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Experimental determination of U diffusion in α -Ti

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α -spectrometry was used in order to measure the diffusion of U in bulk α -Ti in the temperature range 863–1123 K (540–850 °C). A straight Arrhenius plot was found, giving diffusion parameters $Q=297$ kJ/mol and $D_0=5 \times 10^{-3}$ m²/s, which are similar to the α -Ti self-diffusion ones, when measured in Ti samples with a similar impurity content than presently. This behaviour is compatible with the hypothesis of U diffusing via a vacancy-assisted mechanism in the α -Ti lattice and contrasts with older results in which the activation energy is almost a third the self-diffusion one, even lower than the vacancy formation energy.

Keywords: diffusion; U; Ti; α -spectrometry; nuclear materials

1. Introduction

The present work is part of a larger and systematic investigation on U diffusion at infinite dilution in metals. The interest on the subject lies in the fact that the U diffusion coefficients available in the literature are scarce, mostly measured in the 60s and 70s in poorly characterized materials and obtained at high temperatures, far from the ones of current technological interest. Cf [1] for a list of the measurements performed up to 1990. Besides, a quick (probably not exhaustive) literature search (e.g., [2] and the Scopus data base) suggests that there are no measurements of diffusion at infinite dilution in pure metals newer than the ones reported in [1].

Regarding U diffusion in α -Ti, there is a previous measurement performed by Federov et al. [3] with an unreported technique, in an uncharacterized material, in a short temperature range (1020–1124 K). The reported activation energy $Q=114.5$ kJ/mol is less than half the α -Ti self-diffusion one, measured in the purest material nowadays available [4] ($Q_{SD}=303$ kJ/mol). On the other hand, at the lower temperature measured, the U diffusion coefficient is more than two orders of magnitude higher than the self-diffusion one.

In order to extend the temperature region of the diffusion measurements in this system, our first task was to adapt a reliable technique, namely the α spectroscopy, for the determination of U diffusion profiles, in a sub-micrometric depth scale [5]. Here,

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we apply this technique to perform measurements in high purity α -Ti samples, from the α/β transition temperature to the lowest temperature reachable within a reasonable annealing time (around 10^7 s).

2. Experimental method

The measurements were performed in high purity (99.97%) discs of Ti of about 9 mm in diameter and 3 mm thickness. Table 1 reports a complete list of the impurity content as given by the manufacturer, Goodfellow Metals.

The samples were mechanically polished and subjected to an annealing cycle in order to increase their grain size: 1 h at 1473 K followed by 20 days at 1133 K, in highly pure argon atmosphere. This procedure led to samples with at most 3–4 large grains. Subsequently, the samples were mechanically and chemically polished again in order to obtain very flat surfaces. After that a new annealing for 1 day at 1123 K was performed in order to release stresses originated during the process.

Diffusion pairs were built by evaporation of depleted U, 99.97% purity, onto the sample surface, by heating a tungsten filament in a vacuum better than 10^{-6} torr; around 10 nm thick films were so obtained.

The diffusion anneals were performed under dynamic vacuum, 2×10^{-6} torr, when the total annealing time was shorter than 2×10^5 s, or in sealed quartz tubes under high purity argon for longer times. To prevent reactions between Ti and quartz, the samples were wrapped into Ta foils. The diffusion temperatures were controlled within ± 1 K with a Pt-PtRd S type thermocouple.

A silicon base p-n junction surface barrier detector (Camberra PD 150-16-100-AM) was used in order to measure the α spectra, with an active surface of 150 mm^2 and an energy resolution of around 16 keV.

The as-evaporated initial spectra was fitted with a Gaussian function whose width is given by the convolution of the effect of the α emission depth across the U deposit, the electronic noise and the difference in the particle path due to the solid angle subtended between the sample and the active surface of the detector. Other noise contributions, like straggling, could be neglected. In this particular case, the initial width was 45 keV.

Table 1. α -Ti samples impurity content.

Element	Content ($\mu\text{g/g}$)
Ag	nd
Al	<5
Co	nd
Cu	<3
Fe	<4
Ni	<0.2
Pb	<0.2
Si	<0.3
O ₂	<300
N ₂	<12

Note: nd: non detected.

3. Data analysis

A detailed description of the α spectrometry as applied to measure the U diffusion coefficient in metals is given in [5]. We now proceed to applied it to the α -Ti case.

Figure 1 (full line) shows the α particles spectra measured after U deposition, before the diffusion annealing; we focus the analysis on the particles emitted by the ^{238}U isotope. After annealing there is a spectrum broadening towards low energies (Figure 1 dotted line) given by the increase in the emitter distance to the surface due to diffusion, entailing larger energy losses.

