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The segregation kinetics of carbon to a Mo(100) surface: deviations from a parabolic time law due to subsurface enrichment

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Abstract

The segregation kinetics of carbon to a Mo(100) surface is investigated by Auger electron spectroscopy (AES) in the temperature range from 1018 to 1528 K. Strong deviations from a parabolic time law are observed in the primary stages of the experiments; this is more pronounced the lower the temperature. Reaction desorptions from a carburized, annealed surface with additionally adsorbed oxygen show that a multilayer enrichment occurs, markedly influencing the segregation kinetics up to temperatures of about 1400 K. The initially delayed segregation kinetics observed by the AES measurements are simulated by a simple model calculation which takes account of a multilayer enrichment which lowers the mobility of carbon within the C-enriched outermost layers. This is discussed in connection with non-parabolic segregation kinetics reported in the literature. Applying this model allows us to determine the parameters for the volume diffusion of C in Mo quite accurately, despite the deviations from a parabolic time law.

Keywords: Diffusion of C in Mo; Segregation kinetics; Auger electron spectroscopy

1. Introduction

Since the introduction of surface-sensitive sampling techniques such as Auger electron spectroscopy (AES), one common method of determining diffusivities of foreign atoms in a metal is to monitor the segregation kinetics to a surface. Although numerous solutions exist for a great variety of diffusion problems [1,2], the amount of segregated substances is frequently proportional to the square root of time. This situation is often designated as a parabolic time law. This holds for many geometries, initial and boundary conditions, as long as volume diffusion dominates all other observable effects. Strong deviations from a parabolic behaviour occur in the later stages of segregation kinetics approaching equilibrium enrichment as reported and modelled, for example, by Lea and Seah [3] and Rowlands and Woodruff [4]. For the early stages of enrichment experiments, a quasi-linear or 'delayed parabolic' behaviour has been reported to occur in the systems C–Ni, C–Co, S–Pd–Ag, S–Fe, S–Mo and C–Mo_2C [5–10], but this has not yet been sufficiently explained. Since we found similar kinetics of carbon segregation to a Mo(100) surface, the present paper deals with this aspect of our own experimental work and a simple model to explain the observed time-lagged surface enrichment.

2. Experimental setup

The experiments were performed in a standard commercial UHV-chamber pumped by a set of triode pumps (200 l s^{-1}) and a turbomolecular pump with a pumping speed of 240 l s^{-1}. Supported by a Ti-sublimation pump, a base pressure of about 1–1.5 Torr was established after a bakeout for at least 20 h. The pressure of the residual gas was measured by a Bayard–Alpert ionization gauge; its composition was determined by a quadrupole mass spectrometer. The chamber was equipped with a 4-grid LEED optic for low energy electron diffraction (LEED) and a 3 kV sputtergun for sample cleaning. Gases could be dosed into the chamber through bakeable leak valves. AES was performed with a single stage CMA in the dN/dE-mode with a 5 V peak to peak modulation amplitude. The energy of the defocused primary beam was 2 kV. The sample current density was kept very

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low in order to minimize influences on the surface composition.

As a basic measure for surface C concentrations, we used the ratio of the C_{271} to the Mo_{221} Auger peak-to-peak-heights (APPHs), thus avoiding influences by drifts of the secondary electron multiplier in use. After the adsorption of ethylene on a clean annealed Mo(100) surface to the saturation coverage of C upon the surface at room temperature, a C/Mo ratio of 0.36 ± 0.01 was obtained, in connection with a sharp $p(1 \times 1)$ LEED pattern. From the literature, e.g. see Ref. [11], this saturation coverage is well known to be 1 monolayer (ML), i.e. one carbon atom per Mo atom of the surface layer. A further calibration in order to obtain absolute values of carbon amounts, independently of AES, was performed by quantitative reaction desorptions with oxygen adsorbed additionally at room temperature. This experimental procedure is described in detail elsewhere [12], thus only a brief explanation is given here. The number of C atoms removed by the desorptions was determined by comparing the area beneath the flash desorption curves with the area below a curve of a CO pressure burst out of a glass vessel with known volume and CO pressure ('synthetic flash'). This comparison leads immediately to the amount of removed C owing to the fact that carbon reacts with oxygen on Mo(100) surfaces exclusively to CO. If the desorption has removed all the C atoms within the Auger sampling depth, the correlation between carbon amount and APPH ratios before the desorption can be obtained.

