts of the α -phase were obtained. This is peculiar to the above alloys since it is well known that for titanium alloys the transformation $\beta \Rightarrow \alpha + \beta$ is from mono-variant type. This means that for different temperatures different amounts of α - and β -phases are in equilibrium.

This observation will be discussed in more detail in the next section.

3.2. Metallography

The typical microstructures of the alloys studied after isothermal exposure at different temperatures and subsequent quenching are presented in Fig. 3. First it is necessary to point out, that the α -phase covering the β -grain boundary was observed in all cases of isothermal exposure for both alloys. This may be explained by the comparatively low ($\sim 300^\circ\text{C/s}$) cooling rate after β -solution treatment. It has been shown earlier [8] that for the Ti 6-4 alloy the critical cooling rate (V_{cr}) that depresses completely all diffusion processes of alloying element redistribution should be about 400°C/s . From the data published in Ref. [9] it is supposed that for the Ti 6-2-4-2 alloy the critical cooling rate is even higher ($\geq 500^\circ\text{C/s}$). Hence, some diffusion processes may take place during the cooling from the β -field to the temperature of isothermal exposure. These processes cause grain boundary α formation.

3.2.1. Ti 6-2-4-2 alloy

The as-quenched microstructure after isothermal exposure at 950°C was characterised by the presence of a fine grain boundary α -phase (Fig. 3a). The total amount of diffusively grown α -phase was about 8%. The remaining volume fraction was occupied by a martensitic phase, which has been formed from the β -phase on subsequent cooling. The matrix (martensite) microstructure was not homogeneous. This was due to the complex mechanism of the transformation including partial diffusional redistribu-

Fig. 2. Kinetics of the $\beta \Rightarrow \alpha + \beta$ transformation at different temperatures of isothermal exposure for Ti-6Al-4V (a) and Ti-6Al-2Sn-4Zr-2Mo-0.08Si (b) alloys.

Fig. 3. Microstructures of Ti-6Al-2Sn-4Zr-2Mo-0.08Si (a–c) and Ti-6Al-4V (d–f) alloys after different temperatures of isothermal exposure and subsequent quenching. (a) Ti-6Al-2Sn-4Zr-2Mo-0.08Si ($T=950^{\circ}\text{C}$); (b) Ti-6Al-2Sn-4Zr-2Mo-0.08Si ($T=900^{\circ}\text{C}$); (c) Ti-6Al-2Sn-4Zr-2Mo-0.08Si ($T=850^{\circ}\text{C}$); (d) Ti-6Al-4V ($T=920^{\circ}\text{C}$); (e) Ti-6Al-4V ($T=870^{\circ}\text{C}$); and (f) Ti-6Al-4V ($T=850^{\circ}\text{C}$).

tion of β -alloying elements and diffusionless (martensitic) transformation (note that the cooling rate after isothermal exposure, $\sim 300^{\circ}\text{C/s}$, is not high enough for pure martensitic transformation).

A decrease of the temperature of isothermal exposure down to 900°C caused formation of a coarse α -phase covering β -grain boundaries. In addition some amount of

α -phase diffusively nucleated and grown from the boundaries was observed (Fig. 3b). The amount of the α -phase was higher in small β grains as compared to the big ones. This observation may be associated with the influence of the grain boundary energy which is proportional to the grain boundary curvature. The total amount of diffusively formed α -phase at 900°C was 38%.

Lower temperatures of isothermal exposure led to a complete change of the mechanism of α -phase formation. In addition to the grain boundary α -phase (formed on cooling from the β -field to the temperature of isothermal exposure) an α -phase nucleated and grown homogeneously inside the former β grains was observed (Fig. 3c). The total amounts of α -phases were 69 and 80% for 850 and 800°C, respectively. The main difference between specimens exposed at 850 and 800°C was the different dispersion of the α lamellae — finer lamellae were attributed to lower temperatures. This may be explained with the higher contribution from the nucleation process in comparison to the growth when the temperature of isothermal exposure was lower. Nevertheless, in both cases the morphology of α -phase allows one to suppose that it has been formed with partial participation of diffusionless (shifting) processes [8].

