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Growth kinetics of ω particles in β -Ti matrix studied by in-situ small-angle x-ray scattering

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Abstract

Nucleation and growth kinetics of nanoparticles of hexagonal ω phase in a body-centered cubic β titanium matrix in single crystals of β -Ti alloys were investigated by small-angle x-ray scattering measured *in-situ* during ageing at various temperatures up to 450 °C. The experimental data were compared with numerical simulations based on a three-dimensional short-range order model of nanoparticle self-ordering. The x-ray contrast of the particles is caused by an inhomogeneous distribution of impurity atoms (Mo, Fe and Al), whose density profile around growing nanoparticles was simulated by solving the corresponding diffusion equation with moving boundary conditions. From the analysis of the experimental data we determined the mean distance and size of the nanoparticles and confirmed the validity of the $\propto t^{1/3}$ growth law following from the Lifshitz-Slyozov-Wagner theory. From a detailed comparison of the experimental data with simulations we also assessed the diffusion coefficient of the impurity atoms and its activation energy.

Keywords

ω -Ti phase; Ti alloys; small-angle x-ray scattering; self-ordering

1 Introduction

Metastable β titanium alloys are the most prospective and versatile group of titanium alloys, as they exhibit high specific strength and good fatigue and corrosion resistance [1]. Moreover, the complexity of microstructure and phase transformations in these alloys allows to tailor their mechanical properties to the specific needs of individual applications. The properties of β titanium alloys are determined by alloying elements. In metastable β -Ti alloys the temperature of the start of a martensitic transformation is suppressed below room temperature and thus the body-centered cubic (bcc) β phase is retained in a metastable state upon quenching [2]. In a certain composition range, particles of metastable ω phase are formed in metastable β titanium alloys. The ω phase has a hexagonal structure and is observed as particles of a few tens of nanometers in size uniformly dispersed throughout the β matrix. Crystallographically, the ω phase is coherent with the β phase and the two structures obey a relationship [3]

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$$(0001)_{\omega} \parallel (111)_{\beta}, [11\bar{2}0]_{\omega} \parallel [011]_{\beta}. \quad (1)$$

The mechanism of ω phase formation has been described as a shift of two neighbouring $(111)_{\beta}$ planes along the body diagonal of the cubic cell to their intermediate position, while one $(111)_{\beta}$ between two pairs of collapsed planes is left unchanged [4, 5]. At elevated temperatures, particles of ω phase grow by a diffusional process which is accompanied by rejection of β -stabilizing elements from the ω phase into the β matrix [6]. It has been shown recently by small-angle x-ray scattering (SAXS) that the distribution of the ω phase particles in the β matrix is not random but the ω particles are ordered in a cubic superlattice with axes along $\langle 100 \rangle_{\beta}$ directions. This spontaneous ordering has been ascribed to the minimization of the inter-particle elastic energy in the elastically anisotropic body-centered cubic β phase [7].

Growth of nanoparticles and phase transformations in Ti alloys have been performed by P. Fratzl et al. [8, 9, 10], using SAXS *ex-situ*. In these papers it has been demonstrated that the mean particle size grows during ageing as $\propto t^{1/3}$ with ageing time t . However, the growth finally stabilizes reaching a maximum particle size of a few nm. This effect is explained by the influence of elastic interaction between ω particles. The $\propto t^{1/3}$ growth kinetics follows from the classical description of diffusion-limited particle growth by Lifshitz, Slyozov and Wagner [11, 12] (LSW theory).

The main goal of the present work is to study the kinetics of ω phase reaction *in-situ* by measuring SAXS during isothermal ageing at selected temperatures. To our knowledge, very few in-situ SAXS experiments were done on alloys. For example, authors in [13] studied the evolution of Gunier–Preston–Bagaryatskii zones and δ' precipitates in three aluminum alloys during ageing at room temperature and at 150 °C. Further in-situ SAXS was done by Deschamps et al. [14, 15] on Al–Zn–Mg alloys. However, no in-situ SAXS measurements were yet performed on titanium alloys.

The paper is organized as follows. In the following section we describe the sample preparation and the arrangement of the SAXS measurement. Then, we formulate the problem of diffusion of impurity atoms around a growing particle and find its numerical solution. In Sect. 4 we introduce the short-range order model of the spontaneous ordering of particles and bring formulas for the simulation of the intensity of small-angle scattering. Sect. 5 presents the experimental results and its comparison with theoretical simulations and in Sect. 6 we discuss the assumptions and limitations of the used model.

