



Application of α -spectrometry to the study of U diffusion in nuclear reactor materials

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ABSTRACT

An experimental method used to study U diffusion at infinite dilution in materials is presented in this work. The spectra of α particles emitted by U at different depth in the material, after the diffusion annealing, is converted into diffusion profiles combining the knowledge on the stopping power of α -particles coming from particles accelerators into an algorithm developed here.

Details of sample preparation and experimental set-up is given, as much as depth resolution and limits for the diffusion coefficients attainable with this technique. Diffusion of U in Mo and α -Ti are measured at several temperatures in order to check the technique.

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1. Introduction

Data of U diffusion in pure metals (cf Ref. [1] for details up to 1990) and materials used in nuclear reactor such as Zr and their alloys (Zr–Nb, Zircaloy), Hf, Mo, Al, Fe and several steels is scarce, mostly measured in the 60s and 70s in poorly characterized materials and obtained at high temperatures, far from the ones at which reactors work.

The experimental methods used in order to measure the diffusion coefficients were mainly the fission fragment radiography [2,3], the autoradiography [4] and the residual activity [5–8]; sometimes experimental techniques used [9,10] were not reported.

The accuracy of such techniques is low, especially when the diffuser penetration is short, for instance in the sub-micrometer range as is the attainable depth for a reasonable annealing time at temperatures below $0.5 T_f$ (being T_f the melting temperature). These temperatures are usually the ones at which nuclear reactor facilities work.

Let us point out a few consequences of the mentioned limited accuracy in the experimental methods:

- (i) The two available measurements of U diffusion in Mo [5,9] differ between 3 and 4 orders of magnitude at superposing temperatures.
- (ii) A similar difference is also observed for U diffusion in Nb [5,9].
- (iii) The 1.2 eV activation energy measured for bcc γ -U self-diffusion [11,12] seems to be very low for a self-diffusion assisted by vacancy mechanism in metals.
- (iv) Diffusion of U in α -Ti [10] is from 1 to 2 orders of magnitude higher than the self-diffusion measured in less pure α -Ti [13] and from 2 to 3 orders of magnitude higher than self-diffusion in the purest α -Ti [14], whereas the activation energy 1.2 eV and the pre-exponential factor $D_0 = 4.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ are also low if an assisted by vacancy mechanism for diffusion is assumed.

Besides, a quick (probably not exhaustive) literature search (e.g. Ref. [15] and the Scopus data base) suggests there are no measurements newer than the above of U diffusion at infinite dilution in pure metals.

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The aim of this work is to apply and further develop the α -spectrometry to the determination of U diffusion profiles in metals, using as analysis tool the α particles emitted by the disintegration of natural and/or depleted U.

α -Spectrometry has already been used for the determination of diffusion of actinides in nuclear fuels [16] in U oxides [17] and in U nitrides [18] but with two analysis techniques different from the one presented here.

The first one consists in following the decrease in the total activity measured at the surface after the diffusion annealing (see for instance Eq. (1) in Ref. [16]) assuming an exponential loss of energy for the α -particle when moving from bulk to surface. This method is inaccurate since that decrease may result not only from the diffusion processes but also from loss of materials due to the manipulation and/or evaporation during the diffusion anneals; another source of inaccuracy is the lack of reproducibility in the electronic set up during both measurements, before and after annealing, such as geometry conditions, dead times and background. On the other hand exponential attenuation for charged particles is a rather crude approximation.

The second method consists in the determination of the diffuser depth using a better, but still improvable, way to estimate the α -particle energy lost in the sample. A constant value for the energy loss is assumed, the so called stopping power, being it estimated according to an early work by Fano [19] for each element studied.

Nowadays it is well known that the stopping power is not a constant and its dependence with the energy can be precisely determined by the vast knowledge of ion interactions with matter, coming from particle accelerators studies and provided by computational programs such as SRIM 2008 [20].

The goal of the present work is to analyze the spectra of the α particles emitted by the disintegration of natural and depleted U, measured before and after diffusion annealing in several metals by merging the mentioned up to date knowledge of ion interaction with matter into an algorithm developed here in order to obtain U concentration versus depth profiles with a precision of several tens of nanometers.

2. Sample preparation and experimental set up

Application of α -spectrometry was performed in three kinds of pure metal matrixes: Al, α -Ti and Mo, in order to test the technique on materials of technological interest measured before with controversial results.

Disks of about 9 mm diameter and 3 mm thickness of polycrystalline 99.9% purity materials were used. They were provided by Goodfellow Metals. Grain size lies between 0.1 and 1 mm in α -Ti samples and between 0.2 and 0.5 cm for Mo and Al.

Given the short depths to analyze, the samples were polished with diamond paste decreasing the particle size up to a quarter of μm , in order to obtain a mirror surface. The final surface roughness was checked with optical interferometry.

Diffusion pairs were built by evaporation of pure U, 99.97%, onto the samples surface, by heating a tungsten

filament in a vacuum better than 10^{-6} torr; around 10 nm thick films were so obtained.

When natural U (^{238}U 99.284%, ^{235}U 0.711% and ^{234}U 0.0085%) was used, as shown in Fig. 1a) the signal coming from ^{234}U at 4.77 MeV has almost the same height than the one coming from ^{238}U at 4.267 MeV despite the smaller amount of the former. That happens because the activity is proportional to the product between concentration and isotope half life (see, for instance [21]) and there is a four orders of magnitude difference between these half lives (2.48×10^5 and 4.51×10^9 years respectively). So, isotope effect on diffusion might be studied using natural U.

When depleted U (0.2% ^{235}U) was evaporated (see Fig. 1b) the ^{234}U signal is considerable lower (^{235}U is almost not detectable) being the 4.267 MeV α particle coming from ^{238}U the main signal.

In the present measurements, we used depleted U, focusing the analysis only in the ^{238}U peak.

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 filled with high-purity argon for longer times. Diffusion temperatures were controlled within ± 1 K with Pt–PtRd S type thermocouples.

Given the non-destructive character of the technique, successive anneals increasing the time could be performed,

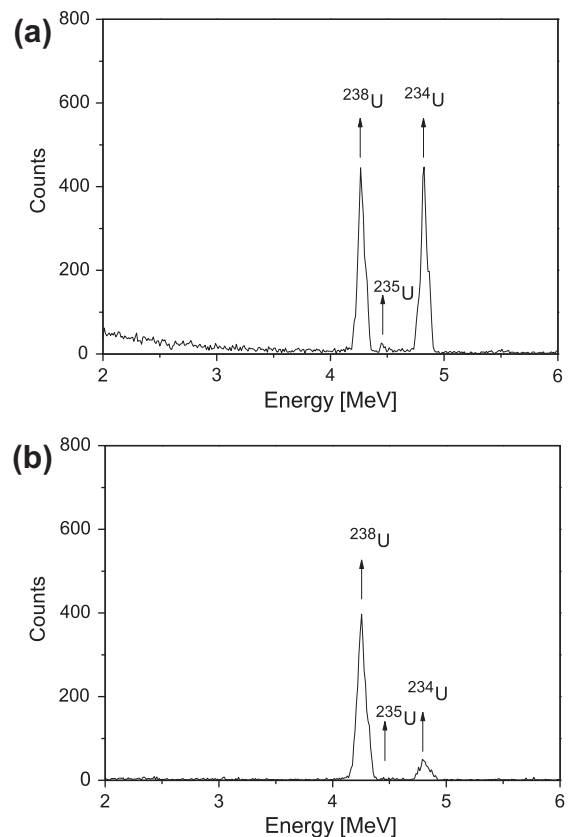


Fig. 1. α Spectra after U evaporation: (a) natural U and (b) depleted U.

in order to detect any kind of initial transitory effects that might mask the actual diffusion process.

Silicon base p-n junction surface barrier detector was used in order to measure α spectra, i.e. Camberra model PD 150-16-100-AM with an active surface of 150 mm² and an energy resolution of around 16 keV. The depletion zone of 100 μ m thickness allows the spectroscopy of all occurring α -particles.

The as evaporated initial spectrum shape could be fitted by a Gaussian function which width is given by the convolution of the effect of the α -emission point across the U deposit thickness, the electronic noise and the difference in the α -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 except for the surface roughness if is not small enough. In this particular case the initial width was 45 keV (full lines in Figs. 2a–2c).

As neither the detector nor the samples are points, the solid angle subtended between them is not unique. In order to test their influence in the peak width we change the sample-detector distance between 2 and 10 cm, inside the vacuum chamber. Of course, an increment in the distance implies an increment in the acquisition time, but not significant variation in the peak width was observed; consequently, a distance of 2 cm between sample and detector was chosen in order to minimize the acquisition time, which typically was between 20 and 40 h.

On the other hand, as we will see in Section 4, all these contributions could be discarded by comparison of spectra before and after diffusion annealings, if the geometry in both measurements is conserved.

3. Measurements

In order to test the technique, measurements in three different metals were performed. Fig. 2a shows the α -spectra for ²³⁸U diffusion in α -Ti at 973 K after 4 h and 28 h anneal. Spectra are normalized by the ratio between acquisition times. The increment in the signal width after each annealing is evident. The area under the peaks, which is proportional to the total amount of U, is conserved after

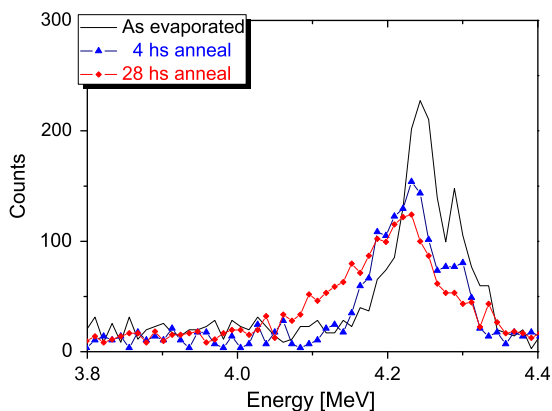


Fig. 2a. α -Spectra for U diffusion in α -Ti after diffusion anneals at 973 K.

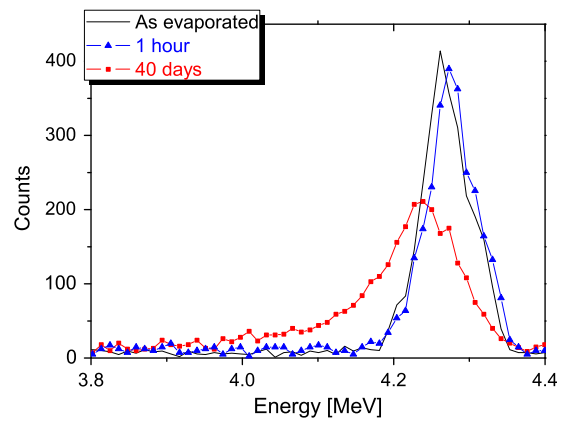


Fig. 2b. α -Spectra for U diffusion in Mo after diffusion anneals at 1373 K.

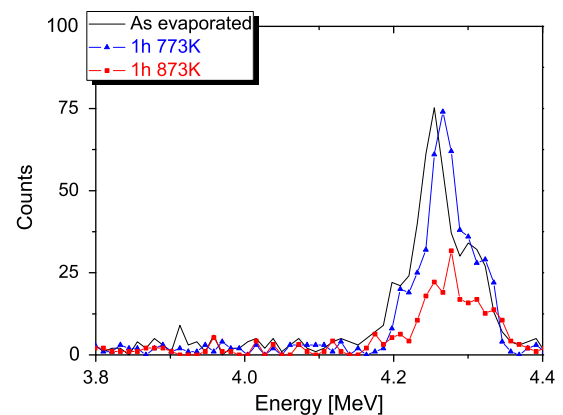


Fig. 2c. α -Spectra for U diffusion in Al.

each annealing, which means that the U loss (by evaporation, manipulation, etc.) is negligible.

Fig. 2b shows ²³⁸U diffusion in Mo for annealings of 1 h and 40 days. The first spectrum shows no differences with the as evaporated one, possibly due to the low diffusion coefficient corresponding to such temperature. There is an increment in the second spectrum. Again the area under the peak is conserved.

Fig. 2c corresponds to Al matrix. ²³⁸U spectra after anneal of 1 h at 773 K is shown with triangles; no significant difference with respect to the as evaporated is observed, the area under the peak is conserved. A second annealing of 1 h at 873 K was performed in the same sample, the corresponding spectrum is shown with squares in Fig. 2c. No increment in the peak width happens but a significant decrement in the peak area can be observed.

In order to make a rough estimation of U diffusion coefficient dependence with temperature in α -Ti, annealings at 1023 K for 3 h and 1073 K for 1 h were also performed.

4. Data analysis and discussion

The broadness in the spectra after annealing process is due to the energy loss of the α -particle emitted from U at

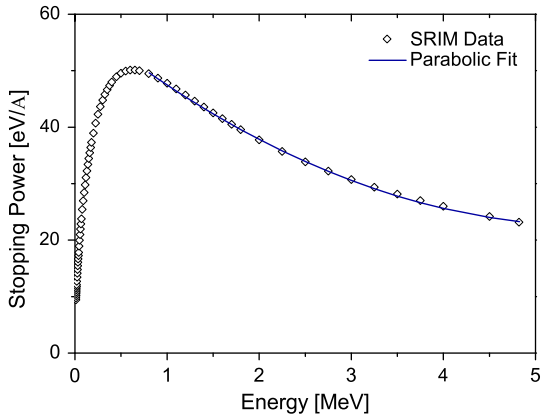


Fig. 3. Stopping power for α -particle in α -Ti.

increasing depths. This energy loss is given by the stopping power (dE/dx) as defined, for instance, in Ref. [22] that can be calculated by the subroutine “stopping range” from the program SRIM 2008 [20] for almost any element in the periodic table and their alloys with an error which is lower than 5% for α particles.

The α -particle stopping power variation with the energy for the particular case of α -Ti is shown in Fig. 3. The solid line is a data parabolic fit valid between 800 keV and 5 MeV:

$$dE/dx(E) = a + b \cdot E + c \cdot E^2 \quad (1)$$

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

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

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:

$$x = \frac{1}{\sqrt{ac - (b/2)^2}} \left[\arctan \left(\frac{cE_0 + b/2}{\sqrt{ac - (b/2)^2}} \right) - \arctan \left(\frac{cE_d + b/2}{\sqrt{ac - (b/2)^2}} \right) \right] \quad \text{if } b^2 - 4ac < 0$$

$$x = \frac{1}{\sqrt{ac - (b/2)^2}} \left[\ln \left(\frac{cE_0 + b/2 - \sqrt{ac - (b/2)^2}}{cE_0 + b/2 + \sqrt{ac - (b/2)^2}} \right) - \ln \left(\frac{cE_d + b/2 - \sqrt{ac - (b/2)^2}}{cE_d + b/2 + \sqrt{ac - (b/2)^2}} \right) \right] \quad \text{if } b^2 - 4ac > 0$$

$$x = \frac{1}{cE_0 + b/2} + \frac{1}{cE_0 + b/2} \quad \text{if } b^2 - 4ac = 0 \quad (3)$$

The values for a , b and c are given in Table 1 for the matrices here studied. The x total error introduced by this procedure is around 5%.

If the amount of U evaporated is lower than its solid solubility in the matrix, the thin film condition applied to the second Fick’s law of diffusion [23] results in a Gaussian shape for the diffusion profile:

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

where C is the U concentration at depth x , C_0 is the initial amount of U by unit of area at the surface, D is the diffusion coefficient at a given temperature, t is the annealing time and t_0 is defined in order to discount the initial (or previous) profile (and also the associated noise) as follows.

Fig. 4 shows the data presented in Fig. 2a for U diffusion in α -Ti at 973 K after Eq. (3) is applied in a semi-log graph versus square depth. As seen, Eq. (4) is followed so that straight lines are obtained. The slope s determined by least square fit is $s = -[4D(t + t_0)]^{-1}$, thus, defining t_0 as $-(4D s_0)^{-1}$, where s_0 is the slope of the as evaporated profile, the value of the diffusion coefficient is extracted:

$$D = \frac{s - s_0}{4t s s_0} \quad (5)$$

Applying Eq. (5) to the as evaporated profile after 4 h anneal a ${}^{\text{U}}D_{\alpha\text{-Ti}}(973 \text{ K}) = 1.4 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}$ is obtained. The same procedure for the 28 h anneal leads to ${}^{\text{U}}D_{\alpha\text{-Ti}}(973 \text{ K}) = 1.5 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}$ and for 28 h anneal against 4 h one ($t = 24 \text{ h}$ in Eq. (5)) ${}^{\text{U}}D_{\alpha\text{-Ti}}(973 \text{ K}) = 1.5 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}$.

We may thus set ${}^{\text{U}}D_{\alpha\text{-Ti}}(973 \text{ K}) = (1.5 \pm 0.1) 10^{-18} \text{ m}^2 \text{ s}^{-1}$. The procedure involving the two annealing times eliminates systematic errors (in particular the electronic noise introduced by the acquisition system) in this way the depth resolution is given directly by the resolution in channels of the spectra after Eq. (3).

In this particular case a minimum depth of 90 nm is necessary in order to distinguish an increment in the peak FWHM with respect to the as evaporated case. Given a maximum reasonable annealing time of 107 s (approximately 3 months) the minimum diffusion coefficient measurable by this technique is in the order of $10^{-21} \text{ m}^2 \text{ s}^{-1}$ since;

$$D_{\min} = \frac{x_{\min}^2}{4t_{\text{MAX}}} \quad (6)$$

which extends in more than four orders of magnitude the ones achievable with the previous techniques reported in the literature for U diffusion studies.

Table 1
Eq. (1) fit coefficients for studied elements.

Element	a (eV \AA^{-1})	b (10^{-5} \AA^{-1})	c ($10^{-12} \text{ eV}^{-1} \text{ \AA}^{-1}$)
Al	42.17114	-0.942631	0.8717008
Ti	59.54170	-1.309878	1.1670195
Mo	85.70145	-1.494486	1.0585821

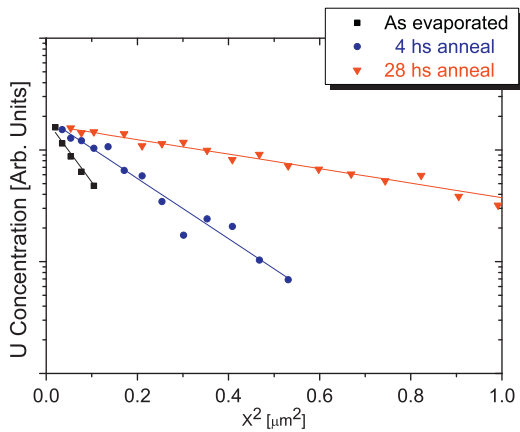


Fig. 4. U diffusion profiles in α -Ti at 973 K after conversion using Eq. (3).

Similar measurements performed at 1023 and 1073 K give ${}^U D_{\alpha\text{-Ti}}(1023\text{ K}) = (4.5 \pm 0.2) 10^{-18} \text{ m}^2 \text{ s}^{-1}$ and ${}^U D_{\alpha\text{-Ti}}(1073\text{ K}) = (2.0 \pm 0.1) 10^{-17} \text{ m}^2 \text{ s}^{-1}$ respectively. Fig. 5 is an Arrhenius plot for U diffusion in α -Ti from this work, together with previous measurements [10] and self-diffusion [11] data for comparison.

At this point it is important to stress that our current aim is to present the technique showing its possibilities and limitations and not to make a precise determination of D in a given system. Then, even when only three points in a short temperature range (but more extended than the one measured by Federov and Smirnov [10]) is not enough in order to get accurate diffusion parameters, it is possible to get a rough estimation of them, $Q = 2.33 \text{ eV}$ and $D_0 = 1.5 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$. Those values are higher than the previous ones, as expected for a substitutional diffuser and similar to the self-diffusion ones [11,12].

When the diffusion of U in Mo was measured at 1373 K, the 1 h first anneal does not show any variation in the α spectrum. From the second one (40 days) it is possible to obtain ${}^U D_{\text{Mo}}(1373\text{ K}) = (6.0 \pm 0.2) 10^{-21} \text{ m}^2 \text{ s}^{-1}$. The increment in spectrum width is proportional to $\sqrt{4Dt}$, for $t = 1 \text{ h}$ it is approximately 9 nm, which is below the technique sensibility, explaining the lack of variation after the first annealing.

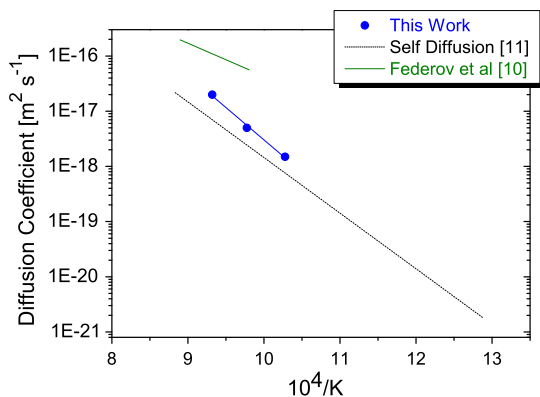


Fig. 5. Arrhenius plot for U diffusion in α -Ti.

Finally, let's analyze the case of U in Al. After the first annealing (1 h at 773 K) there is no variation in the spectrum as in the Mo case. Nevertheless, when the second annealing was performed at 873 K there is also no broadness in the peak, but a significant diminish in the total area. 873 K is a temperature close to the melting point for Al ($T_m = 933.37 \text{ K}$) then a low value for the diffusion coefficient is not expected.

The limitation here is the solid solubility of U in Al; according to Ref. [24] the maximum solid solubility of U in Al is 0.007 at.% at 919 K and less than 0.005 at.% at 623 K. The diminish in the total area under the peak after the second annealing could be due to bulk and/or fast path diffusion, then inside the sample the amount of U gives an alpha signal below the background, whereas the total amount of U distributed along the sample is great enough in order to diminish the U total amount at the surface. Nonetheless, loss of U by evaporation, manipulation, etc. cannot be disregarded. In any case, a minimum solid solubility of U in the matrix between 0.1 and 1 at.% is necessary in order to apply this technique, so no D value could be measured in this case.

The maximum D value attainable with α -spectrometry is given by the ratio between the square of the maximum depth analyzable and the minimum annealing time compatible with a stable temperature during the whole process:

$$D_{\text{MAX}} = \frac{x_{\text{MAX}}^2}{4t_{\text{min}}} \quad (7)$$

As the total amount of U and, consequently the area under the peak, is conserved, the mean limitation to the analyzable depth happens when the peak height falls below the background noise. In our experimental conditions that happens when the Gaussian width increases up to around 3 μm . It is possible to extend the maximum depth to around 10 μm by increasing the total initial amount of U, if the U solid solubility in the studied matrix allows that.

On the other hand, the minimum annealing time in an electric furnace in order to stabilize the sample temperature is not less than 1500 s. Then the order of magnitude of the maximum D measurable is $10^{-15} \text{ m}^2 \text{ s}^{-1}$ for U initial profiles of 10 nm and $10^{-14} \text{ m}^2 \text{ s}^{-1}$ for higher amounts of U. Nevertheless the use of faster heating devices, like infrared furnaces, laser beams, etc. could increase the maximum D_{MAX} to $(10^{-10}/4t) \text{ m}^2 \text{ s}^{-1}$ where t is the minimum annealing time, expressed in seconds, compatible with the heating device.

5. Conclusions

α -Spectrometry was successfully applied to the study of U diffusion in metals.

Diffusion profiles as shallow as several tens of nm are analyzable with this technique, which implies a minimum diffusion coefficient measurable in the order of $10^{-21} \text{ m}^2 \text{ s}^{-1}$.

Determination of U diffusion coefficients at temperatures lower than $0.5 T_f$ is attainable with this technique;

these temperatures are usually the ones at which nuclear reactor facilities work.

A minimum U solid solubility in the studied matrix between 0.1 and 1 at.% is necessary in order to apply this technique.

Data of U diffusion in metals, in particular the constituents of nuclear reactors and nuclear fuels must be revised in the light of the present results.

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