3.2.2. Ti 6-4 alloy

In the specimen exposed at 950°C and then quenched, a diffusively formed α -phase was found on some β grain boundaries as a thin layer covering the boundary. The volume fraction of the α -phase was about 16%. After exposure at 920°C (Fig. 3d) the morphology of the α -phase, obtained as a result of diffusional decomposition of the β -phase, remained the same. Its volume fraction was slightly increased up to 20%. At 900°C a small portion of grain boundary α -phase as well as α plates diffusively grown from them were observed. The volume fraction of the α -phase was about 38%.

At a lower temperature (870°C) the situation is changed principally. Some portions of the α -phase nucleated and grown within the β grains appeared in addition to the grain boundary α -phase (Fig. 3e). The volume fraction of the diffusional α -phase was about 60%. A further decrease of the temperature down to 850°C led to an increase in the amount of homogeneously nucleated (within the former β grains) α -phase (Fig. 3f). Some martensite was found in the regions close to the β -grain boundaries. A decrease of

the temperature down to 800°C and, especially, to 750°C caused further elevation of the amount of diffusion-formed α -phase up to 72 and 82%, respectively.

4. Analysis and discussion

4.1. Thermodynamic equilibria

It is well known from the fundamental theory of the phase transformations that when an alloy is held at a certain temperature for a long time it tends towards and possibly reaches a thermodynamic equilibrium. If this principle is applied here, it can be assumed that in the final stage, when the transformation has been completed, phase equilibria at the corresponding temperatures have been achieved. This means equilibrium amounts of α - and β -phases as well as equilibrium composition of both phases.

As previously mentioned the phase equilibria in titanium alloys are well studied and known. A Ti-database which allows phase equilibria calculations to be performed for multi-component, conventional titanium alloys is available [1]. In this study we calculated the phase equilibria for the compositions and the temperatures used. The calculations were carried out with Thermo-Calc software and using the above-mentioned Ti database. The experimental (from the resistivity study) and calculated results are compared in Table 1.

A good agreement between the experimental and calculated phase compositions was found for the Ti 6-4 alloy (Table 1). The correspondence was better at lower temperatures (750–800°C). At higher temperatures (850–900°C) the calculated equilibrium α amount was slightly lower than that experimentally observed. The differences between the experimental and calculated phase compositions for Ti 6-4 were within the acceptable error range.

The differences between the calculated amount of equilibrium α -phase and the amount experimentally de-

Table 1
Experimental and calculated phase compositions

Alloy	T (°C)	Experimental		Calculated		Al in α (wt.%)	Al in β (wt.%)	V in α (wt.%)	V in β (wt.%)	Sn in α (wt.%)	Sn in β (wt.%)	Zr in α (wt.%)	Zr in β (wt.%)	Mo in α (wt.%)	Mo in β (wt.%)
		α (vol.%)	β (vol.%)	α (mol)	β (mol)										
Ti-6Al-4V	950	22.5	77.5	—	—	—	—	—	—	—	—	—	—	—	—
	900	43.7	56.3	35.9	64.1	6.9	5.8	2.0	6.7	—	—	—	—	—	—
	850	68.9	31.1	62.2	37.8	6.6	5.5	2.4	9.2	—	—	—	—	—	—
	800	79.5	20.5	76.9	23.1	6.5	5.3	2.8	12.2	—	—	—	—	—	—
	750	85.1	14.9	85.0	15.0	6.4	5.1	3.1	15.8	—	—	—	—	—	—
Ti-6Al-2Sn-4Zr-2Mo-0.08Si	930	14.9	85.1	65.8	34.2	6.7	5.1	—	—	1.8	2.1	3.8	4.3	0.56	4.5
	900	42.7	57.3	78.9	21.1	6.5	4.9	—	—	1.9	1.9	3.9	4.3	0.71	6.4
	850	68.2	31.8	89.5	10.5	6.3	4.8	—	—	2.0	1.3	3.9	4.2	0.95	10.0
	800	82.9	17.1	94.2	5.8	6.3	4.6	—	—	2.0	0.81	4.0	4.0	1.1	14.2
	750	87.3	12.7	96.4	3.6	6.2	4.4	—	—	2.0	0.45	4.0	3.6	1.2	18.9
	735	97.7	2.3	96.8	3.2	6.2	4.3	—	—	2.0	0.37	4.0	3.44	1.3	20.4