2 Experimental and data treatment details

For the purpose of this study, two metastable β titanium alloys were used: Ti–15 wt.%Mo and Ti–6.8 Mo–4.5 Fe–1.5 Al in wt.% (hereinafter referred to as Ti-15Mo and LCB, respectively). Single-crystals were grown from these alloys using a floating zone method described in [16]. The resulting ingots were solution treated in an evacuated quartz tube at 860 °C for 4 h and subsequently quenched in water. The single-crystal was then cut into

samples whose surface was parallel with the (001) plane of the bcc β phase. The samples were ground and polished from both sides using SiC grinding papers (grit size 500, 800, 1200, 2400 and 4000) to the thickness of approximately 500 μm . Final polishing was done on a vibratory polisher employing 0.3 μm and 0.05 μm aqueous alumina suspensions and 0.05 μm colloidal silica.

Small-angle x-ray scattering was measured at ESRF, Grenoble, on the high-energy beamline ID15A. A high energy of the primary beam allowed us to measure thicker samples and therefore to obtain better statistics from the bulk by minimizing the influence of sample surface, where the ω phase structure may be in principle different (e.g. as a consequence of mechanical polishing or surface elastic effects). The photon energy was 69.5 keV and the primary beam irradiated the sample at normal incidence. The spot size of the primary beam was set to 120 $\mu\text{m} \times 30 \mu\text{m}$. The scattered beam was detected by a two-dimensional CCD detector (FReLoN) with 2048 $\times$ 2048 pixels. The detector was placed at the distance of 7.8 m from the sample and the pixel size was 24 μm . The acquisition time of one detector frame was 5 – 20 sec depending on the scattered intensity.

The experiments were done in-situ during isothermal annealing (ageing) in a dedicated microtomography furnace equipped with a quartz chamber which allowed evacuation up to 10^{-6} mbar. The samples were heated to the set temperature with the maximum rate the furnace allowed (30 – 40 $^{\circ}\text{C}/\text{min}$) and then the temperature was held for 2 – 8 h. The selected temperatures were 335 $^{\circ}\text{C}$, 370 $^{\circ}\text{C}$, 390 $^{\circ}\text{C}$ and 410 $^{\circ}\text{C}$ for the LCB alloy and 350 $^{\circ}\text{C}$, 370 $^{\circ}\text{C}$, 390 $^{\circ}\text{C}$, 410 $^{\circ}\text{C}$, 430 $^{\circ}\text{C}$ and 450 $^{\circ}\text{C}$ for Ti-15Mo. The scattering angle was calibrated using Ag behenate [17]. The measured intensity was corrected for absorption in the sample and the background scattering was subtracted.

Figure 1 shows the examples of measured 2D intensity maps converted to reciprocal space, for LCB and Ti-15Mo samples aged at 390 $^{\circ}\text{C}$ for 2 h. The four-fold symmetry of the side maxima depicted in the figure demonstrates that the particle positions are self-arranged in a disordered cubic lattice along $\langle 100 \rangle_{\beta}$ directions [7]. It is clearly seen in Fig. 1 that the evolution of the ω particles is quite different in LCB and in Ti-15Mo. The scattered intensity from the ω particles in the LCB alloy (left panel) exhibits the side maxima at smaller Q , which indicates more distant (and probably larger) particles than in the Ti-15Mo alloy (right panel). From the 2D maps we extracted linear intensity scans along $[100]_{\beta}$ direction (denoted by dotted lines in Fig. 1) crossing the side maxima of the scattered intensity. In Fig. 2 we display the time-dependence of the intensities along the cuts of the same samples (390 $^{\circ}\text{C}/2$ h). It is clear that the side maxima move towards the center of the pattern with increasing annealing time. This indicates that the mean particle distance increases. In addition to the strong first-order maxima, additional much weaker second-order maxima appear. These second-order maxima demonstrate relatively small dispersion of the particle distances and/or sizes. As we will show in the next section, the second-order maxima are important for the determination of the data evaluation.

3 Diffusion of impurity atoms during the growth of ω particles

Small-angle x-ray scattering (SAXS) contrast is caused by local variation of the refraction index of the investigated material for the particular x-ray energy. In our case, this difference is caused mainly by the different concentrations of impurity atoms (Mo in Ti-15Mo samples and Mo, Fe, Al in the LCB alloy) in β and ω phases resulting from the diffusion accompanied growth of the ω particles. The contrast of the refraction indexes of the ω and β phases of pure Ti is negligibly small. Therefore, for a detailed analysis of the measured SAXS data, it is necessary to solve the problem of diffusion of the impurity atoms around a growing ω particle. In the description of this process we apply the following simplifying conditions:

1. Only one type of impurity atoms is considered. This assumption is fulfilled in the Ti-Mo alloy. In the LCB alloy the Mo, Fe and Al impurities are replaced by "effective" impurity atoms that give rise to the x-ray scattering contrast. Trace elements such as O, N and H are neglected.
2. The diffusion coefficient D of the impurity atoms does not depend on their density; obviously, this assumption is fulfilled for smaller densities.
3. The concentration ρ_c of the impurity atoms in the ω particle is assumed to be time-independent.
4. The problem is assumed isotropic, i.e. the particles are spherical and the concentration $\rho(r, t)$ of the impurity atoms around the particles depends only on the distance r from the particle center. Therefore we neglect both the anisotropy of the diffusion coefficient (caused by the anisotropy of the host lattice), and the effect of local anisotropic elastic strain around an ω particle on the diffusion of impurities.
5. For the description of the diffusion of the impurity atoms around a given particle we neglect the influence of other particles.
6. The description of the diffusion of impurity atoms does not include the phase transformation $\beta \rightarrow \omega$. The time-dependence of the radius of the growing ω particle $R(t)$ is given and is used as an input in the diffusion problem.

From the last condition it follows that the theoretical description includes *neither* the nucleation of the ω -particles by the martensitic $\beta \rightarrow \omega$ transformation *nor* the subsequent growth of the nanoparticles, and it is restricted only to the problem of the time evolution of the local cloud of impurity atoms around a growing particle, the evolution of which is used as an input. We have treated this problem by solving the standard diffusion equation for the density profile $\rho(r, t)$ of the impurity atoms taking into account the boundary condition at the moving interface between the particle and its neighborhood, i.e., at $r = R(t)$. This boundary condition follows from the conservation of the particle flux at the particle/matrix interface and it contains the constant density ρ_c of the impurity atoms in the particle as a fixed parameter.

In agreement with the classical paper by Ham [18] we divided the sample volume into non-penetrating spherical regions with the radius $R_L(t)$; the volume of one region equals the volume corresponding to a single particle. As we showed in our previous paper [7], the particles create a disordered cubic lattice with the lattice parameter (mean particle distance) $L(t)$ so that $4\pi R_L^3/3=L^3$. The boundary $r=R_L(t)$ is moving as well and we assume that the impurity flux across this boundary is zero.

The boundary value problem (BVP) with moving boundaries was formulated for the first time by J. Stefan [19]; in Ref. [20] several methods are presented for its numerical solution. The details of our calculation are presented in Appendix A.

Figure 3 presents an example of the simulated density profiles. In the simulation we put the diffusion constant $D=0.1 \text{ nm}^2\text{s}^{-1}$, a constant proportionality factor $\zeta=L(t)/R(t)$, and assumed that, in agreement with the LSW theory, the particle is growing according to the dependence $R(t)=R(0)+v_R t^{1/3}$, $R(0)=10 \text{ nm}$, $v_R=1 \text{ nm s}^{-1/3}$. For the calculation of the starting density distribution we used $t_{\text{inc}}=10 \text{ s}$.

The numerical solution of the BVP is rather time consuming so that it was not practical to include the full simulation into a procedure fitting the measured SAXS data to the theory. Instead, we found a suitable parametrization of the BVP results, which made it possible to perform numerical fits. It came out that the second-order polynomial

$$\varrho(r,t) \approx a_0(t) + a_1(t)r + a_2(t)r^2, r \in [R, R_L]. \quad (2)$$

approximates the density profile with a very good accuracy. We chose the coefficients $a_{0,1,2}(t)$ so that the polynomial function obeys the boundary conditions (A.6), the explicit formulas are given in Appendix B. From the comparison of exact and approximate density profiles in Fig. 3(b) it is obvious that the true density profile can be replaced indeed by this simple polynomial function and this approximation improves with increasing time t ; this fact was further used for the fitting of SAXS experimental data. Moreover, as we show in Appendix B, the advantage of the 2nd order polynomial approximation consists in the fact that the shape of the density profile is characterized by a single parameter

$$\varepsilon = \frac{1}{2D} \frac{dR}{dt} \quad (3)$$

describing the influence of the boundary movement on the concentration profile $\varrho(r, t)$.

4 Simulation of SAXS intensity

In the simulation of the SAXS intensity we start from the differential scattering cross-section from a random ensemble of particles [7]

$$\frac{d\sigma}{d\Omega} = \frac{K^4 |\eta|^2}{4\pi^2} \left\langle \sum_{j,k} e^{-i\mathbf{Q} \cdot (\mathbf{r}_j - \mathbf{r}_k)} \Omega_{R_j}(\mathbf{Q}) \Omega_{R_k}^*(\mathbf{Q}) \right\rangle_{\text{positions, sizes}} \quad (4)$$

Here we denoted $\mathbf{Q} = \mathbf{K}_{\text{out}} - \mathbf{K}_{\text{in}}$ the scattering vector, $K = 2\pi/\lambda$, and R_j is the (random) radius of the j -th particle. For the refraction index of x-rays n we used the formula $1 - n(\mathbf{r}, t) = \eta \rho(\mathbf{r}, t)$; the proportionality factor η depends on the nature of the impurity atoms and on the photon energy. The double sum in Eq. (4) runs over the particles in the irradiated sample volume, $\mathbf{r}_j$ is the random position vector of the j -th particle and

$$\Omega_R(\mathbf{Q}) = \int_{|\mathbf{r}| \leq R_L} d^3\mathbf{r} [\varrho(r) - \varrho(R_L)] e^{-i\mathbf{Q} \cdot \mathbf{r}}, \quad (5)$$

is the Fourier transformation of the local contrast of the impurity density around a particle (shape function) including the particle core with radius R and the impurity density ϱ_c . Since the cloud of impurity atoms around a given particle is assumed isotropic, the shape function of the particle is isotropic as well and depends only on the length Q of the scattering vector $\mathbf{Q}$. Assuming the polynomial profile of the density of impurity atoms around a particle introduced in Eq. (2), and the constant density ϱ_c of the impurities in the particle, the shape function can be calculated analytically. The resulting formula is rather cumbersome and is presented in Appendix B. In addition to the radii R and R_L , the shape function contains only the factor ε defined in Eq. (3); the difference $\varrho_s - \varrho_c$ occurring in Eq. (B.1) is included in a multiplicative constant.

The averaging in Eq. (4) is performed over random positions and sizes of the particles, employing the local monodisperse approximation (LMA) [7, 21], i.e. assuming

$$\begin{aligned} \left\langle \sum_{j,k} e^{-i\mathbf{Q} \cdot (\mathbf{r}_j - \mathbf{r}_k)} \Omega_{R_j}(\mathbf{Q}) \Omega_{R_k}^*(\mathbf{Q}) \right\rangle &\approx \\ \left\langle |\Omega_R|^2 \left\langle \sum_{j,k} e^{-i\mathbf{Q} \cdot (\mathbf{r}_j - \mathbf{r}_k)} \right\rangle_{\text{positions}} \right\rangle &= \\ = N^3 \left\langle |\Omega_R|^2 G_R(\mathbf{Q}) \right\rangle_R. \end{aligned} \quad (6)$$

Here $\langle \rangle_R$ denotes the averaging over the particle radii,

$$G_R(\mathbf{Q}) = \frac{1}{N^3} \left\langle \sum_{j,k} e^{-i\mathbf{Q} \cdot (\mathbf{r}_j - \mathbf{r}_k)} \right\rangle_{\text{positions}} \quad (7)$$

is the correlation function of the particle positions for a given particle radius R , and N^3 is the total number of coherently irradiated particles (assumed very large). In Appendix C we present an explicit formula of $G_R(\mathbf{Q})$ assuming a three-dimensional short-range order model.

Taking into account all pre-factors, the flux of scattered x-rays in one detector pixel (number of photons in one second) is

$$J(\mathbf{Q}) = J_{\text{inc}} \frac{K^4 |\eta|^2}{4\pi^2} \frac{T}{L_0^3} \frac{p^2}{Z^2} \langle |\Omega_R(\mathbf{Q})|^2 G_R(\mathbf{Q}) \rangle_R e^{-\mu T}. \quad (8)$$

Here we denoted J_{inc} the flux of the primary x-ray beam, T the sample thickness, p the size of the detector pixel, Z the sample-detector distance, and μ the x-ray linear absorption coefficient. The averaging $\langle \rangle_R$ in Eq. (8) was carried out numerically assuming Gamma distribution of the particle radii with the mean value $R_0 = \langle R \rangle$, order m_R , and rms deviation

$\sigma_R = \sqrt{\langle R^2 \rangle - R_0^2} = R_0 / \sqrt{m_R}$. In the calculation of the average we assumed that the distributions of the particle distances L for various particle radii R 's are similar, i.e. the mean values L_0 as well as the rms deviations σ_L scale with R . Analogously, the density profiles $\rho(r) = \rho(r) - \rho(R_L)$ around various particles are similar, i.e. they scale with R as well. Summarizing this part, we used Eq. (8) for the simulation of the SAXS intensity, the correlation function $G_R(\mathbf{Q})$ was calculated by Eqs. (C.2), (C.1), and the shape function of the particle $\Omega_R(\mathbf{Q})$ was taken from Eqs. (B.2) and (B.3).

The above described theory was employed to fit the measured fluxes $J(Q_x, t)$ corrected to the monitor flux J_{mon} and extracted along the $[100]_\beta$ direction. We tested various fitting strategies and found that the most robust fitting results can be obtained only if we assume *a-priori* that the diffusion coefficient D is time independent. The time evolution of the mean distance $L_0(t)$ of the particles was determined directly from the measured data without fitting. Namely, numerical simulations revealed that the position $Q_{\text{max}}^{(1)}$ of the first (non-central) maximum in the measured data agrees approximately with $2\pi/L_0$, since it corresponds to the first maximum of the 1D correlation function, however it is slightly shifted to smaller $|Q|$ due to the particle shape function. For our range of σ_L and R_0 , the error introduced by this approximation is smaller than 20%. Further, we assumed that the mean particle radius $R_0(t)$ is proportional to $L_0(t)$; the proportionality factor $\zeta = L_0/R_0$ was a fitting parameter and we assumed that its value is time-independent. From our previous SAXS data published in Ref. [7] it follows that $\zeta \approx 2.5$ and its time-dependence is very weak indeed.

Figure 4 presents the SAXS profiles simulated for constant $R_0 = 20$ nm and $L_0 = 60$ nm and various values of ε [see Eq. (3)], other simulation parameters are $m_R = 50$, $\sigma_L = 30$ nm. The curve $\varepsilon = 0$ corresponds to the static case with immobile boundaries and constant density $\rho(r, t) = \rho_s$; with increasing ε (i.e., with increasing growth rate and/or decreasing diffusion coefficient D) the effect of the boundary movement on the scattered intensity increases. The profiles are normalized to the height of the first order peak at $Q = Q_{\text{max}}^{(1)} \approx 2\pi/L_0$. It follows from the figure that the position of the first order is almost identical for various values of ε , while ε affects mainly the height of the second-order peak $Q_{\text{max}}^{(2)}$ on the SAXS profile. Therefore, ε and consequently the diffusion coefficient D can be reliably determined only if the second maximum is present in the measured data. Further, in Fig. 4 we compare the

actual position of the main maximum at $Q_{\max}^{(1)}$ with $2\pi/L_0$ (the dotted vertical line); the deviation $\delta Q^{(1)} = Q_{\max}^{(1)} - 2\pi/L_0$ is indeed small enough so that we can use the approximation $Q_{\max}^{(n)} \approx 2\pi n/L_0$ with the desired accuracy.

The fitting procedure consists of the following steps: (i) In the first step we determine $L_0(t)$ directly from the position $Q_{\max}^{(1)}$ of the first peak in the SAXS data. (ii) We calculate its time derivative dL_0/dt and use it together with $L_0(t)$ as inputs for the fitting. (iii) For a series of time values t we perform the fitting of the measured data to the theory, using (8). In the fitting we use the common fitting parameters D , ζ , m_R and σ_L for all SAXS profiles measured at a given ageing temperature. The scaling factor

$$C = |\eta|^2 |\varrho_s - \varrho_c|^2 J_{\text{inc}}/J_{\text{mon}} \quad (9)$$

and background are fitted for each t independently. Unfortunately, the accuracy of the determined scaling factors $C(t)$ is affected by the poor accuracy of the monitor signal J_{mon} so that it cannot be used for a reliable determination of the time evolution of $\varrho_s - \varrho_c$.

5 Results

Examples of the measured and fitted SAXS profiles extracted from the two-dimensional scattering pattern along a line going through two first-order maxima are presented in Fig. 5 for both alloys (LCB and Ti-15Mo) and the ageing temperature of 390 °C. The figure clearly demonstrates the presence of the first and second-order maxima; the relative height of the second maximum is decisive for the determination of the diffusion coefficient D . The correspondence of the measured and fitted SAXS profiles is fairly good and it improves for longer times t . This fact follows from the polynomial approximation of the true density profile of the impurity atoms; as shown in the previous section, the approximation fits better to the exact profile for longer times.

Figures 6, 7, 8 and 9 summarize the parameters obtained from the fit. In Fig. 6 we present the time evolution of the mean particle distance $L_0(t)$ determined directly from the measured data without fitting. The mean particle distance monotonically increases during annealing and its time dependence can be approximated by the power law

$$L_0(t) = L_0(t_0) + v_L (t - t_0)^{1/3}, \quad (10)$$

following from the LSW theory [11, 12]; in Fig. 6 the fitted power-law curves are plotted by blue lines. The mean distances increase with increasing ageing temperature, except for the 450 °C in the Ti-15Mo alloy; at this temperature we detected a *smaller* mean distance than at 430 °C. We emphasize that the error bars in the graph denote the uncertainties of L_0 following mainly from the finite size of the detector pixel, and not the systematic errors due to the deviation $\delta Q^{(1)}$ discussed in the previous section. The true inter-particle distances could be smaller by 20% at most.

In Fig. 7 we summarized other parameters assumed time-independent in the fitting procedure. The parameter $\zeta = L_0/R_0$ in Fig. 7(a) lies between 2.7 and 3.7. Since the SAXS data are less sensitive to this parameter, its error is relatively large and it is not possible to reveal any dependence of ζ on the ageing temperature T . Figure 7(b) shows the temperature dependence of the rms deviation σ_L of the inter-particle distances; obviously, its value increases with T . Finally, in Fig. 7(c) we plotted the temperature dependence of the order m_R of the Gamma distribution of the particle sizes. The sensitivity of the SAXS data on this parameter is very poor; increasing m_R , the rms deviation σ_R of the particle sizes decreases and the second-order maximum becomes more visible. However, in the range $m_R \in [30, 80]$ almost no changes in the simulated SAXS data can be observed.

Using the L_0 values from Fig. 6 and the parameters $\zeta = L_0/R_0$ from Fig. 7(a) we calculated the mean particle radii R_0 ; the results are plotted in Fig. 8. Since we assumed that the values ζ depend only on the ageing temperature and not on the ageing time, the curves $R_0(t)$ are similar to $L_0(t)$.

Figure 9 shows the Arrhenius plot of the diffusion coefficient D together with published values of Mo diffusion in a β -Ti matrix. From the slope of the data we estimated the activation energy E of the diffusion process assuming the temperature dependence of the diffusion coefficient in the form $D \propto \exp(-E/(k_B T))$ (k_B is the Boltzmann constant). For LCB and Ti-Mo alloys we obtained $E = (1.0 \pm 0.5)$ eV and $E = (2.3 \pm 0.3)$ eV, respectively.

6 Discussion

We have verified the validity of the LSW theory by proving the $\propto t^{1/3}$ dependence of the mean inter-particle distance L_0 and the mean particle radius R_0 . The $L_0 \propto t^{1/3}$ dependence was determined directly from the measured data without fitting, so that this finding is quite robust and does not depend on the assumed structure model. From this dependence it follows that the number of ω particles decreases by a coarsening process as $\propto 1/t$, which is the main result of the LSW theory [11]. In Refs. [8, 9] the same growth kinetics of ω particles in a β Ti-20%Mo alloy was reported, however the authors observed that the particle sizes stabilized after reaching a maximum diameter of approx. 15 nm. The authors explained this stabilization by an attractive elastic interaction between the particles [8]. Such a stabilizing effect was not observed in our experiment – the nanoparticle $\propto t^{1/3}$ growth was observed in both alloy types for all ageing temperatures and in the full range of ageing times; in the case of the highest annealing temperatures their radii exceeded 20 nm. However, in our study we used much shorter ageing times and smaller Mo concentrations than in [8, 9], so probably the effect of stabilization could be observed only after a longer ageing.

In comparison to the previous SAXS investigations on Ti-alloys in [8, 9] our present measurements have been carried out using a synchrotron source, i.e. with much higher flux of primary photons. This was the reason why we were able to detect the second maximum on the SAXS scans, which depends on the shape of the radial profile of the impurity atoms and allows us to estimate their diffusion coefficient D . From the Arrhenius-like plots of D in Fig. 9 we determined the activation energies of the impurity diffusion for LCB and Ti-15Mo

to $E = (1.0 \pm 0.5)$ eV and $E = (2.3 \pm 0.3)$ eV, respectively. The energy value of 2.3 eV as well as the values of D for Ti-15Mo samples compare well with the activation energy and diffusion coefficient of Mo impurities in β -Ti in [22, 23, 24, 25]. The difference between our values of D and those from the literature can be ascribed to the fact that the cited works contain the diffusion data measured at the temperatures above 1000K and we extrapolated their results to our temperature range. From the experimental data published in [22] it follows that with increasing Mo content the diffusion constant decreases. Namely, a decrease of D by approx 20-30% was observed due to an increase of the Mo content from 0 to 10%; such effect is smaller than the accuracy of the D values determined from our data. In the case of the LCB samples, the interpretation of the values of D is not straightforward, since different impurity atoms (Mo, Fe, Al) are present in the samples; these atom types differ both in their diffusion coefficients and in their effect on the x-ray index of refraction. As we stated above, a reliable fit can be obtained only if we assume that D does not change during ageing. This assumption can be justified if we neglect the dependence of the diffusion coefficient on the concentration of impurity atoms, i.e. for small impurity densities.

As we stated above, our data confirm the validity of the LSW theory. From this theory the connection follows between the diffusion coefficient D and the growth factor $v_R \equiv v_L/\zeta$ [see Eq. (10)]:

$$v_R^3 = \frac{8D\sigma}{9k_B T} V_{\text{at}} \varrho_{\text{sat}},$$

where σ is the energy density of the β/ω interface, V_{at} is the atomic volume, and ϱ_{sat} is the saturated concentration of impurity atoms [11]. If we neglect the temperature dependences of ϱ_{sat} and σ , the factor $T(v_L/\zeta)^3$ is proportional to D and the proportionality constant is temperature-independent. In Fig. 10 we have displayed the temperature dependence of this factor as an Arrhenius-like plot. It is obvious that for the Ti-15Mo samples, the points in the plot yield similar activation energies as in Fig. 9. From this fact we conclude that for our ageing times and temperatures the growth rate of the ω nano-particles during ageing is determined mainly by the out-diffusion of impurity atoms from the particle volumes.

However, in the Ti-15Mo alloys we found the value of the growth factor v_L smaller for $T = 450$ °C than for 430 °C. Most likely, more densely packed and smaller α -Ti particles are created at this relatively high ageing temperature, which contribute to the SAXS signal as well. This explanation is in agreement with the results in [9], however from the data presented in our paper it is not possible to decide if the ω particles indeed dissolve or if the effective mean particle radius determined from the SAXS data is influenced by the presence of smaller α -Ti particles. The growth kinetics of the α -Ti particles will be investigated in our forthcoming paper.

It was not possible to determine the mean particle size R_0 and the diffusion coefficient D independently from a single SAXS pattern, since we found that their values are highly statistically correlated. In particular, with increasing R_0 the second-order maximum in a SAXS scan diminishes; a similar decrease in the height of the second maximum can be achieved by decreasing the value of parameter ε defined in Eq. (3). In our previous paper

[16] we used ex-situ SAXS for the study of ω nanoparticles in LCB-Ti single crystals after ageing for three temperatures and various ageing times. We analyzed the SAXS data assuming "naked" particles, i.e., without considering a cloud of impurity atoms around a particle, which contributes to the SAXS shape function as well. This simpler structural model allowed us to determine the mean inter-particle distance L_0 and particle radius $R_0 = L_0/\zeta$ from the SAXS data *independently*. For comparable ageing times and temperatures we found quite similar values of R_0 , but the L_0 values were found somewhat smaller than in the present work. As we pointed out above, in the present paper we could determine L_0 only from the positions of the first intensity maxima and therefore the resulting L_0 values may be overestimated. Moreover, the exsitu data could be affected by processes during quenching the samples from ageing temperature down to room temperature.

In the previous work [16] we also performed Monte-Carlo simulation of the process of self-ordering of the ω -particles assuming that the particles nucleate in the minima of the energy of the elastic inter-particle interaction. We have demonstrated that the distance L_0 of the energy minimum from the particle center scales with the particle radius as $L_0/R = \zeta \approx 2.2$. The simulation of the interaction energy was simplified by assuming that the ω -particles alone are the sources of local elastic deformation, i.e. we did not consider the influence of the cloud of the impurity atoms on the interaction energy. An impurity cloud increases the effective particle radius and consequently the corresponding value of ζ will be larger too. Moreover, the L_0 data in this work are probably overestimated (see the discussion above) so that the ζ values are somewhat larger as well.

7 Summary

We have studied the growth kinetics of ω -Ti nanoparticles during ageing of β -Ti alloys at various temperatures between 310 and 450 °C. The investigation has been performed by high-energy small-angle x-ray scattering *in-situ*. The experimental data have been compared with simulations. The simulation of small-angle x-ray scattering was based on a numerical solution of diffusion of impurity atoms around a growing nanoparticle, and on a three-dimensional short-range order model of the nanoparticle arrangement. The results of the study can be summarized in the following items:

1. The time-dependence of the mean particle distance was determined directly without numerical fitting from the experimental data and it follows the $\propto t^{1/3}$ growth law for all ageing temperatures. This fact indicates that the LSW kinetic theory is applicable for the Ti-alloys under study in the used range of ageing times and temperatures.
2. The particle distance increases with increasing ageing temperature except for the highest temperature of 450 °C and Ti-15Mo samples; at this temperature the effective particle size was probably affected by nucleation and growth of α -Ti particles.
3. The mean particle radius was found proportional to the mean particle distance with the proportionality factor of about 1/3.

4. From the fit of the measured and simulated scattering data we determined the diffusion coefficient of impurity atoms and its temperature dependence. In the case of Ti-15Mo samples, which contain only one type of impurities, the diffusion coefficient and its activation energy compare well with published data.
5. The growth factor of the particle sizes exhibits the same temperature dependence as the diffusion coefficient, therefore in this stage of ageing the particle growth is mediated by the diffusion of impurity atoms.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Examples of SAXS patterns after in-situ ageing at 390 °C for 2 h in LCB (left panel) and Ti-15Mo (right panel). The dotted lines indicate the $[100]_\beta$ directions along which intensity profiles were extracted. The gray scale is logarithmic and its range corresponds to two decades.

Figure 2.

The time dependence of the linear cuts extracted from the 2D SAXS maps in Fig. 1. The horizontal dotted lines indicate the time at which the set temperature was reached, the blue dotted lines denote the positions of the first- and second-order maxima (see the text).

Figure 3.

(a) The time evolution of the density profile $\rho(r, t)/\rho_0$ of impurity atoms around a growing spherical particle (grey area), the white line represents the radius R_L ; see the text for details. (b) Density profiles extracted from the data in panel (a) for 4 values of time t (the parameters of the curves are in s). The red dots represent the polynomial approximation of the density profile (see the text); the curves are shifted vertically for clarity.

Figure 4.

The SAXS profiles simulated for $R_0 = 20$ nm and $L_0 = 60$ nm and various values of ε in nm^{-1} , using Eq. (8). The profiles are normalized to the height of the first peak, the vertical dotted line denotes the value of $2\pi/L_0$.

Figure 5.

The measured (points) and fitted (lines) SAXS profiles extracted from the SAXS data along the $[100]_{\beta}$ direction, samples LCB (left) and Ti-15Mo (right), aged at 390 °C. The curves are shifted vertically for clarity, the parameter is the ageing time in hours.

Figure 6.

The time evolution of the mean inter-particle distance L_0 in LCB (left) and Ti-15Mo (right) alloys for various annealing times (in °C). The blue lines are the $\propto t^{1/3}$ fits according to Eq. (10).

Figure 7.

Dependences of the parameters ζ (a), σ_L (b) and m_R on the ageing temperature (see text for details). The dotted lines are only guides for the eye.

Figure 8.

The time evolution of the mean particle radii R_0 in LCB (left) and Ti-15Mo (right) alloys for various annealing times (in °C). The blue lines are the $\propto t^{1/3}$ fits.

Figure 9. Arrhenius plots of the diffusion coefficient for both alloy types. The dotted lines denoted [a,b,c,d] represent the values of the Mo/ β -Ti diffusion coefficients extrapolated from Refs. [22], [23], [24], and [25], respectively.

Figure 10. Arrhenius plot of the factor $T(v_L/\zeta)^3$, which, according to the LSW theory in [11], is proportional to the diffusion coefficient D .