The samples investigated were disks of 0.6 mm thickness and 6.4 mm diameter cut perpendicular to the ⟨100⟩-orientated axis of a high-purity Mo single-crystal rod. The orientations of the top and bottom planes turned out to be within 0.5° of ⟨100⟩ after mechanically grinding and polishing them to a mirror finish. The disks were mounted to Ta-wires by electron beam welding and the wires clamped between jaws of a copper sample holder. Sample heating was achieved by a current through the wires and the sample itself. The unavoidable effect by the heating current on the APPH ratios was taken into account by a calibration described in detail elsewhere [12,13]. The temperature of the sample was measured by a chromel–alumel thermocouple spot welded to the back of the sample.

The untreated sample was cleaned in UHV by extended anneals, until no further segregation of impurities other than carbon (notably sulphur, oxygen and calcium) appeared. A further anneal in a flowing O_2 atmosphere reduced the carbon content until the segregation kinetics of the C atoms to the surface were slow enough to be monitored accurately by AES. After this procedure the overall carbon concentration was less than 1 at. ppm as confirmed by a sample cleaned identically and analysed by the 'Max-Planck Institut für Reinststoffe' laboratory at Dortmund. This is equal to a total carbon content of less than the equivalent of 4 ML for the whole sample.

3. Experiments and results

The segregation kinetics of C to the Mo(100) surface were investigated within the temperature range from about 1000 to 1528 K. The high temperature limit is a consequence of the C-enrichment becoming too fast to be reasonably recorded by AES, even at the very low bulk concentrations. At low temperatures, however, the adsorption of hydrocarbons and CO noticeably influences the results of the measurements. By monitoring the carbon uptake from the residual gas on a totally clean sample it turned out that a noticeable adsorption did not occur with the experimental setup at temperatures above 1000 K and experimental times up to 4 h.

Prior to each experimental run the sample was annealed for 1 h at 1528 K in order to achieve an equilibrated carbon concentration within the bulk. The sample was then set up to the desired diffusion temperature within a few seconds and the surface under investigation sputtered by 3 kV argon ions for only 30 s. This short sputtering time lowered the carbon amount at the surface, but did not remove it completely. Thus, the unavoidable depletion of the very low total carbon amount by the performance of several subsequent diffusion experiments, as well as the sputter damage, could be limited. Moreover, it turned out that even by prolonged sputtering a total disappearance of the C-Auger peak could not be achieved. Figs. 1(a) and 1(b) show the C-to-Mo APPH ratios for 1018, 1305, 1391 and 1528 K plotted against the square root of time. These ratios are normalized to the value of 0.36 determined for 1 ML of carbon upon the surface. The C/Mo APPH ratios shown in Fig. 1(b) towards the end of the experiment (approaching equilibrium) are surprising, being in this case higher for the higher temperature. This fact is due to the total carbon amount being higher in the experiment at the higher temperature, as discussed in Section 5. Within experimental error, the enrichment at 1528 K shows a parabolic behaviour until the surface concentration has reached 75% of the equilibrium value. In contrast, at lower temperatures a pronounced time delay of the carbon enrichment occurs; this is more pronounced the lower the sample temperature. That this effect is not due to sputter damage as proposed in the literature, e.g. as for the system sulphur–nickel [14], was checked in the following manner:

(a) a clean, annealed Mo surface was Ar-ion sputtered at the particular temperatures of the diffusion experiments, but for prolonged times (5 min), leading