ected by the resistivity experiments were significant for the Ti 6-2-4-2 alloy (Table 1). No reasonable explanation for this observation was found. In order to clarify this discrepancy additional experiments were carried out. Samples from both alloys were treated according to the same heat treatment process (see Section 2). Thereafter the samples were studied by means of quantitative metallography. The results are plotted in Fig. 4. Again, acceptable correspondence for the Ti 6-4 alloy was observed (Fig. 4a). For the Ti 6-2-4-2 alloy the experimental results from the metallography study were in agreement with the experimental results of the resistivity study and in disagreement with the calculated phase equilibria (Fig. 4b). Thus we tend to believe that the experimentally observed α -amounts are the correct ones and the calculated values for Ti 6-2-4-2 are unrealistically higher. It should be admitted that the curve, tracing the kinetics at a high temperature (see curve corresponding to 930°C in Fig. 2b), had a tendency to increase with the time prolongation. This may indicate that the transformation at this temperature was still incomplete. Possibly a very slow transformation process was still in progress but it was undetectable with the experimental technique used. Nevertheless, it is very unlikely that even when the time is significantly prolonged the experimental amount of α -phase (~15%) will reach the amount calculated (~65%).

One may conclude that for both alloys there is a better correspondence between the calculated and experimentally observed α -amounts at lower temperatures.

4.2. Kinetics of the transformation

The analysis of the resistivity experimental data was made within the framework of the Avrami theory by

means of the JMA equation [10–13]. This equation traces the kinetics of the transformation giving a relation between the fraction of transformed material and the time. For isothermal transformations this equation has the following popular form:

$$f = 1 - \exp(-kt^n) \quad (1)$$

where f is the product volume fraction which varies with time t , k the reaction rate constant and n the Avrami index that describes the nucleation and growth mechanisms.

In the present study the kinetics of the $\beta \Rightarrow \alpha + \beta$ phase transformation in Ti 6-4 and Ti 6-2-4-2 alloys were modelled by adapting the classic JMA theory. For this particular case the above equation can be written in the form:

$$\frac{f_{\alpha}(t)}{f_{\alpha}^{\max}} = y = 1 - \exp(-kt^n) \quad (2)$$

where $f_{\alpha}(t)$ is the amount of α -phase after a time t , $f_{\alpha}^{\max}$ is the maximum (equilibrium) volume fraction of the α -phase at the corresponding temperature of the transformation and y is the 'degree of the transformation'.

It must be pointed out that the JMA equation traces the transformation from its start and does not describe the pre-processing stages and the incubation time. Hence, the time should be treated not as an absolute time but as relative to the start of the transformation. Here the above was taken into account by simple subtraction of the incubation times at the corresponding temperatures.

Eq. (2) was used to analyse the experimental data by means of logarithmic plots, where $\ln(\ln(1/(1-y)))$ is plotted versus $\ln(t)$. The slope of the resulting straight line is the Avrami exponent ' n ', while from the intercept the

Fig. 4. Experimentally observed and calculated α -phase amounts for Ti-6Al-4V (a) and Ti-6Al-2Sn-4Zr-2Mo-0.08Si (b) alloys.

' k ' value can be calculated. Such plots are presented in Fig. 5 for some of the temperatures applied in the present study. It was found that for all the temperatures used the experimental measurements were described very well by straight lines when the plots were in the above coordinate system. This means that the JMA theory can be applied to describe the kinetics of the $\beta \Rightarrow \alpha + \beta$ phase transformation in near- α titanium alloys under isothermal conditions. Moreover, the mechanism of the transformation does not change in the course of the transformation. It has been shown recently [6] that in near- β titanium alloys (Ti 10-2-3 and β -CEZ) the mechanism of the transformation changes during the course of the transformation when the transformation takes place at low temperatures (350°C). This was indicated by the obvious change of the line slope. Such effects were not observed here for near- α titanium alloys. In both alloys the transformations were well described by single straight lines for all temperatures applied.

Using the above plots ' n ' and ' k ' values for all applied temperatures were derived in both titanium alloys studied (Table 2).