This energy loss is given by the stopping power (dE/dx) as defined, for instance, in [6]; it was calculated by the subroutine ‘stopping range’ from the program SRIM 2008 [7] for an α particle moving in Ti between 10 KeV and 5 MeV, with an error lower than 3%.

The α -particle stopping power variation with the energy for this particular case is shown in Figure 2. The solid line is a data parabolic fit valid between 800 KeV and 5 MeV:

$$dE/dx(E) = a + bE + cE^2 \tag{1}$$

being $a = 59.54170 \text{ eV \AA}^{-1}$, $b = -1.309878 \cdot 10^{-5} \text{ \AA}^{-1}$ and $c = 1.1670195 \times 10^{-12} \text{ eV}^{-1} \text{ \AA}^{-1}$.

Then, when the α -particle is emitted by a ^{238}U atom from a distance x to the surface:

$$x = - \int_{E_0}^{E_d} \frac{dE}{dE/dx} = - \int_{E_0}^{E_d} \frac{dE}{a + bE + cE^2} \tag{2}$$

where E_0 is the energy of the α -particle when emitted (4.267 MeV) and E_d is the detected energy when arriving at the surface.

Analytic integration of expression (2) is straightforward, giving a relationship between the U depth and the detected energy:

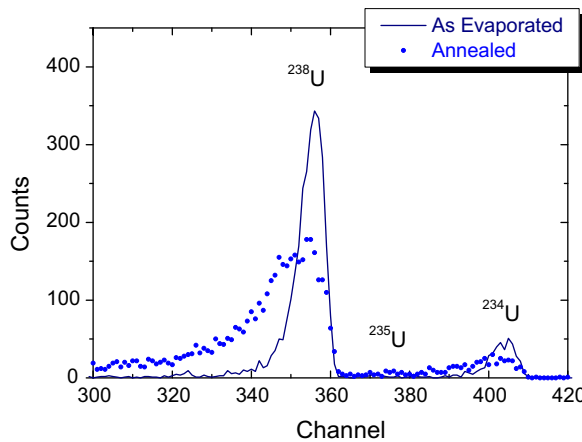


Figure 1. (colour online) α spectra, before and after annealing.

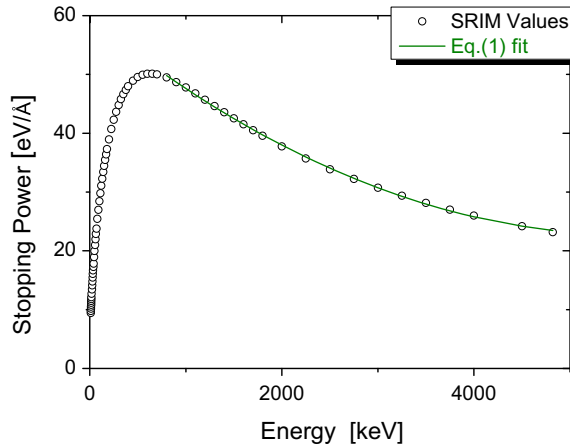


Figure 2. (colour online) α particle stopping power dependence with energy in Ti matrix.

$$x(E_d) = \frac{1}{\sqrt{ac - (b/2)^2}} \left[\arctan \left(\frac{cE_0 + b/2}{\sqrt{ac - (b/2)^2}} \right) - \arctan \left(\frac{cE_d + b/2}{\sqrt{ac - (b/2)^2}} \right) \right] \quad (3)$$

when $(b^2 - 4ac) < 0$ as in the present case.

Equation (3) shows a bijective correspondence between energy lost and depth and, consequently, with the spectrum channel number. On the other hand, the amount of U at each depth is directly related to the number of counts cumulated in that channel.

So, for all the information in order to obtain a typical diffusion profile, concentration versus depth is now available.

4. Results and discussion

Given the initial thickness of the as deposited U, a Gaussian shape solution to Fick's law is proposed:

$$C(x) = \frac{C_0}{\sqrt{\pi D(t + t_0)}} \exp \left(\frac{-x^2}{4D(t + t_0)} \right) \quad (4)$$

where C is the U concentration at depth x , C_0 is the initial amount of U per unit of area at the surface, D is the diffusion coefficient at a given temperature, t is the annealing time and t_0 is a fitting parameter coming from the initial profile, used in order to deconvolve its initial width as described in [5].