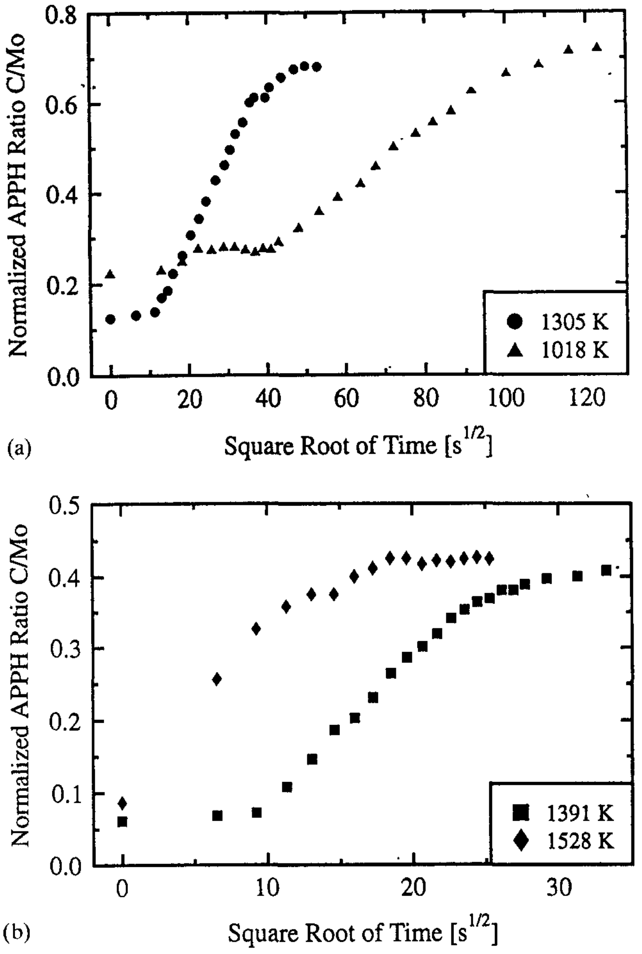

Fig. 1. Normalized C/Mo Auger signal height ratio during the segregation of carbon plotted vs. the square root of time. The higher equilibrium (final) value for the higher temperature in (b) is due to the higher bulk concentration in this experiment.

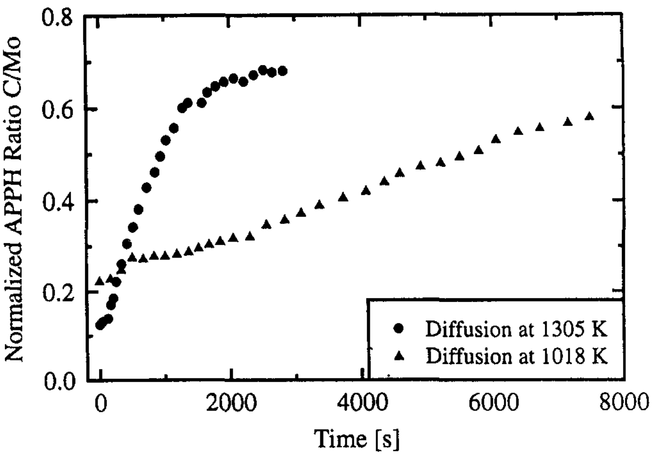

Fig. 2. Normalized C/Mo APPH ratio during the segregation of carbon to the Mo(100) surface plotted vs. a linear time scale.

to the disappearance of the initial p(1 × 1) LEED structure. After stopping the sputter procedure the p(1 × 1) reappeared within several seconds, at most within a few minutes. Sputter defects of the surface itself are obviously annealed too fast to represent a sufficient explanation for the time lag of the enrichments;

(b) in addition, the enrichment experiment with the most pronounced time lag (at 1018 K) was repeated without argon ion sputtering in order to avoid any sputter damage at all. The surface and near-surface carbon was now removed from the annealed surface by the adsorption of a suitable amount of oxygen at room temperature and subsequent desorption of CO. As soon as all the oxygen is consumed the C-AES signal increases in the usual way. The kinetics of this C-enrichment to the surface turned out to be almost identical to the behaviour observed after an initial sputtering procedure.