It is apparent that the Avrami indexes (n) for all temperatures used in both alloys are within the narrow range of 1.15–1.60. This corresponds to the mechanism of the $\beta \Rightarrow \alpha + \beta$ transformation in titanium alloys, namely that β -grain boundaries are the nucleation sites and the α -phase has a plate-like morphology. No clear tendency in the ' n ' and ' k ' values was observed.

It must be pointed out, however, that although the above plots are the most usual means of deriving of the JMA kinetics parameters such a free approach may be misleading. In this respect it should be mentioned that acceptable good fittings, between the experimental and the calculated fractions were possible for any ' n ' value ranging within 1.2–1.5 and for all curves in Fig. 2. Since ' n ' is correlated with the nucleation and growth mechanisms (the geometry of the transformation) the next conclusion in this work was that the mechanism of the transformation does not change in the applied temperature ranges. This conclusion is valid for most transformations over an appreciable temperature range [14]. Thereby the next step was to fit the experimental data in Fig. 2 to the JMA theory (Eq. (2)) by setting the n value free but constant for all the temperatures used. This was performed by optimisation computer program trying to minimise the 'sum square error' between the experimental and calculated fractions for all temperatures. From such calculations the values of $n=1.31$ for Ti 6-4 and $n=1.44$ for Ti 6-2-4-2 were obtained. The calculated rate constant values (k) for these cases are plotted in Fig. 6.

The temperature dependence of the rate constant was not monotonic in the above cases (Fig. 6). For both alloys there was an abnormality at about 900°C. Apparently the transformation could be considered as having two somewhat different kinetics above and below 900°C. Within both temperature intervals and in both alloys the rate constant increased with decreasing temperature (increasing

undercooling). Such a characteristic is usual for phase transformations taking place on cooling. These results were in agreement with the results from the metallography study of samples after isothermal exposure at different temperatures (see Section 3.2). It was found that the microstructures of the α -phase produced above and below 900°C were different. For the temperatures above 900°C the α -phase was mainly grain boundary nucleated and grown (Fig. 3a,b,d). For a high degree of undercooling (temperatures below 900°C) mixed mechanisms of the transformation were observed. The main part was homogeneously nucleated (within the former β -grains) and plate-like grown α -phase (Fig. 3c,e,f). Small amounts of the grain boundary α were observed as well.

These observations implied that the Avrami indexes (' n ' values) are different for the kinetics of the $\beta \Rightarrow \alpha + \beta$ transformations above and below 900°C. For example for grain boundary nucleation after saturation $n=1$ and for diffusion-controlled growth of plates under the assumption that all particles were present at $t=0$ and had negligible initial dimensions $n=3/2$ [14].

Following the above reasoning the resistivity data were fitted to the JMA equation assuming different ' n ' values for $\beta \Rightarrow \alpha + \beta$ transformation for temperatures above and below 900°C. The derived kinetics parameters as well as the different mechanisms of the α -phase nucleation and growth for both studied alloys are summarized in Table 3.

In Fig. 7 the calculated (from the JMA theory) and the experimental (from the resistivity measurements) transformation kinetics were compared for different constant temperatures and for both alloys studied. Calculated fractions were based on Eq. (2) using the ' n ' and ' k ' values given in Table 3. A very good correspondence between the calculated and the experimental curves was found. This correspondence gave us confidence in the obtained JMA kinetic parameters. These parameters can be used in the heat treatment practice of titanium alloys to predict and trace the course of $\beta \Rightarrow \alpha + \beta$ transformation in Ti 6-4 and Ti 6-2-4-2 alloys at different isothermal conditions.

The approach described above using two different mechanisms and, respectively, two different ' n ' values of the $\beta \Rightarrow \alpha + \beta$ transformation in Ti 6-4 is different from the approach used in S. Malinov, Z. Guo, W. Sha, A. Wilson (unpublished research); in that work the kinetics of the same transformation have been modeled during continuous cooling on the base of differential scanning calorimetry experiments. A single n value for the entire temperature interval of the transformation has been attributed to continuous cooling conditions. In the following some explanation of the different approaches is given.