Typical diffusion profiles $\ln [C(x)]$ versus x^2 were build, as we mentioned in the previous section. They are shown, for each temperature studied, in Figure 3. In all cases, straight lines were obtained, thus Equation (4) is satisfied as expected. Diffusion coefficients are obtained from:

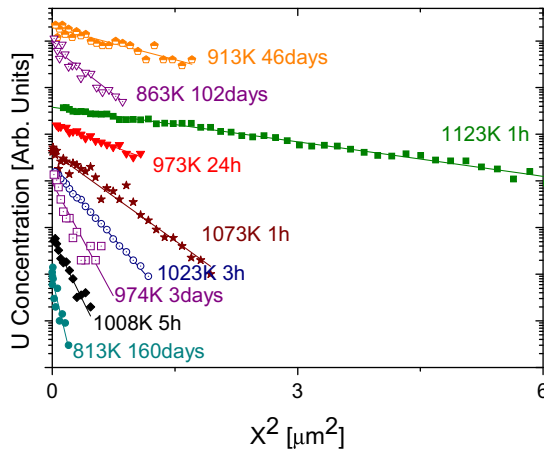


Figure 3. (colour online) U diffusion profiles in α -Ti.

$$D = \frac{s - s_0}{4ts_0} \tag{5}$$

where s is the slope of the diffusion profile and s_0 is the one of the as-evaporated initial profile.

A complete list of temperatures, diffusion annealing times and D values for each temperature is given in Table 2.

Figure 4 is an Arrhenius plot [$\ln(D)$ vs T^{-1}] for all those D values. They nicely fall on a straight line, so that the activation energy Q and the pre-exponential factor D_0 were obtained from the slope and the intercept, respectively. The temperature dependence of the U diffusion coefficient in α -Ti results therefore:

$$D(T) = (5 \pm 2) * 10^{-3} \exp\left(\frac{-(297 \pm 20)kJ/mol}{kT}\right) m^2 s^{-1} \tag{6}$$

Also in Figure 4, α -Ti self-diffusion [4] in samples with the similar amounts of impurities than here is shown for comparison, together with the previous U diffusion

Table 2. D values measured for each temperature.

Temperature K	t (10^4 s)	D ($m^2 s^{-1}$)
1123	0.36	$(1.0 \pm 0.2) \times 10^{-16}$
1073	0.36	$(1.7 \pm 0.3) \times 10^{-17}$
1023	1.08	$(3.3 \pm 0.6) \times 10^{-18}$
1008	1.8	$(1.8 \pm 0.3) \times 10^{-18}$
973	8.64	$(7.0 \pm 1.0) \times 10^{-19}$
924	25.92	$(8.8 \pm 2.0) \times 10^{-20}$
913	397.44	$(5.3 \pm 0.8) \times 10^{-20}$
863	881.28	$(6.8 \pm 1.0) \times 10^{-21}$
813	1382.4	$(4.0 \pm 1.0) \times 10^{-22}$

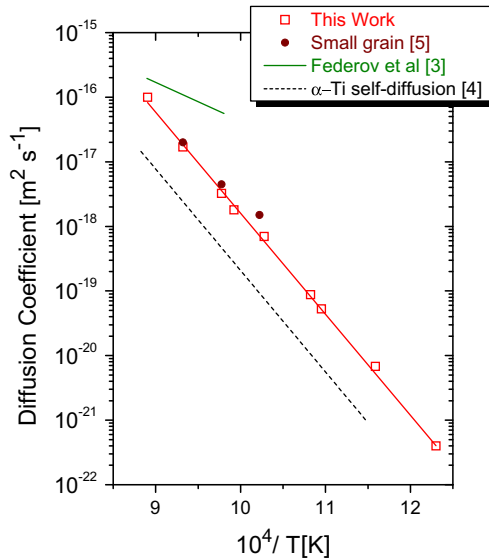


Figure 4. (colour online) Arrhenius Plot for U diffusion in α -Ti.

work [3] and 3 points measured in our laboratory in samples with small grains (around 0.1 mm) used in [5] in order to test the technique.

As can be observed, diffusion parameters for self-diffusion $^{\text{SD}}Q=303$ kJ/mol and $^{\text{SD}}D_0=1.35 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$ are similar to those obtained here, which is compatible with U being substitutional in the α -Ti matrix and a diffusion mechanism assisted by vacancies. D values are systematically higher than the self-diffusion ones, but within the same order of magnitude, also compatible with a vacancy mechanism.

Diffusion parameters for U diffusion from previous work [3] $Q=114.5$ kJ/mol and $D_0=4.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ are very different from the ones that measured here. Also, the diffusion coefficients are systematically higher than the present ones, being almost two orders of magnitude higher at the lowest temperatures.