Plotting the experimental results at 1018 and 1302 K vs. a linear time scale (Fig. 2) shows a quasi-linear C-enrichment which persists longer for the lower temperature. Such a behaviour is in contradiction to the classical foreign atom depletion extending from the surface. Since the results of equilibrium segregation experiments [13] suggest noticeable subsurface enrichments of carbon in addition to the surface segregation, we investigated the depth distribution and the mobility of carbon near the surface again by reaction desorptions with oxygen. In these experiments the carbon enrichment in the near-surface region was performed by the adsorption of ethylene, followed by distinct anneals, leading in equilibrium to the same depth distribution of C atoms as occurs with equilibrium segregation. Since a description of these experiments is given in detail elsewhere [12], only the results important for the diffusion considerations are reported here.

A clean annealed Mo(100) surface was saturated with one ML of carbon by ethylene adsorption at room temperature, which yielded a carbon amount similar to that of the diffusion experiments. This was followed by distinct anneals (denoted below as preanneals) within the temperature range of the diffusion experiments and by a room temperature adsorption of oxygen to saturation. Annealing times of 5 min turned out to be sufficiently long for establishing equilibrium within the carbon-enriched subsurface layers. Thus the carbon distribution in this region can be assumed to resemble the distribution occurring with equilibrium segregation. A subsequent temperature flash caused the reaction to CO and its desorption which was monitored by the quadrupole mass analyser. The desorption curves obtained with these experiments were compared with those of an experiment without a preanneal. A preanneal strongly influences the shape of the desorption curve (Fig. 3). The higher the temperature of the anneal the more distinctly a second, delayed desorption peak occurs. This peak is due

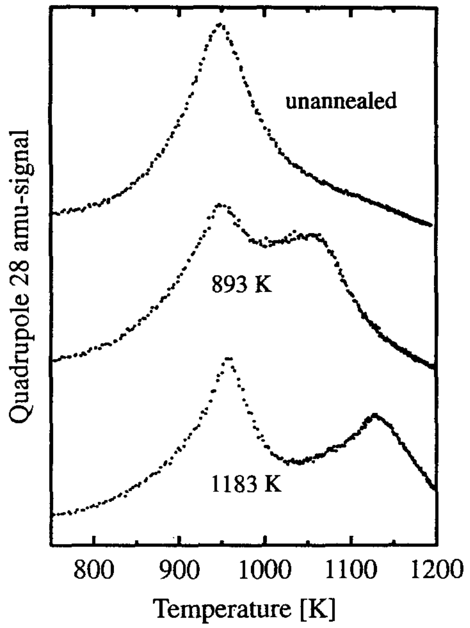

Fig. 3. 28 a.m.u. (atomic mass units) signal of the reaction desorptions of CO without a preanneal (upper curve) and after preanneals (below). The area below the curves corresponds to $7 \pm 0.7 \times 10^{14}$ CO molecules; 1 ± 0.1 ML of carbon has been removed by the desorptions respectively.

to a considerable part of the total carbon amount now distributed in the subsurface region as the consequence of the preanneal. Before its reaction to CO this C has to be resupplied to the surface by diffusion. The resupply is a function of the mobility of C atoms, their concentration and their respective distances from the surface. Quick runs of the C-AES signal monitored simultaneously with the desorptions show that after the preanneals the distribution of the C atoms is extended to depths larger than the sampling depth of AES. The depth of this distribution of about 15 Å can be estimated by model calculations [12], yielding about ten subsurface layers enriched with C atoms. This depth combined with the time required for the C supply shows that the carbon diffusion is markedly slowed down in the C-enriched subsurface region.

If the samples were sputtered at the end of the preanneal under the same conditions as in the diffusion experiments, the desorption curves were the same as those obtained without sputtering. This fact indicates that the carbon resupply quickly establishes a depth distribution similar to that after the heat treatment alone. This feature is important for choosing the initial conditions of the model calculations described below.

Thus, the segregation kinetics of C to a Mo(100) surface measured by AES are strongly influenced by a multilayer enrichment, having the following consequences:

(a) there are diffusion traps combined with enhanced barriers in the vicinity of the surface. How this explains the observed segregation kinetics is discussed below;

(b) the C to Mo ratios of the APPHs do not represent an immediate measure for surface concentrations because the additional carbon enrichment contributes to the total carbon Auger signal.

As an additional check of statement (b) we applied the usual formula

$$n_A \sim \int_0^\infty n_E(z) \exp\left[-z\left(\frac{1}{\lambda_p} + \frac{1}{\lambda_E \cos\theta}\right)\right] dz \qquad (1)$$

to a heavily carburized sample: n_A is the resulting Auger signal height for element A; $n_E(z)$ is the atomic density at depth z where Auger electrons with energy E are emitted; λ_E is the inelastic mean free path of those Auger electrons [15]; θ is the angle between the surface normal and the direction towards the entrance slits of the CMA; λ_p is the inelastic mean free path of the primary electrons [15].

Assuming the highest C concentration reported in the literature, i.e. one C atom per Mo atom, for at least the sampling depth of Auger electrons Eq. (1) yields a C/Mo APPH ratio of 2.3 times the value for the surface monolayer, in excellent agreement with the experimental C/Mo APPH ratio of this sample, 2.28 times the value for a single monolayer upon the surface. This supports that:

(1) using the mean free paths of [15] is correct;

(2) the assumption of a maximum carbon concentration of one C atom per Mo atom in the near-surface region is quite correct.

4. Modelling a multilayer enrichment

The basic effect of trapping carbon near the surface on the segregation kinetics can be understood in the following manner. Starting the diffusion experiment means that a fraction of the originally segregated carbon is removed by Ar-ion sputtering or desorption as CO, reducing the carbon amount on the surface as well as within the subsurface region. C atoms diffusing from the bulk must pass several subsurface layers before they reach the surface. They are consumed for an enrichment of the surface as well as for refilling the traps in the subsurface region. The refilling effect dominates the kinetics mainly at the beginning of the experiment. A pronounced time lag is observed by AES only if at least a considerable part of the traps have distances from the surface that are larger than the sampling depth of AES.

For the numerical calculations the half of the sample pointing towards the CMA is modelled by two regions, namely the bulk and a number N of discrete outermost atomic layers in which carbon atoms are trapped. In the calculations N is varied from 5 to 15, in agreement with the results of the reaction desorptions and the results of the equilibrium measurements [13]. Within the bulk, diffusion occurs without trapping.

The energy level E_i for a carbon atom in a subsurface site i is deep (according to carbide formation) compared with an interstitial site in the Mo matrix, thus keeping the concentration of the $(N+1)$th layer (the outermost 'bulk layer') near zero. Then the amount $j(t)$ per second and unit area of carbon supplied to the subsurface region by the bulk can be expressed by the simple relation

$$j(t) = \frac{\sqrt{D}c_0}{\sqrt{\pi t}} \tag{2}$$

where D denotes the bulk diffusion coefficient and c_0 the initial bulk concentration.

Despite the small size of the sample, Eq. (2), valid for semi-infinite diffusion sources, can be used. This is checked by using the series of the expansion from Ref. [2]

$$j(t) = \frac{2Dc_0}{b}\sum_{n=0}^{\infty} \exp(-D(2n+1)^2\pi^2 t/4b^2) \tag{3}$$

with b denoting half the sample thickness. The results obtained by Eq. (3) agree with those from Eq. (2) for the sample under investigation until the AES C signal approaches equilibrium. The bulk diffusion coefficient is obtained from the results in the next section. The initial conditions are chosen as follows. At the end of the high temperature anneal, prior to sputtering, the depth distribution of the carbon atoms and their total amount within the whole sample are determined by a modified Langmuir–McLean formalism. This analysis exploits the strong segregation-induced bulk depletion which leads to the pronounced measured deviations from a classical Langmuir–McLean behaviour, as described in detail in a previous paper [13]. The subsequent sputtering process lowers the carbon concentrations only in the outermost layers, but to a degree unknown a priori. In the bulk the number of C atoms and their distribution are assumed to be unaffected, owing to the short time for cooling down, sputtering and annealing of the sputter defects. In agreement with the experimental result that a C distribution close to local equilibrium is established among the subsurface layers within a very short time after sputtering, the new initial conditions are chosen neglecting sputter effects. For the subsurface region plus the surface, the carbon distribution is now governed by a Langmuir–McLean formalism decoupled from the bulk and representing a new local equilibrium. The total C amount in this region is determined so that the application of Eq. (1) yields the C/Mo APPH ratios measured immediately after the sputter procedure. The subsequent diffusion process within the subsurface layers is simulated numerically. The carbon fluxes between layer i and layer j are calculated according to

$$s_{i,j} = \nu\theta_i(1-\theta_j)\exp(-E_{i,j}/RT) \tag{4}$$

where R denotes the universal gas constant, T is the temperature in kelvin, ν is a frequency factor of about 10^{13} s^{-1} magnitude and $E_{i,j}$ is the energy barrier to move a carbon atom from layer i to layer j.

As a value for the segregation enthalpy (the potential for carbon upon the surface), we insert 45 kcal mol^{-1} determined by equilibrium segregation measurements [13]. The θs denote the C concentrations in the layers in units of C per Mo atom. The 1 in the term $(1-\theta)$ in Eq. (4) reflects the assumption of a maximum C concentration of unity, in agreement with the results of the AES calibration for the most heavily carburized sample and the maximum concentration reported in the literature [16]. The time development of the θ_js is calculated using the Runge–Kutta scheme:

$$\theta_j(t+\Delta t) = \theta_j(t) + (s_{j+1,j} + s_{j-1,j} - s_{j,j+1} - s_{j,j-1})\Delta t \tag{5}$$

Here $j=0$ denotes the surface and $j=N$ the layer adjacent to the bulk where the net diffusion flux out of the bulk $s_{N+1,N} - s_{N,N+1}$ is given by Eq. (2). The parameters of the calculation were varied until the resulting carbon to molybdenum APPH ratios calculated by Eq. (1) agreed with the experimental results. Performing these calculations, the energy levels E_i and the diffusion barrier heights $E_{i,j}$ were varied over a wide range. As the bulk diffusion coefficient can be roughly estimated by the slopes in Figs. 1 its variation could be held smaller. The experimental results were, in addition, checked as follows. The final equilibrium C/Mo APPH ratios of each experiment lead, applying again a Langmuir–McLean treatment for the whole sample, to a total C amount. Within experimental error, this amount was equal to the amount of carbon determined for the whole sample before sputtering minus the carbon removed by sputtering (estimated by the decrease of the C/Mo ratios during sputtering).

The experimental results can be reproduced by the calculations only if the parameters inserted are within the following detailed ranges.

The number of carbon enriched, trapping subsurface layers is 10 ± 5; the energetic level for carbon within these layers is 37 ± 3 kcal mol^{-1} deeper than in an interstitial bulk site, in agreement with the results of [13].

The approximate heights of the outermost diffusion barriers are 70 kcal mol^{-1} at 1018 K, 80 kcal mol^{-1} at 1305 K, 90 kcal mol^{-1} at 1391 K and less than 70 kcal mol^{-1} at 1528 K, owing to the disappearance of any noticeable enrichment delay.

Obviously, the diffusion barriers for C atoms within the carbidic subsurface layers increase with increasing temperature up to at least 1391 K; they then decrease with further increase in temperature. This fact might at first sight look rather strange, but in the literature, e.g. see Refs. [10,17–20], many peculiarities are also reported in connection with C diffusion in bulk carbides of molybdenum. A similar transition to remarkably lowered diffusion barriers with increasing temperature is reported for C in bulk Mo-carbides [17] and coincides with the transition from orthorhombic α-Mo_2C to the disordered β-Mo_2C [16], all within the same temperature range. Moreover, the values for the barrier heights found by our treatment are in reasonable agreement with those for the C diffusion in α- and β-Mo_2C reported in Ref. [17] (114 and 68 kcal mol^{-1} respectively). Until now it has been impossible to decide whether this coincidence is merely an accident or the lowering of the diffusion barriers is, for example, caused by the higher amount of interstitial vacancies in β-Mo_2C. There is obviously too little information available about molybdenum carbide, especially subsurface carbides.

5. Determination of the bulk diffusion coefficients

The most usual procedure for determining diffusion coefficients from segregation kinetics is to calculate them by regarding the amount of solute *m(t)* supplied from the bulk per unit area:

$$m(t) = 2c_0(Dt/\pi)^{1/2} \tag{6}$$

which is easily obtained by integrating Eq. (2).

This kind of procedure is quite correct for high segregation enthalpies and a parabolic behaviour according to Eq. (2). For our results, only the first condition is generally fulfilled. Therefore, except for the experimental result at 1528 K, the bulk diffusion constants cannot be evaluated immediately by Eq. (6) owing to the deviations from parabolic behaviour. The calculation introduced above in Section 4, however, yields not only subsurface diffusion barriers, but also values of the bulk diffusion parameters when searching for the best fit to the measured curves. As an additional complication we had to take into account the depletion of bulk carbon amounts during the sequence of our diffusion experiments due to the C atoms sputtered at the beginning of each experiment. Therefore, the bulk concentration was determined for each diffusion run separately by taking the temperature-dependent equilibrium segregation level at the last stage of the diffusion experiments as a measure for the total amount of solute at the given temperature [13]. By using this procedure, it turned out that the initial carbon amount of 0.64 ppm for the (first) diffusion experiment at 1528 K had decreased to 0.37 ppm for the 1391 K experiment (see also Fig. 1(b)), in agreement with the experimental sequence and, moreover, agreeing reasonably with the loss of sputtered carbon estimated from the decrease of the C-Auger signals during the sputter procedures.

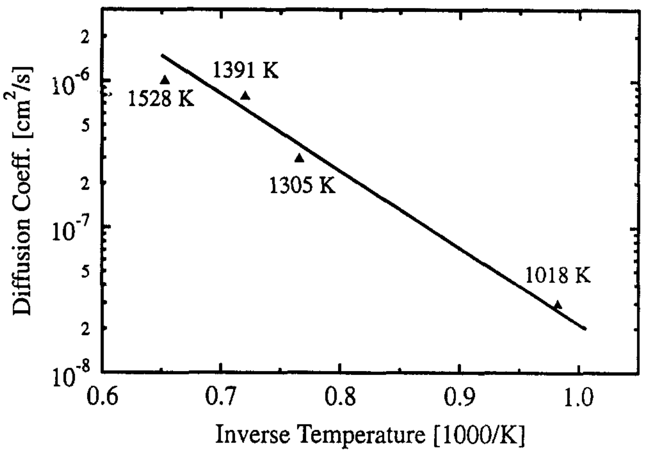

Fig. 4. Arrhenius plot of the bulk diffusion coefficients determined by a set of subsequent experiments.

The Arrhenius plot of the resulting bulk diffusion constants is shown in Fig. 4. From this plot an activation energy for the bulk diffusion of very dilute carbon in molybdenum of 25.5 ± 2 kcal mol^{-1} is determined. Owing to the depletion of carbon by the subsequent experiments, the diffusion constants could be evaluated reliably within an experimental sequence only for the four temperatures shown. Nevertheless, the slope in Fig. 4, and therefore the activation energy for the bulk diffusion, can be obtained quite accurately.

6. Discussion

The segregation kinetics obtained by the present investigation qualitatively resemble those reported by du Plessis et al. [21]. There, the non-parabolic behaviour is shown to be the consequence of the foreign atom depletion during a quite extended initial sputtering procedure. This kind of explanation can, however, be ruled out for the present results. The sputtering time is very short compared with the duration of the whole experiment and, moreover, the reaction desorptions show that after sputtering there is no depletion, but an enrichment of the foreign atoms beneath the surface. A time delay obtained in a plot vs. the square root of time can obviously be caused by a depletion as well as by a subsurface enrichment. There are some results reported in the literature suggesting the latter (enrichment) effect. Two of them are discussed briefly.

Mojica and Levenson [5] reported the bulk-to-surface precipitation of carbon at the surface of a polycrystalline Ni-ribbon. The time dependence showed two distinct regions: the first (A) with a carbidic lineshape of the differentiated C-Auger signal and the B-region obviously due to the formation of graphitic patches on the surface. Consider region A: for the two enrichment curves at the lower temperatures presented in Figs. 2 and 3 of Ref. [5] a quasi-linear increase of the carbon APPHs is observed followed by a pronounced plateau until the beginning of region B. Even within the range of the plateau the decrease of the Ni APPHs continues. The authors' interpretation of this fact is that during the plateau the number of carbon atoms within a depth of about 10 Å remains constant. It becomes evident that during the initial quasi-linear enrichment the subsurface region has been supplied with C atoms far above their solubility; this is more pronounced the lower the temperature. This fact agrees qualitatively with the temperature-limited stability of thin Ni-carbide films [22], and with the initial enrichments reported in this paper. In connection with these observations we note that Zdansky et al. [23] explained their experimental results as a transition of surface carbon to subsurface Ni-carbide.

Hamilton and Blakely [6] investigated the C segregation to a Co(0001) surface. They observed an abrupt disappearance of the carbon AES signal between 983 and 1023 K which they attributed to a phase transition at the surface of the Co-crystal. In addition, the segregation kinetics observed by step-changing the temperature from 1023 to 983 K showed a pronounced enrichment delay. The enrichment obtained in those measurements is remarkably slower and shows a pronounced time lag compared with a curve due to the treatment by Lea and Seah [3]. In connection with this fact it is of interest that carbon has been presumed to enrich in subsurface layers of cobalt [24].

The solute–matrix systems in which such delayed enrichments are reported have several facts in common with the C–Mo system: the small solubility in the matrix connected with high segregation enthalpies of the solute and the existence of several phases, some of them being unstable. Time lags in segregation kinetics might, therefore, in many cases be a consequence of phase transitions in the surface region and/or due to solute enrichments beneath the surface leading to the formation of subsurface phases.

A conversion of surface carbon to a subsurface state has also been reported by Overbury [25] for a Mo(111) surface and by Mullins and Overbury [26] for a W(100) surface, which in its structural and chemical behaviour is similar to Mo. It should be noted, however, that those subsurface enrichments are extended only to depths well within the detection limit of AES. This should be due to the different treatment causing the subsurface state, the anneal at only 600 K and/or the additional adsorption of oxygen.

A reduced diffusion immediately below a surface has also been reported for the systems C–W(100) [27] and O–Zr(0001) [28]. In those papers the reduced diffusion is explained using a one-dimensional layer-by-layer model with enhanced diffusion barriers, in a manner similar to the treatment introduced in the present paper.

The model assumptions we made for our calculations are obviously rather crude: the modelling has been performed on the basis of a simple one-dimensional layer-by-layer model; thus, (more realistic) three-dimensional C–C interactions leading to the formation of subsurface states are not involved. However, the results of equilibrium segregation [13] and extended reaction desorption studies [12] can be reproduced by the same assumptions and values of the parameters inserted. Moreover, there is to date, to the author's knowledge, no real physical model to calculate the formation of subsurface carbides and the mobility of carbon in those layers within a reasonable computing time. In contrast, a frame for the development of such a model is given by the results stated above. Carbon concentrations close to unity in a number of subsurface layers can easily be modelled by attraction forces due to carbide formation, e.g. by a model of a regular random solution. Such a model, however, must fail in the low concentration ranges necessary to explain the experimental results. The attractive interactions have to be unrealistically large and strongly dependent on the C concentration. Thus, we assume the subsurface carbides to be clusters or precipitates growing from carbidic islands upon the surface in a manner similar to that proposed by Sunderland and Slavin [29] for the W(15 × 3)R14^0–C structure.

7. Conclusions

By the treatment of segregation kinetics of C to a Mo(100) surface introduced in this paper, it is possible to separate effects of bulk diffusion from the slower diffusion in the outermost atomic layers. The latter is mainly caused by subsurface enrichments of carbon acting as diffusion traps. Owing to the low C mobility in carbides, the enrichment investigated by AES becomes additionally hindered. Despite large deviations from a parabolic behaviour it is possible to determine diffusion constants with reasonable precision. The determination of the diffusion parameters turns out to be most sensitive to the bulk amount of the solute, which is hard to determine experimentally but can be traced in the computations because of the significant bulk depletion. Comparing the present results with delayed enrichments reported in the literature leads us to the conclusion that noticeable deviations from a parabolic time law should be expected for systems of transition metals in which several phases exist in combination with a very low solubility of the solute in the metal matrix.

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