The mechanisms of the transformations are different for continuous cooling and isothermal conditions with respect to the nucleation and growth conditions. This difference is significant for phase transformations taking place on cooling in titanium alloys. In the case of continuous cooling at each temperature the transformation starts and proceeds in conditions of microstructure, which has been

Fig. 5. Plots of $\ln(\ln(1/(1-y)))$ against $\ln(t)$ for deriving of the JMA parameters for Ti-6Al-4V (a,c,e) and Ti-6Al-2Sn-4Zr-2Mo-0.08Si (b,d,f) at different temperatures. (a) Ti-6Al-4V at 750°C; (b) Ti-6Al-2Sn-4Zr-2Mo-0.08Si at 750°C; (c) Ti-6Al-4V at 850°C; (d) Ti-6Al-2Sn-4Zr-2Mo-0.08Si at 850°C; (e) Ti-6Al-4V at 950°C; and (f) Ti-6Al-2Sn-4Zr-2Mo-0.08Si at 930°C.

Table 2

JMA kinetic parameters for Ti–6Al–4V and Ti–6Al–2Sn–4Zr–2Mo–0.08Si alloys obtained by $\ln(\ln(1/(1-y)))$ versus $\ln(t)$ plots

Alloy	Temperature of the transformation (°C)	<i>n</i>	<i>k</i>
Ti–6Al–4V	950	1.41	0.017
	920	1.39	0.024
	900	1.21	0.046
	870	1.34	0.025
	850	1.38	0.022
	800	1.34	0.026
	750	1.40	0.028
Ti–6Al–2Sn–4Zr–2Mo–0.08Si	930	1.15	0.032
	900	1.53	0.014
	850	1.53	0.012
	800	1.36	0.024
	750	1.60	0.013
	735	1.30	0.059

formed at previous stage(s). For example at 850°C the studied transformation on continuous cooling is in conditions of nucleation sites that already exist (grain boundary α formed on cooling from β -transition to the current temperature) which are preferable sites for further growth. In the case of isothermal exposure the sample is cooled rapidly from the β -field to the temperature of isothermal exposure (850°C). At this temperature spontaneous nucleation (mainly homogeneous) and growth take place. In other words in the cases of isothermal exposure when the undercooling is high the amount of the α -phase formed and grown within the former β -grains will be higher as compared to the grain boundary α (see Fig. 3f). These two different mechanisms result in a somewhat different morphology of the α -phase formed and imply a difference in the Avrami indexes derived from continuous cooling and

isothermal experiments. Nevertheless both approaches and models have their own importance and area of application.

4.3. Time–temperature–transformation diagrams

Using the resistivity results on the kinetics of $\beta \Rightarrow \alpha + \beta$ transformation at different constant temperatures complete isothermal transformation diagrams were designed. These diagrams, also known as time–temperature–transformation (TTT) diagrams, give the relationship between the temperature (plotted linearly) and the time (plotted logarithmically) for a fixed fractional amount of transformation to be attained. Such diagrams are usually used in alloy heat treatment practice. In most cases only the ‘start’ and the ‘end’ of the transformation are plotted in these diagrams. However, it must be emphasized that times corresponding to the start and the end of the transformation are difficult to be measured experimentally. For this reason in our calculations we used transformed fractions of 5 and 95% for the start and the end of the transformation, respectively (Fig. 8). It should also be noted that for the studied titanium alloys the ‘end of transformation’ does not correspond to the situation where the initial phase (β -phase) completely transforms to the new phase (α -phase). At each temperature a different phase composition ($\alpha + \beta$ mixture) is the final product (see Section 4.1). Hence, the start and the end of the transformation should not be read as 5 and 95% of the α -phase but as a 5 and 95% degree of transformation. Iso-lines were calculated and plotted on the same diagrams (Fig. 8), showing the real amounts of the α -phase.

In addition, available in the literature TTT diagrams for the studied alloys are plotted in the same figures. From the resistivity study we found that the kinetics of the $\beta \Rightarrow \alpha + \beta$ transformation at isothermal conditions in Ti 6-4 and Ti

Fig. 6. Calculated JMA rate constants for $\beta \Rightarrow \alpha + \beta$ transformation in Ti–6Al–4V (a) and Ti–6Al–2Sn–4Zr–2Mo–0.08Si (b) alloys assuming constant Avrami indexes (*n*).

Table 3

JMA kinetic parameters for two different mechanisms of the $\beta \Rightarrow \alpha + \beta$ transformations in Ti 6-4 and Ti 6-2-4-2 alloys at different temperatures of isothermal transformations

Alloy	Temperature of the isothermal transformation	α -Phase morphology	JMA parameters	
			n	k
Ti-6Al-4V	950	Grain boundary α -phase + some amounts of α -plates nucleated and grown from the grain boundaries.	1.1	0.045
	920			0.055
	900			0.068
	870	Mixed: homogeneously nucleated and plate-like grown α -structure + grain boundaries nucleated and grown α -phase (Fig. 3c).	1.35	0.025
	850			0.024
	800			0.025
	750			0.033
Ti-6Al-2Sn-4Zr-2Mo-0.08Si	930	Grain boundary α -phase + some amounts of α -plates nucleated and grown from the grain boundaries.	1.15	0.035
	900			0.043
	850	Mixed: homogeneously nucleated and plate-like grown α -structure + grain boundaries nucleated and grown α -phase (Fig. 3f).	1.48	0.013
	800			0.017
	750			0.018
	735			0.044

6-2-4-2 alloys are very similar in the temperature range of 800–900°C (Fig. 8a,b). However, the published TTT diagrams in Ref. [15] for these alloys are very different especially in regard to the ‘end’ of the transformation. For the Ti 6-2-4-2 alloy the ‘end’ of the transformation in the above temperature range is at 5–10 s (see dot lines in Fig. 8b) while for the Ti 6-4 alloy it is at >500 s (see dot lines in Fig. 8a). We do not agree with such a high difference in the kinetics of the $\beta \Rightarrow \alpha + \beta$ transformation in these two alloys at isothermal conditions. In this respect it is worth mentioning that in our previous study on the same trans-

formation using differential scanning calorimetry (S. Malinov, Z. Guo, W. Sha, A. Wilson, unpublished research) we found that the Ti 6-2-4-2 and Ti 6-4 alloys have a very similar kinetics of the $\beta \Rightarrow \alpha + \beta$ transformation at continuous cooling.

The curves presenting the end of the $\beta \Rightarrow \alpha + \beta$ transformation showed a small deviation from the usual ‘C-shape’ of such diagrams for both alloys. This may be due to incomplete transformations at high temperatures (>900°C). Probably a very slow process of transformation will still occur if the time is prolonged. But this process

Fig. 7. Experimental and calculated kinetics of the $\beta \Rightarrow \alpha + \beta$ transformation at different temperatures for Ti-6Al-4V (a) and Ti-6Al-2Sn-4Zr-2Mo-0.08Si (b) alloys.

Fig. 8. Calculated time–temperature–transformation diagrams for Ti–6Al–4V (a) and Ti–6Al–2Sn–4Zr–2Mo–0.08Si (b) alloys plotted together with TTT diagrams published in the literature (Ref. [15]).

was beyond the accuracy of the experimental technique used. For the Ti 6-4 alloy no ‘nose’ point for the start of the transformation was found. Two possible reasons for this observation are suggested:

- The vanadium content of the alloy studied was higher than the normal for the Ti 6-4 alloy. Vanadium causes a decrease of the β -transition temperature, which itself will cause a ‘shifting down’ of the TTT diagrams [16]. Hence, before the ‘nose’ point appears the mechanism of the transformation is altered from pure diffusional (above 800–850°C) to diffusional with partial participation of diffusionless (shifting) processes (it is peculiar of titanium alloys that there is not a sharp boundary between diffusional and diffusionless (martensitic) transformations [8]).
- Preprocessing and even early stages of the transformation may take place on cooling from the β -region to the temperature of the isothermal exposure. This is more likely to happen at lower holding temperatures. Since the incubation periods for the studied transformations are very short (a few seconds) this effect may contribute to the experimental absence of the ‘nose’ point.

For the Ti 6-2-4-2 alloy a TTT diagram was calculated on the basis of an artificial neural network model [16]. The

start of the $\beta \Rightarrow \alpha + \beta$ transformation from neural network model predictions and from resistivity experiments is compared in Fig. 9. Good correspondence between the results obtained in different ways was found.

Fig. 9. Calculated start of the $\beta \Rightarrow \alpha + \beta$ transformation in Ti–6Al–2Sn–4Zr–2Mo–0.08Si alloy (TTT diagram) from resistivity experiments and from artificial neural network predictions.

5. Summary and conclusions

- Study of the thermodynamics of $\beta \Rightarrow \alpha + \beta$ transformation showed good correspondence between the experimental and the calculated phase equilibria for the Ti–6Al–4V alloy and disagreement for the Ti–6Al–2Sn–4Zr–2Mo–0.08Si alloy.
- On the basis of resistivity experiments the kinetics of the $\beta \Rightarrow \alpha + \beta$ transformation were modeled under isothermal conditions. The JMA kinetic parameters were derived for different temperatures. A good agreement between the calculated and the experimental transformed fractions was found out.
- Two different mechanisms of the $\beta \Rightarrow \alpha + \beta$ transformation under isothermal conditions were observed in the alloys studied. For temperatures above 900°C mainly grain boundary α was nucleated and grown. For temperatures below 900°C the main part was a homogeneously nucleated and grown α -phase.
- Time–temperature–transformation diagrams were designed for the $\beta \Rightarrow \alpha + \beta$ transformation in Ti–6Al–4V and Ti–6Al–2Sn–4Zr–2Mo–0.08Si alloys. Iso-lines were calculated and plotted tracing the amounts of the α -phase.

Acknowledgements

This work was carried out within the framework of project ‘Modeling the Evolution of Microstructure during Processing of Titanium Alloys’ sponsored by the UK Engineering and Physical Sciences Research Council under grant number GR/M 19932. The authors appreciate the assistance of Dr. A.F. Wilson from Timet UK Ltd. in supplying the alloys and providing the chemical analysis.

References

- [1] N. Saunders, Titanium '95: Science and Technology, in: P.A. Blenkinsop, W.J. Evans, H.M. Flower (Eds.), Proceedings of the Eight World Conference on Titanium, The Institute of Materials, London, 1996, pp. 2167–2176.
- [2] R. Boyer, G. Welsch, E.W. Collings, Materials Properties Handbook: Titanium Alloys (Ed.), ASM International, Materials Park, OH, 1994.
- [3] J.L. Murray, Phase Diagrams of Binary Titanium Alloys (Ed.), ASM International, Materials Park, OH, 1987.
- [4] ASM Handbook, Vol. 3. Alloy Phase Diagrams, ASM International, Materials Park, OH, 1992.
- [5] P. Villars, A. Prince, H. Okamoto, Handbook of Ternary Alloy Phase Diagrams (Ed.), ASM International, Materials Park, OH, 1995.
- [6] S. Bein, J. Bechet, J. Phys. III 6 (1996) C1–99.
- [7] E. Laude, E. Gautier, S. Denis, Titanium '95: Science and Technology, in: P.A. Blenkinsop, W.J. Evans, H.M. Flower (Eds.), Proceedings of the Eight World Conference on Titanium, The Institute of Materials, London, 1996, pp. 2330–2337.
- [8] V.N. Gridnev, O.M. Ivasishin, P.E. Markovsky, V.L. Svechnikov, Phys. Metals 3 (7) (1987) 508.
- [9] Y.C. Huang, S. Suzuki, H. Kaneko, T. Sato, in: R.I. Jaffee, N.E. Promisel (Eds.), The Science, Technology and Application of Titanium Alloys, Pergamon, London, 1970, pp. 695–699.
- [10] M. Avrami, J. Chem. Phys. 7 (1939) 1103.
- [11] M. Avrami, J. Chem. Phys. 8 (1940) 212.
- [12] M. Avrami, J. Chem. Phys. 9 (1941) 177.
- [13] W.A. Johnson, R.F. Mehl, Trans. Am. Inst. Min. Metall. Eng. 135 (1939) 416.
- [14] J.W. Christian, The Theory of Transformation in Metals and Alloys: Equilibrium and General Kinetic Theory, 2nd Edition, Pergamon, Oxford, 1975, pp. 525–548.
- [15] G.F. VanderVoort, Atlas of Time-temperature Diagrams for Nonferrous Alloys (Ed.), ASM International, Materials Park, OH, 1991.
- [16] S. Malinov, W. Sha, Z. Guo, Mater. Sci. Eng. A 283 (2000) 1–10.