Keeping in mind that vacancy energy formation in α -Ti is between 150 kJ/mol (according to experimental measurements [8]) and 200 kJ/mol (given by *Ab initio* calculations [9,10]), the Q value obtained by Federov et al., is incompatible with a vacancy-assisted diffusion mechanism. Such low values (approximately one third $^{\text{SD}}Q$) are usually attributed to some kind of interstitial mechanism, which is not expected in this case, according to semi-empirical rules (e.g., [11]) asserting that the higher the ratio between the ionic radii of impurity and the matrix, the lowest the probability to fill an interstitial position in the lattice.

Comparison with our 3 previous points for samples of smaller grain size shows a slight increment in the diffusion coefficients with respect to present ones, higher for the low temperature and almost negligible for the highest one. In this case, the influence of grain boundary diffusion in the measurements is small given the short penetration profiles (around or less than a μm) with respect to the grain size (around 0.1 mm), but the trend is of increasing the slope in the Arrhenius plot and, in consequence, obtain an activation energy higher than the corresponding to bulk diffusion.

For all the above reasons, it seems very likely that in the previous measurements reported in [3], the actual bulk D values were masked by the diffusion in some kind of short circuits such as grain boundaries, dislocations, etc. When the techniques used involve analysis of deeper diffusion profiles than presently, such an effect could be much more evident, resulting in the measurement of an effective diffusion profile, which is a composition of several mechanisms.

On the other hand, it is well known that in α -Ti even a few tens ppm of ultra-fast impurities, such as Fe, Co, and Ni, has the same effect: to increase D values and Arrhenius slopes (see for instance [4,12]). Even though the impurity content is not reported in [3], α -Ti samples with as low impurity level as used in this work were not commercially available until the 90s.

In order to exemplify the combination of those effects, in Figure 5 we show measurements of α -Ti self-diffusion using IBS (Ion Beam Sputtering), a technique with a similar depth resolution than the used in this work, in samples with a content of 2 ppm of Fe as impurity, full line [4] and 50 ppm dotted line [13], where the increase in Q value (and the decrease in D_0) due to the fast impurity effect is evident.

In addition, an early measurement in polycrystalline samples [14] (with a reported Fe content of 30 ppm), but using an abrasive sectioning technique, is also shown as square symbols in Figure 5. An additional order of magnitude of increment in D values can be observed. If, for instance, we considered the annealing time reported in [14] for 1013 K experiment (2,619,900 s) the Gaussian width $\sqrt{4Dt}$ is around $0.8\ \mu\text{m}$ extrapolating from [4] or around $2.5\ \mu\text{m}$ from [13], the real depth must be something in between. Being each slab width no thinner than $2\ \mu\text{m}$, it means that after the first or second diffusion profile point, most of the bulk contribution was consumed and, consequently, the effect of short circuits become dominant.

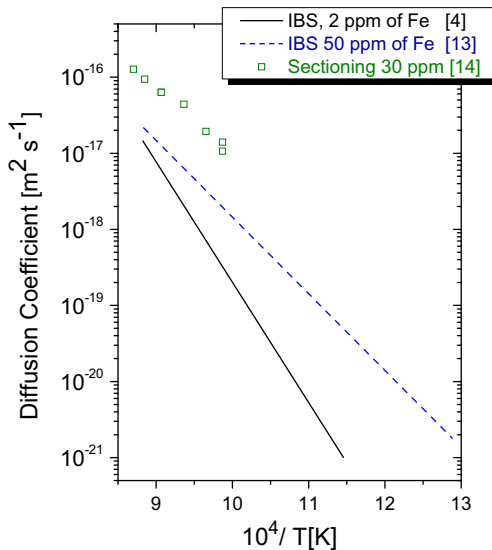


Figure 5. (colour online) α -Ti Self-Diffusion with different amount of impurities and techniques.

5. Conclusions

U diffusion in α -Ti in the temperature range 813–1123 K was determined using α spectrometry, a sub-micrometric technique capable to extend the temperature range of measurements below half the melting point.

The diffusion parameters Q and D_0 obtained were close to the self-diffusion ones measured in α -Ti samples with the same kind and content of impurities than the present ones. This behaviour is compatible with a mechanism of diffusion assisted by vacancies.

Comparison with previous measurements shows significant differences that could be explained arguing these previous D values as coming from a convolution of U diffusion in bulk with short-circuit diffusion and/or the effect of ultra-fast impurities present in those former samples in higher amounts than currently.

In light of these results, it seems necessary to measure again U diffusion at infinite dilution in metals and their alloys, not only trying to reach lower temperatures, but also to verify whether previous measurements suffer from the same problems, given they were performed around the same epoch, with lower spatial resolution techniques or in samples with higher amounts of ultra-fast impurities.

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