Uranium Diffusion in Metals Used in Nuclear Facilities - A New Approach

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Abstract. Diffusion at infinite dilution of U in metals, with particular emphasis in those used in nuclear facilities, is revisited. Early works present some particularities such as activation enthalpies lower than the vacancy formation enthalpy in the matrix, large differences with self-diffusion in the base material, up to four orders of magnitude differences between measurements performed by different authors in similar temperature ranges, etc. In particular U self-diffusion was qualified as abnormal when compared with other metals. Recent studies by means of α-spectrometry reveal a normal behaviour: activation enthalpies and pre-exponential factors similar to the self-diffusion one and diffusion coefficient values in the same order of magnitude than self-diffusion. The possible influence of short circuits, impurities and/or uncertainties in the techniques used in the early works is discussed in order to explain the differences obtained.

Introduction

The study of U diffusion at infinite dilution in metals, in particular the ones used in the nuclear industry, is indispensable in order to comprehend and understand the behaviour of materials inside nuclear reactors, which are to a great extent determined by diffusion processes. Creation of different types of defects in the crystal structure during irradiation, coarsening of finely dispersed precipitate in heat-resistant alloys, diffusion creep and other interactions are only a few examples of the effect of diffusion on the properties of metals and alloys.

Reactor materials are employed under extremely complex conditions of temperature, irradiation, load, aggressiveness of the surrounding medium, etc. Under these conditions, migration of atoms in the crystal lattice is one of the decisive factors leading to performance degradation.

The particular study of diffusion at infinite dilution, the determination of actual values of diffusion coefficients D at different temperatures and the diffusion parameters Q (activation enthalpy) and D_0 (pre-exponential factor), brings fundamental information on properties of the various defects present in those materials. This information constitutes also a basic ingredient for thermodynamic databases that feed computational programs used to model the behaviour of structural and fuel materials

The early works

Before 2012 the main corpus of data for U diffusion at infinite dilution in pure metals was compiled in handbook [1] up to 1990, and handbook [2] up to 2008. This data was scarce, mostly measured in the 1960s and 1970s decades, sometimes in poorly characterized materials and obtained at high temperatures, far from the ones at which reactors work. They are listed in Table 1 and plotted in Arrhenius type graph in Fig. 1: log D vs T_m/T, being T the temperature in K and T_m the melting point of the matrix. Detailed plots for each metal matrix are given further on in order to separate and clarify the data.

The experimental methods used in order to measure the diffusion coefficients were mainly the fission fragment radiography, the autoradiography and the residual activity, sometimes experimental techniques used were not reported. All this information is also given in Table 1.

Table 1: U diffusion coefficients at infinite dilution in metals. ΔH^F_V taken from handbook [3] unless otherwise mentioned in the text

Matrix	T[K]	D_0 [m²s⁻¹]	Q [kJ/mol]	ΔH^F_V	Experimental method	Ref/Year
γ-U	1073-1323	1.8×10^{-7}	115.1	164-191	Mechanical sectioning + residual activity	[4]/1959
	1075-1342	2.33×10^{-7}	119.3		Mechanical sectioning+ residual activity	[5]/1960
β-U	973-1028	1.35×10^{-6}	175.8		Mechanical sectioning+ residual activity	[6]/1959
	973-1023	2.8×10^{-7}	185.1		Mechanical sectioning+ residual activity	[7]/1968
α-U	853-923	2.0×10^{-7}	167.5		Mechanical sectioning+ residual activity	[8]/1962
Mg	773-893	1.6×10^{-9}	114.7	77-87	Residual activity	[9]/1968
β-Ti	1188-1298	2.0×10^{-7}	138.1	Phonon - softening	Fission fragment radiography	[10]/1967
	1173-1473	5.1×10^{-8}	122.7		Residual activity	[11]/1970
	1173-1773	1.6×10^{-9} 2.0×10^{-6}	89.2 192.6		Not specified . 2 exponential fit	[12]/1978
α-Ti	1020-1124	4.1×10^{-11}	114.5	150-200	Residual activity	[12]/1978
β-Zr	1223-1573	8.5×10^{-9}	111.4	Phonon - softening	Residual activity	[13]/1970
	1223-1773	3.0×10^{-10} 3.0×10^{-5}	82.5 242.8		Direct Sectioning, 2 exponential fit	[14]/1971
Nb	1773-2273	8.9×10^{-6}	321.5	255.7	Residual activity	[15]/1965
	1993-2373	5.0×10^{-10}	321.1		Not specified	[16]/1971
Mo	1773-2273	7.6×10^{-11}	319.9	289-347	Residual activity	[15]/1965
	2073-2373	1.3×10^{-14}	316.5		Not specified	[16]/1971
V	1373-1773	1.0×10^{-8}	257.1	202.6	Residual activity	[16]/1971
Ta	1873-2423	7.6×10^{-9}	353.4	270-280	Residual activity	[16]/1971
	2186-2530	1.03×10^{-10}	117.2		Fission fragment radiography	[18]/1977
W	2245-3000	1.8×10^{-6}	389.4	357-396	Out-diffusion	[19]/1968
	-	D_0 and Q dependence with the grain size				[20]/1969
	1973-2473	2.0×10^{-7}	433.3		Not specified	[16]/1971
	2407-2608	3.34×10^{-8}	259.2		Fission fragment radiography	[18]/1977
γ-Fe	1223-1348	7.0×10^{-9}	133.2	135-178	Thin layer+fission fragment radiography	[10]/1967
Ni	1248-1348	1.0×10^{-4}	236.1	172	Autoradiography	[21]/1971
Al	798-898	1.0×10^{-5}	117.2	64-74	Autoradiography	[22]/1968
α-Th	963-1150	2.21	332.0		α emission	[23]/1967

These techniques require U penetration profiles of at least some tens of μm in order to get reliable results. At temperatures below 0.5 T_m D values are usually below 10^{-17} m²/s in most metals, thus achieving diffusion depths of tens of μm may require annealing times forbiddingly large (several years), which explain the lack of information at lower temperatures at which nuclear reactor facilities usually work. On the other hand, those measurements were mostly performed in polycrystalline samples and, as it is well known, when the diffusion path (given by $\sqrt{4Dt}$ being t the annealing time) is in the same order of magnitude than the grain size, influences of diffusion through short circuits is unavoidable.
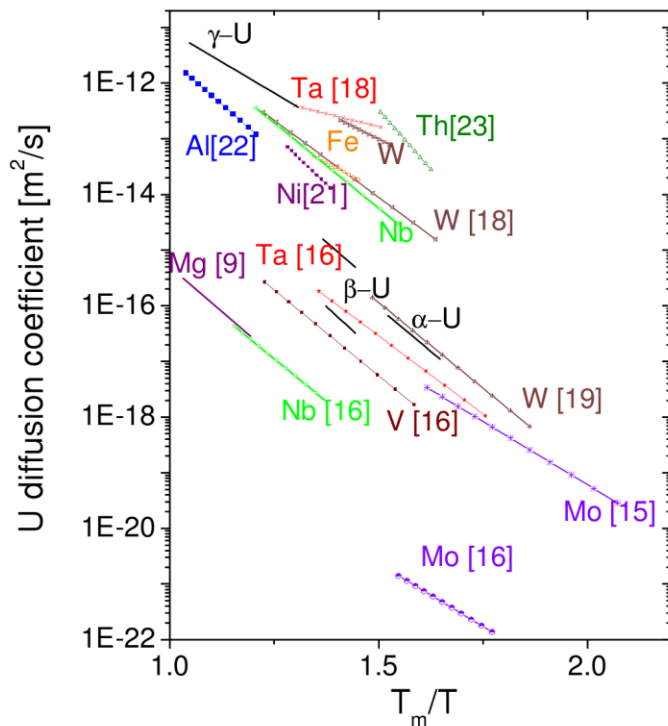
Figure 1: U diffusion in metals before 2012

Keeping all these facts in mind, let's analyze some peculiarities that appear in Table 1 data corresponding to those early works. The first remarkable fact is the 115.1 (119) kJ/Mol activation enthalpy measured for bcc γ-U self-diffusion [4, 5]; Q is lower than the vacancy formation enthalpy ΔH^F_V for U, which is between 150 and 200 kJ/mol [35]; being Q the formation enthalpy of the defect responsible for the diffusion jump plus the migration enthalpy of this jump, such a low Q value is incompatible with a self-diffusion assisted by a vacancy mechanism.

Another intriguing issue came from the analysis of the U diffusion in Nb and Mo data. There are two works in which U diffusion is studied in both materials in a superposed temperature range [15, 16]. They get similar Q, 321.5 [15] and 321.1 [16] kJ/mol for Nb and 319.9 [15] and 316.5 kJ/mol [16] for Mo, nevertheless D values differ between 3 to 4 orders of magnitude at superposing temperatures for both materials, which is reflected in the D_0 values reported in Table 1.

Also in several elements Q values seem to be very low, even lower than ΔH^F_V in the matrix. For instance, diffusion of U in α-Ti [12] is representative of all the anomalies observed in the early works. Here Q=114 kJ/mol is lower than ΔH^F_V in α-Ti (between 150 kJ/mol [24] and 200 kJ/mol [25, 26]), and D values are 2 or more orders of magnitude higher than the self-diffusion ones, therefore U diffusion in α-Ti seems to be incompatible with a diffusion via vacancy mechanism, which is not predicted by any semi-empirical rule relating diffusion of an impurity with atomic radius larger than the matrix.

All those peculiarities leave us wondering if the measurements reported are effective diffusion coefficients that combine the effect of short circuits, impurities, etc. rather than actual bulk diffusion coefficients at infinite dilution.

Performing a literature search (e.g. Defect and Diffusion Forum journal and Scopus database) there are no measurements reported before 2012 of U diffusion at infinite dilution in pure metals different from the above; in particular and relevant for the nuclear industry, there are no data in the low temperature hcp α-phase of Zr or its alloys.

At this point, for all those reasons, we think it was necessary to develop and apply a reliable technique capable to measure sub-micrometric diffusion profiles, revisiting the subject, and aiming at improving and enlarge the corpus of data when possible. Then we developed in 2012 a new implementation of α-spectrometry applied to the determination of diffusion profiles [27].

The α-spectrometry technique

Even when α-spectrometry has already been used for the determination of diffusion of actinides in nuclear fuels [28-30] the data analysis performed in these works consist in following the decrease in the total activity measured at the surface after the diffusion annealing and/or considering the α particle loss of energy (the so called Stopping Power as defined in [31]) as constant. This kind of data treatment can led to some uncertainties, as is detailed in ref. [27].

Nowadays it is well known that the stopping power has an important dependence on energy; that was precisely determined in particle accelerators studies and can be easily obtained from

computational programs such as SRIM 2008 [32]. The whole process is essentially the same as that involve in the [4]He ion in Rutherford Backscattering Spectrometry (RBS) technique [30], for the path out, after the ion collision.

Let's see what happens in a real measurement, i.e. the U diffusion in α-Zr at 1074 (801ºC) as an example. After thermal evaporation of depleted U onto the α-Zr sample surface a thin film of approximately 10 nm is formed; the corresponding α spectrum consists in the narrow peaks (one for each U isotope) shown in Fig. 2 (full line). After 4 hours of annealing, focusing the analysis on the [238]U peak, there is broadening towards low energies (dots) given by the increase in the emitter distance to the surface due to diffusion, entailing larger energy losses. Finally, as the technique is a non destructive one, a further annealing of 19 hours (23 hours in total) originates a higher broadening shown in Fig. 2 as dotted line.
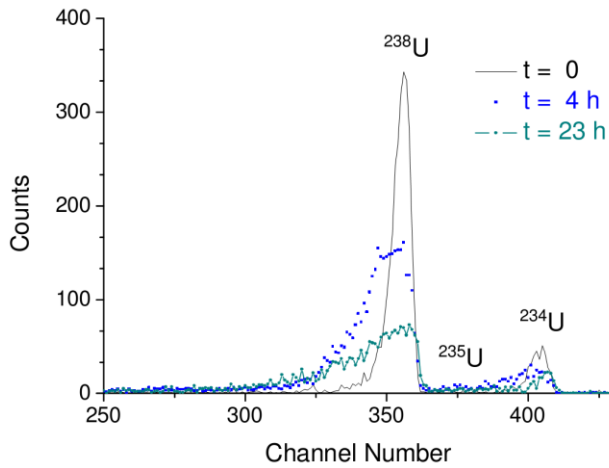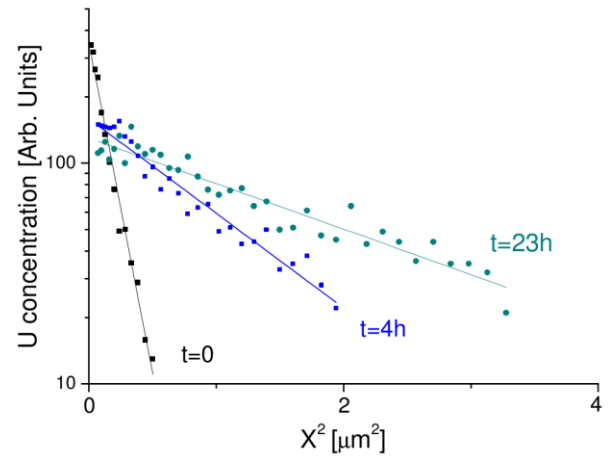

Figure 2: U spectra in α-Zr annealed at 1074K   **Figure 3:** Profile α-Zr annealed at 1074K

The energy loss of the α-particle through the solid matrix can be calcualted from the stopping power (dE/dx) whose dependence on energy in the electronic range, between 800 keV and 5 MeV, has a parabolic behaviour:

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

In our example for Zr: a = 66.9913848 eV Å^{-1}, b = -1.5731277 10^{-5} Å^{-1} and c = 1.4080616 10^{-12} eV^{-1} Å^{-1} (see Fig.4 in ref. [33]). For any other material a similar fit can be made using the corresponding data for dE/dx given by SRIM.

When the α-particle is emitted by a [238]U atom from a distance x to the surface, x is given by:

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

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 sample surface. Eq.(2) can be analytically integrated, giving a unique correspondence between energy loss and depth as shown in ref.[27].

Then, spectra in Fig. 2 can be converted into standar diffusion profile, C vs x, being $C(x)$ the U concentration at a given depth. Given the small initial thickness of U, the corresponding solution to Fick's law is the Gaussian function (provided the U solubility in the matrix is large enough):

$$C(x) = \frac{\kappa}{\sqrt{\pi D(t + t_0)}} \exp\left(\frac{-x^2}{4D(t + t_0)} \right) \tag{3}$$

where κ is the initial amount of U per unit of area at the surface, D is the diffusion coefficient at the given temperature, t is the annealing time, and t_0 is a fitting parameter coming from the initial profile (before the diffusion annealing) used in order to perform a deconvolution to its initial width as described in [27].

Typical diffusion profiles log $[C(x)]$ vs x^2] are presented in Fig. 3. In all three cases shown, straight lines were obtained, that means all the deposited U diffuses in solid solution in the α-Zr matrix, thus Eq. (3) is satisfied as expected. Diffusion coefficients are obtained from:

$$D = \frac{s - s_0}{4\,t\,s\,s_0} \qquad (4)$$

where s is the slope of the diffusion profile and s_0 is the one of the as-evaporated initial profile (or the previous annealing profile). In this particular case D can be determined 3 times: (1) using s from the 4 hours profile and s_0 from the as-evaporated, (2) 23 hours and the as-evaporated,(3) 23 hours and 4 hours. In all 3 cases we obtain the same value $^{U}D_{Zr}(1074\ K) = (4.5 \pm 0.5) \times 10^{-18}$ m^2/s.

All the data obtaining using α-spectrometry are listed in Table 2.

Table 2: U diffusion in metals measured with α-spectrometry

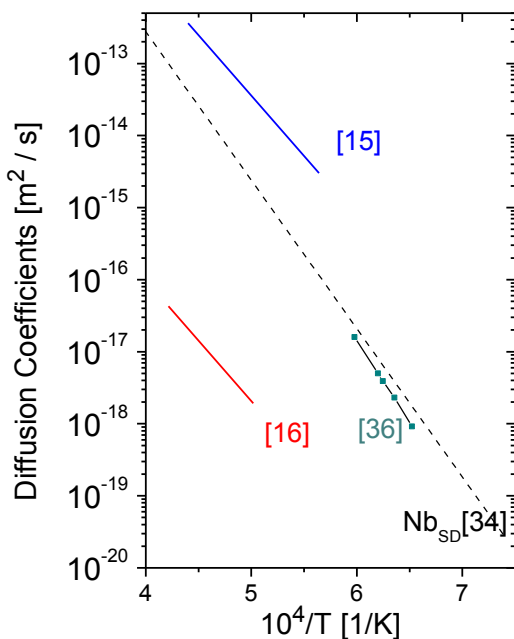| Matrix	T[K]	D_0 [m^{2}s^{-1}]	Q [kJ/mol]	ΔH^F_V [kJ/mol]	Ref/Year
α-Ti	863-1123	$(5\pm2) \times 10^{-3}$	297 ± 20	150-200	[42]/2013
Nb	1533-1673	$(2.5\pm1) \times 10^{-4}$	423 ± 10	255.7	[36]/2016
α-Zr	1123	$(1.4 \pm 0.4) \times 10^{-17}$		Non Arrhenius behavior	[33]/2015
	1113	$(1.0 \pm 0.3) \times 10^{-17}$			
	1093	$(6.3 \pm 0.6) \times 10^{-18}$			
	1074	$(4.5 \pm 0.5) \times 10^{-18}$			
	1030	$(1.4 \pm 0.3) \times 10^{-18}$			
	1029	$(1.1 \pm 0.4) \times 10^{-18}$			
	983	$(2.5 \pm 0.3) \times 10^{-19}$			
	913	$(4.8 \pm 0.8) \times 10^{-20}$			
	863	$(1.5 \pm 0.3) \times 10^{-21}$			
	813	$(1.0 \pm 0.3) \times 10^{-22}$			
Zry-4	843-1093	$(3.2\pm1.1) \times 10^{-2}$	316 ± 9	-	[48]/2017

U diffusion in Nb

Figure 4: U diffusion in Nb. Nb$_{SD}$ dotted line

There are three measurements of U diffusion in Nb, two summarized in Table 1 and a new one using α-spectrometry [36]. They are presented altogether in the Arrhenius plot of Fig.4; Nb self-diffusion [34 and references therein] was also plotted for comparison.

Measurements in [15] were performed in polycrystalline samples of 99.55 % purity using the residual activity technique in a high temperature range 1773-2273 K. *D* values are more than one order of magnitude higher than the self-diffusion ones. Extrapolation to the lower temperatures measured for self-diffusion increases this difference to almost 3 orders of magnitude.

Besides, the *Q* = 321.5 kJ/mol obtained seems too low for a diffusion assisted by vacancy mechanism, since ΔH^F_V in Nb is between 290 [37] and 350 kJ/mol [38], according to experimental measurements. Fedorov *et al.* in page 78 of ref. [17] claim that such a low *Q* value is a common issue in body-centered cubic metals "that may be easily explained if it is considered that the impurity atoms significantly deform the lattice of the base metal" (sic).

The second work [16] studies U diffusion in a narrower: 1993-2373 K, but close, temperature range than the previous one, by means of the there called "layer-removal method" without any further specification. A similar $Q = 321.1$ kJ/mol was found, but with $D_0 = 5 \times 10^{-10}$ m^2/s 4 orders of magnitude lower than the 8.6×10^{-6} m^2/s reported in [15] which is reflected in Fig. 4, where D values are more than 3 orders of magnitude lower than those from self-diffusion, In both cases we do not have access to the original Russian papers but to the English translation [16, 17]; such a difference is hard to explain.

Recently, using α-spectrometry, U diffusion in Nb in 1533-1673 K (1260-1400ºC) temperature range was measured [36]. Arrhenius law is obeyed with parameters are very close to the self-diffusion ones; $Q = 423 \pm 10$ kJ/mol and $D_0 = (2.5 \pm 1) \times 10^{-4}$ m^2/s. Q is higher than ΔH^F_V in bcc Nb, therefore the diffusion process is compatible with substitutional diffusion without the need of any significant deformation of the Nb lattice by U. Besides, D values for U are sligthly lower than the self-diffusion ones (squares in Fig. 4), which is the standard behaviour for substitutional heavier elements diffusing in a ligther matrix.

Given the large grain size (of few mm) of the Nb samples used in [36] (see Fig.1 there) and the sub-micrometer range of the analyzed depth, all short circuits contributions can be neglected. On the other hand, even when the grain size of samples was not reported in [15], it is very likely that their D values were convoluted with diffusion along short circuits explaining both, the low activation enthalpy and the high D values. As we will see, this behaviour is a common issue in other metals measurements.

U diffusion in Mo was also presented in the English translation of the Russian works [15] and [16] and it has the same qualitative behaviour than Nb: lower Q than the Mo self-diffusion [36,39] (488 kJ/mol) and even lower than ΔH^F_V (between 289-347 kJ/mol [3]), similar Q values between both measurements (319.9 and 31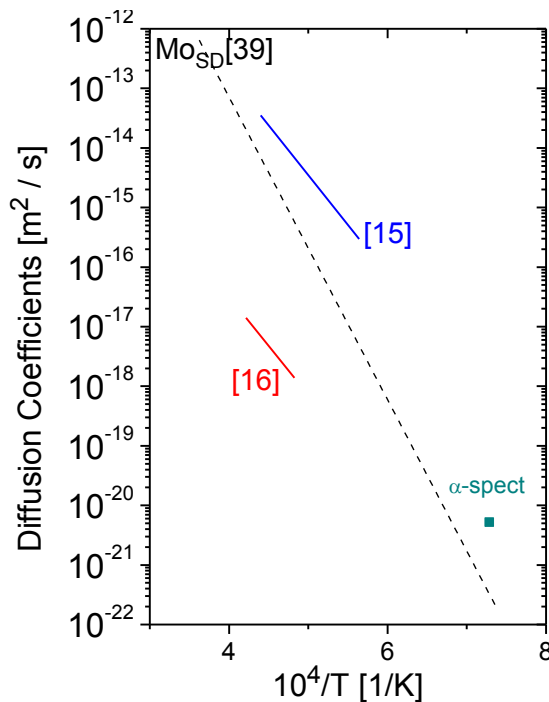6.5 kJ/mol respectively) but around 4 orders of magnitude difference between D_0 values and consequently between U diffusion coefficients measured in almost the same temperature range.

Figure 5: U diffusion in Mo. Mo$_{SD}$ dashed line

Presented here for the first time, in order to check which is the most reliable measurement, only one measurement at 1373 K annealed 40 days was made using α-spectrometry for U diffusion in Mo. The Mo sample has a small grain size (around 10 μm) and 99.9 % purity, with an impurity content listed in Table 3, as provided by Goodfellow metals.

A spectrum with a large low energy tail was obtained, indicating that diffusion via short circuits happens at the same time that the bulk diffusion. The obtained value for this effective diffusion coefficient (5.4×10^{-21} m^2/s) is shown in Fig. 5 as a single square. It is more than 1 order of magnitude higher than self-diffusion at the same temperature due to the grain boundary diffusion contribution; probably, measurements in samples with a larger grain size would be closer to self-diffusion, which is work in progress.

Table 3: Mo impurities content [μg/g]														
Al	Ca	Cr	Cu	Fe	K	Mg	Pb	Si	Ti	W	C	H	N	O
<20	<20	<50	<20	50	<2	<20	<30	<50	<30	10	40	5	10	30

U diffusion in α-Ti

Diffusion in the low temperature α-phase of Ti is a test case for our current approach to the study of U diffusion in nuclear materials, since our laboratory has a large body of work on this metal matrix. Due to the α/β phase transition it is not possible to extrapolate D values from measurements at high temperatures; as $T_{\alpha/\beta} = 1155$ K equals $0.68T_{m\alpha}$ (the hypothetical melting temperature of the α-phase) D values below 10^{-17} m²/s are expected for substitutional diffusers, thus depth profiles of at most a few μm are achievable for reasonable annealing times (10^7 s ≈ 4 months). Studies in an extended temperature range in α-Ti require a sub-micrometric analysis technique; direct sectioning, residual activity, and other techniques needing diffusion profiles of several tens of a μm depth can only be applied at temperatures close to $T_{\alpha/\beta}$ and their results must be carefully analysed, as we show further on.
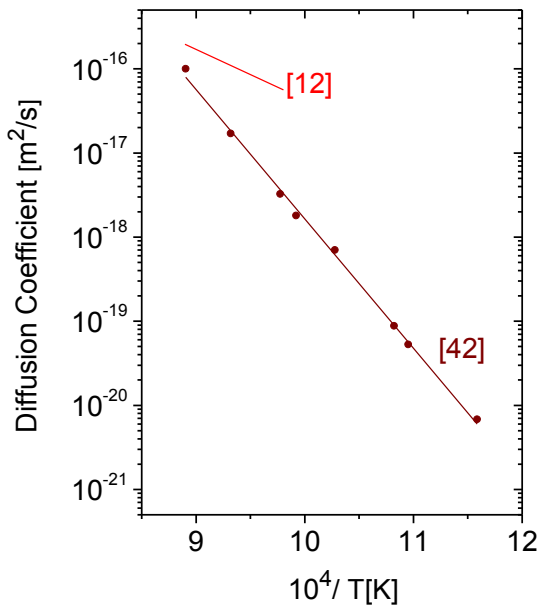

Figure 6: U Diffusion in α-Ti

An attempt to measure U diffusion in α-Ti was made in [12] unfortunately neither the method used, nor the characterization of the α-Ti samples is provided in the English translation of that work. Measurements were performed in a narrow temperature range, 1020-1124 K (747-851ºC), Q=114 kJ/mol was reported, lower than $\Delta H^F{}_V$ in α-Ti (between 150 kJ/mol [24] and 200 kJ/mol [25, 26]), and D values are from 1 to 2 orders of magnitude higher than the self-diffusion measured in low purity α-Ti [40] and from 2 to 3 orders of magnitude higher than for the purest α-Ti [41]. As a matter of fact Q for U diffusion from [12] is almost one third of $Q = (303 \pm 2)$ kJ/mol for self-diffusion [41].

In our new measurements using α-spectrometry [42], a normal Arrhenius plot is obtained, as shown in Fig. 6. A larger temperature range, 863 to 1123 K (540 to 850ºC) than previous works was studied, obtaining Q=(297±20) kJ/mol, $D_0 = (5±2)×10^{-3}$ m²/s similar to the self-diffusion ones measured in the purest α-Ti samples [41], the same material used in [42]. Also D values for U diffusion are of the same order of magnitude than the self-diffusion in the whole temperature range, as expected for a substitutional diffuser in a metal matrix.

As we pointed out, α-Ti is an interesting case since a similar evolution in time for the measurements can be observed analysing the self-diffusion data in the literature. They go from low Q and D_0 values and large diffusion coefficients, when measured using direct sectioning [43] in a short temperature range, to lower D values and higher diffusion parameters when sub-micrometric IBS (Ion Beam Sputtering) technique is used [40], and the impurity content is reduced [41], as can be seen in Fig. 7.

It is well known that in α-Ti even a few tens ppm of ultra-fast impurities, such as Fe, Co, and Ni, also increase D values and decrease Q and D_0 parameters (see for instance [41], [44]). Therefore the amount of ultra-fast impurities, in particular Fe; ranging from 50 μgr/gr in [40] to 2 μgr/gr in [41], must be kept in mind during the analysis.

Figure 7: α-Ti Self-Diffusion

Early data [43] obtained with direct sectioning, requires to analyze depths of several tens of μm. This work reports the amount of impurities (30 μgr/gr of Fe), the annealing times and the diffusion profiles. Let's take the case in which the sample was annealed at 1013 K during 2619900 s: The average diffusion path is given by $(4Dt)^{1/2}$, if we use $D(1023\ K)$ coming from [41] instead of the corresponding from [43] to this path, it amounts to around 0.8 μm, if instead we use $D(1023\ K)$ from [40] $(4Dt)^{1/2} \approx 2.5$ μm; the difference comes from the different Fe content in the samples since both measurements were performed in the same laboratory with the same IBS technique. The amount of Fe present in [43] was 30 μgr/gr, so the depth corresponding to bulk diffusion must be somewhere in between. Being each sectioning chip no thinner than 2 μm, it means that after the first or second diffusion profile points, most o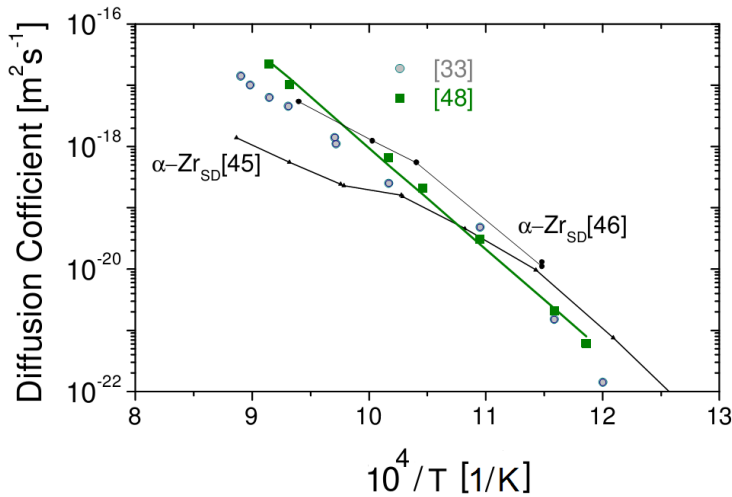f the bulk contribution was consumed and, consequently, the effect of short circuits become dominant. As a matter of fact, large tails in the diffusion profiles are observed and reported in [43], so those values correspond to an effective diffusion coefficient combining the effect of ultra-fast impurities content and short circuits on the self-diffusion of α-Ti, not to the actual bulk self-diffusion at infinite dilution given in [41].

Even though the impurity content is not reported in [12], α-Ti samples with 2 μgr/gr of Fe were not commercially available until the 1990s; comparing Fig. 6 and Fig. 7 it is straightforward to observe that the differences for U diffusion between [12] and [42] are quite similar to those found for α-Ti self-diffusion. Consequently the data measured in [12] corresponds to effective diffusion coefficients rather than to the actual bulk U diffusion, indeed reported in [42].

U diffusion in W is also interesting to analyze. In the English translation [17] of [20] Table 34 page 79, the effect of W grain size on U diffusion parameters is reported. For grain size between 75-170 μm: $Q = 282.1$ kJ/mol, $D_0 = 3.6 \times 10^{-8}$ m^2/s; for grain size 8000 μm: $Q = 342.5$ kJ/mol, $D_0 = 2.4 \times 10^{-7}$ m^2/s, and for single crystal $Q = 376.8$ kJ/mol and $D_0 = 1.8 \times 10^{-6}$ m^2/s.

Further on the same ref.[17], it is claimed that the rather large dispersion among the data for W reported here in Table 1, Q between 256 kJ/mol and 433 kJ/mol and D_0 between 10^{-6} and 10^{-8} m^2/s should be attributed to different experimental methods, different base metal purities, etc. In other words, the hypothesis here sustained that some of the early works report effective diffusion coefficients rather than bulk U diffusion at infinite dilution in those metals, is suggested even in those early works, when carefully examined. Unfortunately no new measurements using α-spectrometry in well characterized W samples are available yet.

U diffusion in α-Zr and Zircalloy-4 (Zry-4)

U diffusion in α-Zr was recently measured using α-spectrometry technique [33], no previous data were reported in the low temperature hcp phase of Zr. As in the case of α-Ti the α/β phase transition does not let to extrapolate D values from measurements at high temperatures; being $T_{\alpha/\beta} = 1136$ K $(0.62T_{m\alpha})$ also D values must be equal or below 10^{-17} m^2/s, then conventional techniques require very large annealing times in order to achieve suitable depth profiles.

Also, as in the case of α-Ti, the presence of few tens of ppm of ultra-fast impurities, in particular Fe, increases diffusion coefficients significantly. Both metals are in the same column of the periodic table and share an electronic structure combining unpaired d and s valence electrons and several thermodynamic properties. Nevertheless, whereas self and substitutional diffusion in α-Ti follows

Figure 8: U diffusion in α-Zr and Zry-4

the Arrhenius law, when both are studied in α-Zr for a large enough temperature range, the Arrhenius law is not obeyed; a downward curvature, that also can be interpreted as a break around 1000 K, is observed (see [44] and references therein).

As shown in Fig. 8, U diffusion was not the exception. A break can be observed at around 1000 K not so strong as for the α-Zr self-diffusion measured in [45] using samples with lower amount of Fe (20 μgr/gr), but similar to self-diffusion data from [46], measured in samples with 160 μgr/gr, almost the same Fe content as in [33].

Again, when α-spectrometry is used and sub-micrometric depth profiles are measured in polycrystalline samples with grain sizes several orders of magnitude larger than the depth, and low and well identified amount of impurities, there are no significant differences between self and U diffusion in the base metal.

Regarding the non-Arrhenius behaviour, it is a common observation when diffusion is measured in α-Zr for a large enough temperature range (from $T_{\alpha/\beta}$ down to at least 873 K) and the key in order to understand this outcome seems to be the presence of the ultra-fast impurity Fe. Theoretical work establishing the existence of a complex vacancy-Fe mechanism with lower formation enthalpy than the vacancy, together with migration enthalpy lower than the simple atomic jump to a vacancy was reported in [47], suggesting an explanation to the enhancement of the D values due to the Fe presence. Furthermore a possible explanation for non Arrhenius behaviour for ultra-fast impurity diffusion was recently given in [26] based on *ab initio* calculations. Diffusion behaviour of ultra-fast diffusers: Fe, Co and Ni in both α-Ti and α-Zr matrices were modelled. The migrating species may adopt any of three states: (1) a highly mobile interstitial, (2) (relatively) immobile quasi-substitutional and (3) (relatively) immobile trapped at impurities dumbbell configuration. A dissociative mechanism was postulated and so the explanation for the differences between both matrices relies on the relationship among binding energies of these states in each matrix. Extrapolation to U diffusion in is not straightforward but the experimental results in [33] and [42] point into that direction.

No diffusion parameters were assigned to U diffusion in α-Zr even when sometimes, in the literature, Q values are assigned to non-Arrhenius systems from the slope of the Arrhenius curve at a given temperature. This procedure is not always correct. The slope of the Arrhenius curve is defined as the derivative of D/D_0 with respect to $1/T$ which is directly $-Q$/K for well behaved Arrhenius systems, but when Q depends on temperature $Q = Q(T)$ the slope has an additional term which includes the derivative of $Q(T)$ with respect to $1/T$ that can be positive or negative. Thus a higher slope at low temperature than close to $T_{\alpha/\beta}$, as in the case of U diffusion in α-Zr, not necessarily implies higher Q values at those low temperatures (see e.g. [33] for the case of diffusion in ferromagnetic α-Fe).

U diffusion in Zry-4: was also studied [48]. Samples of Zry-4 were annealed together with pure α-Zr in order to avoid systematic measurement errors when comparing. The results are also shown in Fig. 8; they are consistently higher than for U diffusion in pure α-Zr, but within the same order of magnitude.

Zry-4 is an alloy that for all practical purposes can be considered as monophasic; even when small precipitates are present at equilibrium, they are a minor proportion of the total volume and tend to be in grain boundaries and/or dislocations.

The moderate increase in D values can be partially ascribed to the smaller grain size of Zry-4 (few tens of μm) with respect to pure α-Zr (several tens of mm); nevertheless being the diffusion depth profiles measured in [48] one order of magnitude lower, between 0.6 and 1.8 μm, this effect should not be very significant.

On the other hand, ultra-fast impurities are present in Zry-4 in higher amounts, 32 μgr/gr of Ni and 2100 μgr/gr (0.21 wt%) of Fe. The increment of D must be related to this higher amount of ultra-fast impurities, even when such an effect is non-linear and probably has a saturation point, presumably reached in the experiment.

Remarkable is the qualitative difference between both matrices, U diffusion in Zry-4 obeys the Arrhenius law nicely, Fig. 8, with Q = (319 ± 9) kJ/mol and D_0 = (3.2±1.1)×10^{-2} m^2/s, normal values for a metallic alloy. The supersaturation of Fe together with the presence of other alloying elements constituent of Zry-4 might be anchoring the vacancy-Fe complex partially responsible for the diffusion in pure α-Zr, even at temperatures close to $T_{\alpha/\beta}$, only one diffusion mechanism seems to be operative.

Another interesting fact informed in [48] is that the alloying elements in Zry-4 diminish the U solubility, which is reflected in the complementary error function used to fit diffusion profiles below 763 K, presenting surface U retention.

U self-diffusion

It is interesting to revisit the early works where U self-diffusion was measured, in particular the ones by Adda *et al* in all 3 phases: the bcc γ-phase of high temperature (1048-1407 K) [4], in the tetragonal β-phase (941-1048 K) [6], and the orthorhombic α-phase (below 941 K) [8].

In [4] one finds a careful description of the techniques used at the time. Samples are well characterized and diffusion along grain boundaries and surface are avoided in the experiment, nonetheless a low Q = 115.1 kJ/mol is obtained. Also the authors made a plot of Q vs T_m for self-diffusion in metals, with the data available at that time, obtaining a linear behaviour from which γ-U self diffusion Q value drops strongly; Adda *et al* estimate that this activation enthalpy must be between 230 kJ/mol and 250 kJ/mol in order to be in line with the other metals. They relate this "anomaly" of U with elastic characteristics of the γ-phase.

Measurements were made in diffusion couples of natural U and U enriched at 20 %. After diffusion anneals they cut chips parallel to the interface and count α particles emitted by the remaining sample. Being both, matrix and diffuser, α emitters, they get a convolution of signals. The deconvolution of these signals was made by simple rule of three, disregarding the dependence of the stopping power on the energy (unknown at that time) and the differences in energy among U isotopes (about 0.5 MeV between ^{238}U, 4.267 MeV, the main emitter of the matrix, and ^{234}U, 4.77 MeV, the main source of α particles coming from the diffuser). This simplification entails an uncertainty that can not be easily estimated without having access to the original spectra. All the data listed in Table 1 for U self-diffusion compiled in handbooks [1] and [2] were measured in the same way. There are other measurements applying more uncertain techniques, such as [49] using the decrease in surface activity method, that were ignored in the handbooks and we are not going to analyse them here.

Since then the idea of U anomaly was established up to current days. Recently [35], ΔH^F_V in depleted U was measured by means of positron annihilation (PAS) in the orthorhombic α-phase. They found a strong dependence in the values upon the O content of the U samples, ranging from 55 kJ/mol (0.55±0.02 eV) in oxidize samples, to 155 kJ/mol (1.6±0.2 eV) after O removal by heating the samples three times at 1200 K; the successive increases in ΔH^F_V were observed after each heat treatment. The authors claim that this 155 kJ/mol is a lower limit to ΔH^F_V since complete removal of O was not achieved. Ab-intio VASP calculations were also presented in this work, 191 kJ/mol (1.98 eV) was obtained for pure U, 164 kJ/mol (1.7 eV) for a vacancy near neighbour to a substitutional O and 77 kJ/mol (0.8 eV) for an interstitial O.

They also measured by PAS the migration enthalpy of O in α-U, ΔH_m = 58 kJ/mol (0.6±0.1 eV) that can be considered as a lower limit to the migration enthalpy for U. According to those values we expect Q for α-U self-diffusion no lower than 250 kJ/mol, in contrast to 167.5 reported in [8], if the usual vacancy mechanism for self-diffusion is considered.

Also recently [50] an EAM (embedded-atom model) was used to deal with self-diffusion in γ-U (and γU-Mo), the authors propose a self-interstitial mechanism as responsible for the low Q measured in [4].

Those works are just examples on how present this topic is nowadays. Irrespective of those low Q values being the effect of uncertainties in the measurements, result of O presence, or a self-interstitial mechanism, new measurements of U self-diffusion in any of its phases would be interesting work. The combination of α-spectrometry with other nuclear techniques could be the proper tool to accomplish such a task.

Finally let's remark that in [4] