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Equilibrium segregation of sulfur to the free surface of single crystalline titanium

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Abstract

Equilibrium segregation of sulfur to the free surface of single crystalline titanium from 560°C to 800°C was investigated using Auger electron spectroscopy (AES) measurements. To describe the concentration evolution in the sulfur overlayer, Fick's first law was modified by adding a local function $df(x)/dx$, to the concentration gradient to drive the segregation starting from an initially homogeneous distribution. The diffusion equation thus derived was solved for the case $f(x) = a_s \exp(-x/d_s)$. It was found that the solution leads to an AES intensity evolution for segregants, $I_S(t) = I_S^\infty (1 - e^\alpha \operatorname{erfc}(\sqrt{\alpha}))$, $\alpha = Dt/d_s^2$, which fits the experimental results extremely well. An exponentially decaying distribution of sulfur beneath the titanium surface at equilibrium was revealed by sputter depth profiling, which in turn justifies our modification to Fick's first law. Without referring to the detailed kinetics, an activation energy $E_a = 718$ meV/atom was determined by comparing the sulfur concentration evolution at different temperatures.

1. Introduction

Constituent atoms of small surface free enthalpy in a multicomponent system have the tendency to accumulate at the surface to reduce the overall free enthalpy of the system, thus resulting in a localized enrichment of this constituent. In particular, the surface free enthalpy of elements from the IVa, Va and VIa groups, which are solid at room temperature, is considerably lower in comparison with those of metals [1]. Therefore it is not surprising that impurities such as P and S, and also Au in some Au-containing alloys, would seep out of the metal matrices to form an overlayer and even to display some patterns [2]. Recently, this phenomenon has found a novel application on the microscopic scale, i.e. in surfactants to facilitate layer-by-layer epitaxial film growth [3], in which the surfactant atoms struggling through the fresh-borne layer reduce to some extent the stress at the interface. The locality of segregation to the surface, interface

and grain boundary has already been experimentally confirmed [4]. In the case of equilibrium segregation to a free surface, which is reproducible simply by re-establishing the identical physicochemical conditions, the segregant concentration deviates from the bulk value only in a depth determined by the structural width of the free surface.

Much effort has been devoted to the study of segregation-related phenomena over the past decades. Segregation to a free surface starting from a homogeneous bulk distribution has attracted extensive investigation [5–8]. Most diffusion models for segregation follow the pioneering work of Mclean [5]. Due to the congenital deficiency of these diffusion models, however, some tricks that are generally untenable from the viewpoint of mathematics have to be played in order to obtain a seemingly reasonable solution. It has long been recognized that the linear relation thus derived between the surface concentration of the segregant and $(Dt)^{1/2}$, where D is the diffusion coefficient and t is the time, is quite annoying since the surface concentration is unlimited at $t \rightarrow \infty$ [6]. Deviations from this behaviour have been observed by many authors [4]. Moreover, the solutions to those models cannot provide a reasonable concentration profile for the segregating species. An analytical formulation of the concentration depth profile induced by segregation, to the best of our knowledge, is not to be found in the literature.

On the other hand, the composition and structure of a surface, which are the key factors influencing the material properties, often manifest strong dependence on the history of thermal treatment, and consequently on the segregation behaviour of impurities. Notably, even a small amount of impurities can provoke remarkable changes in the mechanical and physical properties of metals. Titanium is a metal that has found wide industrial applications. It has similar characteristics to steel but it is much lighter. Unfortunately, titanium always contains some impurities that have a particularly high mobility even at low temperatures. For instance, even at 560 °C the sulfur atoms already begin to segregate at a considerable rate, resulting in an electron-spectroscopically detectable amount of sulfur within an hour. Enrichment of sulfur at the surface could drastically alter a wide range of the properties of titanium.

In this paper we are concerned with the equilibrium segregation of scanty sulfur impurity to the free surface of single crystal titanium. The surface concentration of sulfur was monitored by Auger electron spectroscopy (AES) from 560 °C to 800 °C each for 70 min. A phenomenological model for equilibrium segregation is proposed and solved under boundary conditions concerning overlayer formation. It is found that, when the driving force contains an exponentially decaying function in addition to the concentration gradient, the solution approaches a temperature-independent constant at $t \rightarrow \infty$, and fits the experimental curves perfectly well. Atomic force microscopy observation was applied to verify the formation of a sulfur overlayer on titanium at segregation equilibrium. Further, the sulfur distribution beneath the titanium surface was sputter depth profiled with the view of justifying the assumed driving force. Without referring to the detailed kinetics of segregation, the activation energy can be derived generally by comparing the concentration evolution of the impurities at the surface. For sulfur in titanium in this experiment, the activation energy $E_a = 718$ meV/atom. To facilitate our discussion, the model analysis is presented ahead of the measurement results.

2. Model and solution

In this section we first give a brief review of the conventional diffusion models for segregation, analysing the difficulties that these models confront; then a new model is proposed and solved to explain the experimental results displayed in the later sections.

2.1. Difficulty of conventional diffusion models

By conventional diffusion models of segregation we mean those in which either the concentration gradient itself or a functional of it that vanishes at zero concentration gradient, e.g. the gradient of chemical potential, is considered the responsible driving force. The various conventional diffusion models and their solutions were reviewed by Plessis [6]. In the case when segregation is driven by the concentration gradient, the net material flow $J(x, t)$ is given by Fick's first law

$$J = -D \frac{c(x, t)}{x} \quad (1)$$

where D is the diffusion coefficient and $c(x, t)$ is the concentration of segregating atoms. The governing equation for segregation then reads

$$c_t(x, t) - Dc_{xx}(x, t) = 0. \quad (2a)$$

Equation (2a) is classified as the diffusion problem in 1+1 dimensions [9]. It is well defined with two boundary conditions and one initial condition. For segregation to a free surface starting from an initially homogeneous distribution, equation (2a) can be solved with the initial condition

$$c(x, 0) = c_0 \quad x \geq 0 \quad (2b)$$

where c_0 is the bulk concentration. The boundary condition at infinity generally takes the form

$$c(\infty, t) = c_0 \quad (2c)$$

implying that segregation is local. The boundary condition (2c) is adopted for all models discussed in this article, and will not be particularly stressed in the following sections.

The solution to equation (2a) depends on the choice of the boundary condition at $x = 0$. If we choose

$$c_x(0, t) = 0 \quad (2d)$$

i.e., no segregant atoms pass through the surface as happens in some alloys of transition metals, then the only possible solution to equation (2a) is $c(x, t) = c_0$. Segregation does not take place at all! To circumvent such a difficulty, an alternative boundary condition

$$c(0, t) = 0 \quad t > 0 \quad (2e)$$

has been introduced [6]. Physically, this means that all the segregating atoms arriving at the surface are removed instantaneously. In this case the solution to equation (2a) reads

$$c(x, t) = c_0 \operatorname{erf} \left(\frac{x}{\sqrt{4Dt}} \right). \quad (3)$$

The value of $c_x(0, t)$ is then employed to construct an overlayer of segregating atoms in order to explain the experimental results.

Some other tricks for dealing with the boundary conditions at $x = 0$ have also been introduced to solve other variants of the diffusion model [6]. However, all of them confront one or a few of the following inconsistencies:

- (a) The value of $c(x, t)$ vanishes at $t \rightarrow \infty$ for any finite x , i.e., the segregating species will be drained completely. The equilibrium for thermal segregation can never be achieved. This contradicts the observation that segregation is a local event.
- (b) The surface concentration diverges at $t \rightarrow \infty$.

- (c) The continuity at $x = 0$ is violated. The concentration at $x > 0$ in the direct vicinity of the overlayer drops abruptly to a value less than the bulk concentration. Furthermore, no model has a proper solution $c(x, t)$ that can be taken as the resulting concentration profile in the matrix material.

That the conventional diffusion models are impractical for the description of segregation is quite easy to understand from the physical point of view. At equilibrium there should not be any net material flow, so the driving force for segregation must vanish. The concentration gradient, or similarly the chemical potential gradient, acting alone as the driving force leads indubitably to a homogeneous equilibrium distribution irrespective of the boundary and initial conditions. The pitfall lies in the misuse of Fick's first law to the description of diffusion phenomena. It should be borne in mind that Fick's first law is only valid when the motion of the particles is sufficiently randomized, and the environment for the particle motion on both sides of an imaged partition is identical. Most diffusion processes can be well approximated by Fick's first law, *except when the concentration is extremely low, very high, or changes suddenly in a short distance, so that the statistical reasoning is no longer applicable* [10]. Intuitively, in the case of segregation to a free surface, interface or grain boundary where the particle motion is anisotropic, a material flow other than that defined by Fick's first law is expected. Notably, it is required to be nonzero at a vanishing concentration gradient.

2.2. Modified diffusion model

In order to describe segregation with a diffusion model, Fick's first law needs to be modified. The material flow $J(x, t)$ assumes the form of an explicit function of the coordinate x so as to be able to signify the locality of segregation. For equilibrium segregation to a free surface by which the anisotropy for particle transport arises from a relaxed structure near the surface, as a bold assumption, Fick's first law can be replaced by

$$J(x, t) = -D \left(\frac{c(x, t)}{x} - \frac{df(x)}{dx} x \right) \quad (4)$$

where $f(x)$ is a function contingent upon the structure distortion and the interaction between diffusates and matrix. It should deviate from a constant value only within the near-surface region. Since there is no net material flow at equilibrium, the concentration profile at equilibrium, from equation (4), is given by

$$c(x, \infty) = f(x) + \text{constant}. \quad (5)$$

This implies that $f(x)$ can be experimentally determined by depth profiling the equilibrium concentration distribution. Similar material flows as in equation (4) have been applied to treat other diffusion-relevant phenomena. For instance, the material flow for carrier transport in a semiconductor in the presence of an external electric field contains a drift component in addition to the diffusion term

$$J_e(x) = -D \frac{\partial c(x, t)}{\partial x} + \mu E c(x, t) \quad (6)$$

where E is the electric field strength and μ the carrier mobility [11].

Hence the segregation process to a free surface starting from a homogeneous distribution is governed by the equation

$$c_t(x, t) - D c_{xx}(x) = D f_{xx}(x) \quad (7a)$$

with the initial condition

$$c(x, 0) = c_0 x \geq 0 \quad (7b)$$

and a proper boundary condition at $x = 0$. For any limited, continuous function $f(x)$ defined on the positive half space, equation (7a) is analytically solvable [9], giving a physically reasonable result.

To show this we solve equation (7a) for the case

$$f(x) = a_s \exp(-x/d_s) \quad (8)$$

where a_s is a parameter designating the strength of segregation, and d_s denotes the characteristic depth of structure distortion that causes segregation. The plausibility of equation (8) will be justified later. Accordingly, equation (7a) is rewritten as

$$c_t(x, t) - Dc_{xx}(x, t) = -Da_s/d_s^2 \exp(-x/d_s) \quad (7a')$$

By choosing the boundary condition at $x = 0$ it is evidently desirable to distinguish whether the segregating atoms penetrate the matrix surface to build up an overlayer or not (figure 1). This is of course an idealization of the reality. We first consider the simpler case when no segregating atoms exude, i.e. $J(0, t) = 0$, hence

$$c_x(0, t) = -a_s/d_s \quad t > 0. \quad (7c)$$

Equation (7a') with boundary condition (7c) can be easily solved using the Laplace transformation method,

$$c(x, t) = c_0 + a_s e^{-x/d_s} - \frac{2a_s}{\pi} \int_0^\infty \frac{e^{-r^2(Dt/d_s^2)} \cos(rx/d_s)}{1+r^2} dr. \quad (9)$$

This is an analytically continuous function of x and t . It can be readily seen that

(a) $c(x, t)$ is bounded at $t \rightarrow \infty$,

$$c(x, \infty) = c_0 + a_s \exp(-x/d_s). \quad (10)$$

This is the concentration profile of the segregant at equilibrium. The material flow defined in equation (4) thereafter vanishes everywhere.

(b) $c(x, t)$ differs from c_0 only in a shallow region beneath the surface.

(c) $c(x, t)$ reproduces the initial condition (7b). The last two terms in equation (9) cancel out at $t = 0$, since [12]

$$\int_0^\infty \frac{\cos(\alpha x)}{\beta^2 + x^2} dx = \frac{\pi}{2\beta} \exp(-\alpha\beta) \quad \text{for } \alpha > 0, \beta > 0. \quad (11)$$

By setting $x = 0$ in equation (9) one obtains immediately the temporal variation of the segregant concentration at the surface,

$$c(0, t) = c_0 + a_s - a_s e^\alpha \operatorname{erfc}(\sqrt{\alpha}) \quad \alpha = Dt/d_s^2. \quad (12)$$

This approaches the steady-state value $c_0 + a_s$ asymptotically, as shown in figure 2.

In the case that an overlayer forms on the surface, the material flow at $x = 0$ might be nonzero. We consider the simplest situation that

$$c_x(0, t) + a_s/d_s = -mc(0, \infty) - c(0, t)/d_s \quad (7c')$$

equation (7c') implies that the material flow out of the surface stops when the surface concentration $c(0, t)$ comes to a steady-state value $c(0, \infty)$. This is reasonable when a 'braking' mechanism exists that eventually terminates the outflow of the segregating atoms. For convenience and simplicity, the proportionality factor is chosen as m/d_s so that m is dimensionless.

The solution to equation (7a') with boundary condition (7c') looks somewhat complicated

$$c(x, t) = c_0 + a_s e^{-x/d_s} - \frac{2a_s}{\pi} \int_0^\infty \frac{e^{-r^2 Dt/d_s^2} (1+m)[m \sin(rx/d_s) + r \cos(rx/d_s)]}{(1+r^2)(m^2+r^2)} r dr. \quad (13)$$

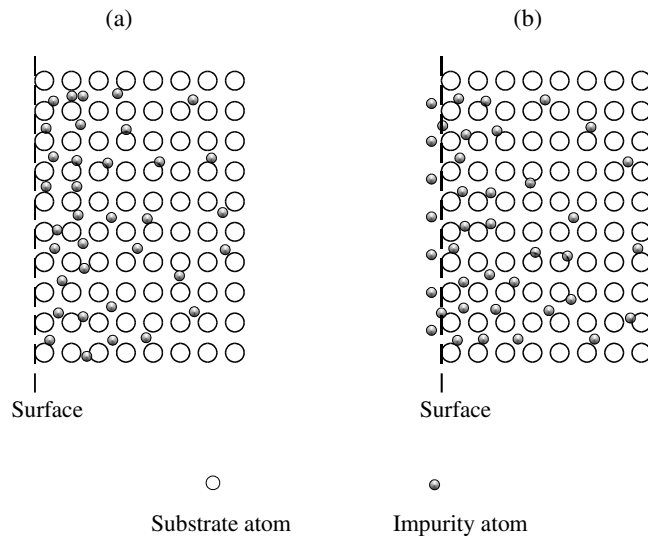


Figure 1. Schematic illustration of segregation to a free surface. (a) The original surface is retained; (b) an overlayer of the segregating species is formed.

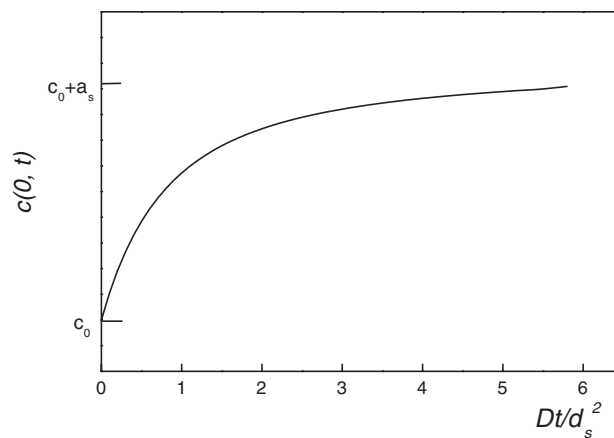


Figure 2. Evolution of the surface concentration given by equation (12).

Yet we can verify with satisfaction that this function is local and bounded due to the rapidly attenuating exponential term in the integral. Moreover, it also reproduces the initial condition since the last two terms in equation (13) cancel out at $t = 0$ by virtue of the equality

$$\frac{2}{\pi} \int_0^{\infty} \frac{(1+m)[m \sin(rX) + r \cos(rX)]}{(1+r^2)(m^2+r^2)} r dr = e^{-X}. \quad (14)$$

Setting $x = 0$ in equation (13) yields the temporal variation of the segregant concentration at the surface

$$c(0, t) = c_0 + a_s - \frac{2a_s}{\pi} \int_0^{\infty} \frac{e^{-r^2 Dt/d_s^2} (1+m)r^2}{(1+r^2)(m^2+r^2)} dr. \quad (15)$$

The atomic concentration of the segregating atoms in the overlayer, defined in a thickness of d_{over} , is given by the integral

$$c_{over}(t) = -\frac{1}{d_{over}} \int_0^t J(0, \tau) d\tau$$

$$= \frac{a_0 d_s}{d_{over}} \frac{m}{m-1} (1 - e^\alpha \operatorname{erfc}(\sqrt{\alpha})) - \frac{1}{m-1} (1 - e^{m^2 \alpha} \operatorname{erfc}(m\sqrt{\alpha})) \quad (16)$$

$$\alpha = Dt/d_s^2 \quad m \neq 1.$$

Clearly, $c_{over}(\infty) = a_s d_s / d_{over}$ because of the vanishing term $e^\alpha \operatorname{erfc}(\sqrt{\alpha})$.

In summary of this section, the modified diffusion equation (7a) has been solved under two distinct boundary conditions. The boundary condition (7c') provides only an oversimplified picture of the percolation of the segregating atoms. However, it is very encouraging to note that the solution exhibits no contradiction to the nature of segregation. Later we shall see that this model is justified by the experimental data obtained for the sulfur segregation to the surface of titanium.

3. Experimental details

AES monitoring of the segregation process was performed on the surface of a single crystalline titanium sample containing minor sulfur impurities. The sample was cut along the basal plane. The bulk concentration of sulfur was estimated to be below 3.0 ppm from secondary neutral mass spectroscopy measurements. Note that the surface free enthalpy at room temperature for S (0.078 J m^{-2}) is roughly 3% of the value for Ti (2.57 J m^{-2}) [1], hence the sulfur-titanium system provides an ideal case for the study of segregation exhibiting overlayer formation.

The experiment was carried out in the chamber of a Scanning-Auger-Microprobe (PHI, SAM590A), in which the base pressure was maintained at 4×10^{-10} mbar. The pressure would have increased to 1.0×10^{-8} mbar once the ion gun was in operation. Before being introduced into the UHV chamber, the sample was polished with diamond paste of grain size down to 250 nm. A Ni/NiCr thermocouple was used to control the temperature of the sample mounted on a tantalum target holder which was heated from inside. The Auger transitions were excited with a coaxial electron beam operated at 5 keV. For the cleaning and removing of the sulfur overlayer, 1 keV Ar^+ -ions were employed to sputter the target at a current density of around $10 \mu\text{A cm}^{-2}$.

First the atomic force microscope (AFM, Park Instruments) was employed to verify the existence of the sulfur overlayer. Figure 3 displays the AFM images taken on different locations of the titanium surface maintained at 750°C for three hours until the AES intensities for both titanium and sulfur were stabilized. We see that sulfur gives rise to different patterns due to its tendency to bond in chained molecules. A discussion of the structure and formation mechanism of these sulfur patterns is beyond the scope of this article. For the time being we are satisfied with the knowledge that sulfur indeed forms an overlayer covering the titanium surface at thermal equilibrium.

The segregation process was monitored at temperatures below 850°C to avoid the phase transition of titanium (hcp to bcc) at 882°C but above 550°C so that the segregation proceeds fast enough. In the experiment the sample was heated to a definite temperature in about 10 min, but a few hours more were required for the whole system, including the manipulator, sample, heating station and analyser, to be stabilized under high temperature. Since segregation already took place during heating of the sample, the sulfur atoms that had arrived at the surface were removed before measurement. After prolonged sputtering the AES signal of sulfur at 152 eV became negligible. Note that the sputtering process left behind a microprofile of sulfur,

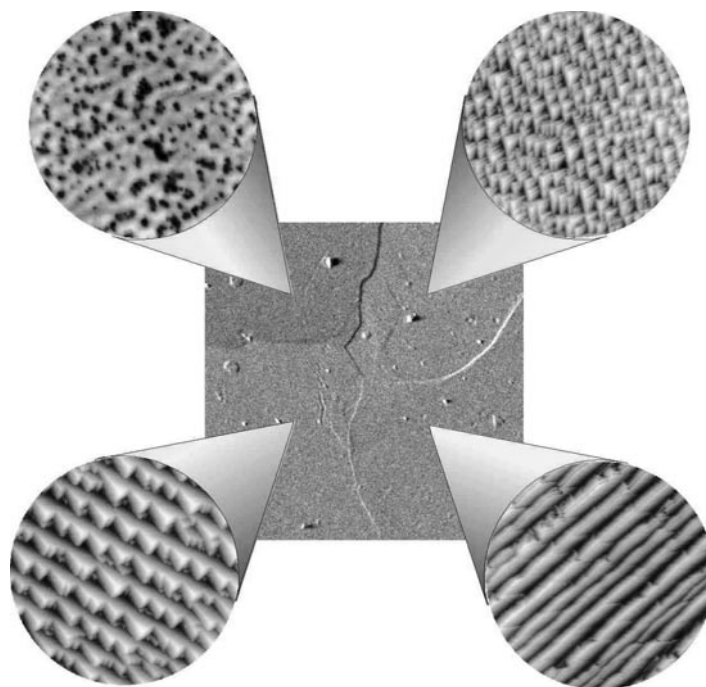


Figure 3. AFM images of the sulfur overlayer on titanium surface exhibiting patterns. The images were taken in contact mode over a range of 1 μm .

therefore the status after sputter cleaning corresponds to an initial condition, instead of being a constant c_0 , given approximately by

$$c(x, 0) = c_0 - c_1 \exp(-x/r) \quad c_1 < c_0. \quad (17)$$

The parameter r depends on the nature of the ion–target interaction. For a small r (roughly 1 nm in this experiment) and an almost vanishing c_0 and c_1 , the solution to the diffusion equation differs from the one starting from a constant initial distribution only during the short beginning period. It was seen that the sulfur AES signal increased only slowly at the beginning due to sputter cleaning, but it reached normal segregation in just one minute or so.

4. Quantification of AES data

By applying AES to investigate segregation, the spectral data cannot be related to the surface concentration or the coverage straightforwardly. Quantification of the spectral data deserves extreme care because the information depth of the Auger electrons is generally comparable to the characteristic distribution of the segregating atoms. For sulfur segregation to the surface of titanium, the formation of the sulfur overlayer is of main concern, but the AES intensity for sulfur originates both in the overlayer and beneath the titanium surface.

On the other hand, sulfur atoms segregate in titanium through the interstitial mechanism. Despite the significant enrichment of sulfur in the near-surface region, the atomic concentration of titanium is subjected to only slight variation. This is verified by the observation that during the experiment, the intensity of the Ti LMM Auger peak was not sensitive to the sulfur concentration. We measured an intensity reduction for the Ti LMM Auger peak of only

12% after 200 min at 690 °C, and this intensity reduction for Ti can be mainly attributed to the attenuation of Auger electrons by the sulfur overlayer. Consequently, the concentration of titanium can be taken as unchanged in the following quantification.

The Auger intensity for Ti is given by

$$I_{Ti}(t) \propto [1 - \gamma_{Ti,over}(t)]\lambda_{Ti}c_{Ti} \quad (18a)$$

where λ and γ denote the inelastic mean free path and the attenuation factor, respectively, and the subscript 'over' specifies the parameters associated with the overlayer. At segregation equilibrium, $\gamma_{Ti,over}$ approaches the value $(1 - e^{-d_{over}/\lambda_{Ti,over}})$. By comparing the Ti Auger peak intensity at segregation equilibrium with the initial value, the overlayer thickness d_{over} can be estimated. At 755 °C, some 70% of the intensity of the Ti LMM Auger peak remained after prolonged segregation. Assuming a layer distance of about 0.3 nm for the S overlayer and therefore a $\lambda_{Ti,over}$ of 1.38 nm, we can estimate the overlayer to be roughly two monolayers thick.

The Auger intensity for S is approximated by

$$I_S(t) \propto c_{over}(t)\lambda_{S,over}(1 - e^{-d_{over}/\lambda_{S,over}}) + [1 - \gamma_{S,over}(t)] \int_0^\infty c(x,t)e^{-x/\lambda_S} dx \quad (18b)$$

where the first term comes from the overlayer and the integral term denotes the contribution of the S atoms in the matrix. For $c(x,t)$ given in equation(13),

$$\int_0^\infty c(x,t)e^{-x/\lambda_S} dx = c_1 - c_2g(t) \quad (19)$$

where

$$g(t) = \int_0^\infty \frac{e^{-r^2Dt/d_s^2}}{(1+r^2)(m^2+r^2)[1+(r\lambda_S/d_s)^2]} r^2 dr \\ \approx (d_s/\lambda_S)^2 \int_0^\infty \frac{e^{-r^2Dt/d_s^2}}{(1+r^2)(m^2+r^2)} dr \quad (20)$$

showing the same time dependence as $c_{over}(t)$ in equation(16). Since $\gamma_{S,over}(t)$ increases only slowly from zero to a small value, $(1 - \gamma_{S,over})$ in equation (18b) can be taken as constant. Substituting the integral in equation (19) into equation (18b), one obtains

$$I_S(t) \approx I_S^0 + \epsilon c_{over}(t) \approx \epsilon c_{over}(t). \quad (21)$$

Since $I_S^0 \propto c_0$ is negligible. Here ϵ is a proportionality factor incorporating the parameters d_s , λ and γ . This demonstrates that the Auger intensity for S is approximately proportional to the overlayer concentration though it originates from both the overlayer and inside the titanium. Substituting $c_{over}(t)$ in equation (16) into equation (21), for $m \gg 1.0$, we have

$$I_S(t) \approx I_S^\infty [1 - e^\alpha \operatorname{erfc}(\sqrt{\alpha})] \quad \alpha = Dt/d_s^2. \quad (22)$$

5. Results and discussion

5.1. Experimental data

The segregation process of sulfur in titanium was monitored starting from a homogeneous distribution at 565, 600, 660 and 75 °C by AES for 70 min. The variation of the S LVV Auger intensity is shown in figure 4, where all the curves can be well fitted with the function in equation (22). By contrast, the function

$$I(t) = I_S^\infty(T) [1 - e^{-kt}] \quad (23)$$

which has been applied to fit experimental curves similar to those depicted in figure 4, though with different I_S^∞ values, works only for small t [8]. The function in equation (22) fitted our data satisfactorily throughout the whole time range and, noticeably, with a unique temperature independent I_S^∞ . This is in agreement with observations at higher temperatures on many other systems [4, 6, 13]. The uniqueness of the parameter I_S^∞ is not readily inferred from the data acquired at low temperatures.

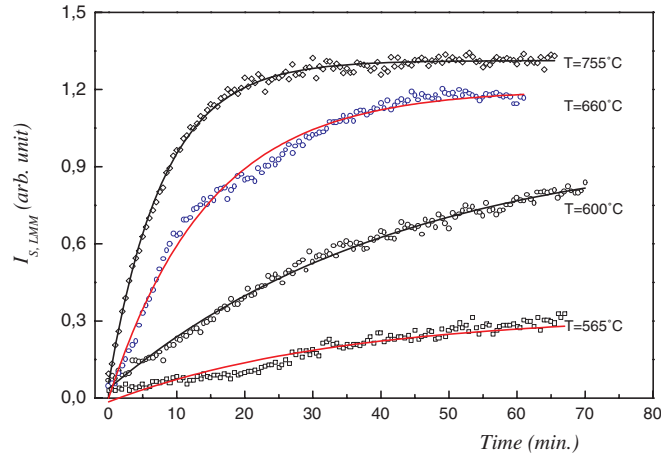


Figure 4. Peak-to-peak intensity of the S LVV Auger transition as a function of time during segregation at different temperatures.

In all the physical processes described by the diffusion equation, the temperature plays a role by changing the diffusion coefficient, and thus scaling the time. The solution to the problem is a function of Dt so long as the driving force is not an explicit function of the time t . Therefore, segregation should evolve in essentially the same manner at different temperatures, except that the time is scaled with respect to the corresponding diffusion coefficient. This is a basic feature of the diffusion process. Figure 5 depicts the curves from figure 4 with the abscissa accordingly scaled to that at 600 °C. It can be readily seen that they merge into one single curve as expected.

Similar curves to those in figure 4 were obtained by measuring the Auger intensity of the segregating atoms versus temperature T , with the sample heated at different heating rates [13]. Such results are quite comprehensible from the above discussion. The varying heating rates imply different sample temperatures at the moment t thus corresponding to distinct values of Dt . Consequently, the $I(T)$ curves measured for a sample heated at different heating rates should be of the same form when properly scaled.

5.2. Activation energy

One immediate application of the scaling feature for segregation is to calculate the activation energy from experimental curves in figure 4 without considering the details of kinetics. Since the temperature dependence of the diffusion coefficient follows an exponential law

$$D(T) = D_0 \exp(-E_a/kT) \quad (24)$$

in which E_a is the activation energy and k is the Boltzmann constant, we have the relation

$$\exp(-E/kT_n) = \sigma_{n,r} \exp(-E/kT_r) \quad (25)$$

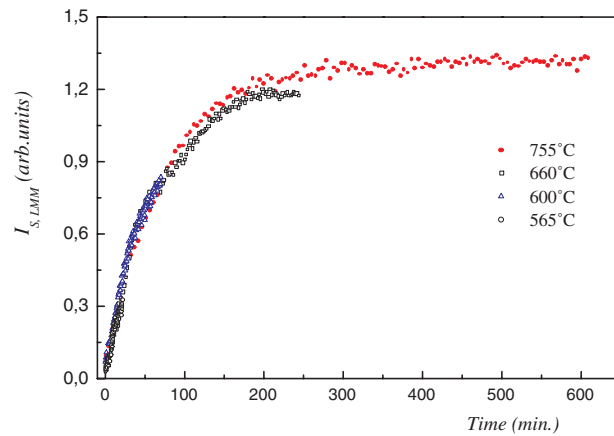


Figure 5. The same curves drawn with data from figure 4. Time scaling factors are 9.3, 4.0 and 0.32 for the curves at 755, 660 and 565 °C, respectively, with reference to the curve at 600 °C.

where $\sigma_{n,r} = D(T_n)/D(T_r)$ is the time scaling factor for the $I(t)$ curve at T_n in reference to that at the reference temperature T_r . Thus E_a can be determined by linearly fitting the plot $\ln(\sigma_{n,r})$ versus $1/kT_n$. From the curves in figure 4, we obtain $E_a = 718$ meV/atom. Khan has derived a value of about 925 meV/atom for E_a for sulfur segregation in single crystalline titanium by fitting his experimental data with expression (23).

It is worth noting that $\sigma_{755^\circ\text{C}, 565^\circ\text{C}} \approx 30$, i.e., one needs almost 40 hours to carry out a measurement at 565 °C compared with only 70 min at 755 °C. The prohibitively large time scale at low temperature prevents the measurement from being carried out up to equilibrium. The data obtained at low temperatures, if not acquired for a sufficiently long time (as, unfortunately, is often the case), correspond to very small values of the argument Dt . In this case, the experimental data can be fitted with many simple functions such as \sqrt{t} , t or $(1 - e^{-kt})$ depending on the range of time and the preset tolerance. This may lead to erroneous conclusions in the undertaking to infer the kinetics of segregation.

5.3. Concentration profile

As previously mentioned, the concentration profile at equilibrium is directly related to the form of the driving force responsible. Therefore, the equilibrium concentration profile, when experimentally determined, may help justify our model. To do this, we sputter depth-profiled the sulfur distribution in titanium with 1 keV Ar⁺-ions. The sample temperature was kept at 755 °C for three hours to reach the segregation equilibrium. Prior to the depth profiling, the weakly bonded sulfur overlayer was removed by a scanning electron beam. The sputter time profile $I_S(t)$ in figure 6 can be described with an exponential function

$$I_S(t) = I_0 e^{-t/\tau}. \quad (26)$$

The measured $I_S(t)$ curve is not straightforwardly related to the initial concentration profile $c(x, t = 0)$ (here $t = 0$ denotes the beginning of sputtering), as shown by investigations on the sputter depth profiling technique [14–16]. Yet, based on simulations on the sputtering process where the preferential sputtering effect and radiation enhanced diffusion are concerned, we can conclude with confidence that the temporal profile (26) evolves either from a constant initial distribution (this possibility is excluded for the case discussed here) or a monotonic, slowly

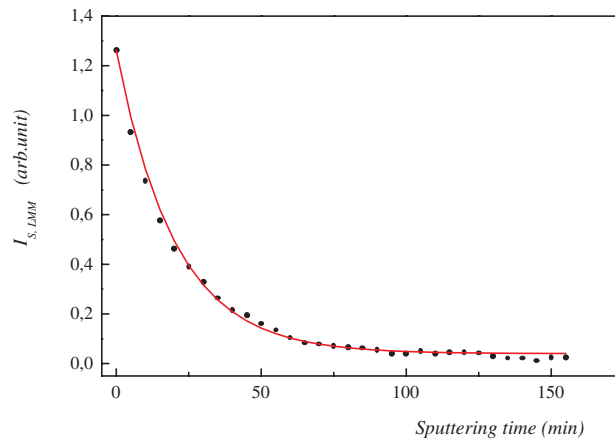


Figure 6. Sputter time profile of the equilibrium sulfur distribution induced by segregation at 755 °C.

decreasing depth profile which can be roughly given by

$$c(x, t = 0) = c_0 + a_s \exp(-x/d_s). \quad (27)$$

This provides substantial support to our assumption of the driving force for segregation in equation (10)

From figure 6 it was determined that $\tau \approx 20$ min. By sputtering of the Ti/S system with 1 keV Ar⁺-ions of current density at $10 \mu\text{A cm}^{-2}$, assuming a total sputtering yield of 1.0 at/ion and taking the atomic density to be 5.66×10^{22} at cm^{-3} for titanium, this corresponds to a sputter removal of about 5 nm. This indicates that segregation is indeed a local event that takes place only in the first few tens of atomic layers.

6. Summary

The equilibrium segregation of sulfur to the free surface of single crystalline titanium between 560 and 800 °C was monitored by AES and a diffusion model was formulated to explain the experimental results. In this model a driving force composed of the concentration gradient plus an additional exponential term is proposed. Both the solutions for the cases with and without overlayer formation are bounded local functions, and in particular they give a reasonable concentration profile inside the matrix. It is also predicted that the concentrations in the overlayer at different temperatures approach a unique equilibrium value. This is experimentally confirmed by observations on different systems. Sputter depth profiling reveals an exponentially decaying distribution of the segregating atoms inside the matrix, providing a substantial support to our diffusion model.

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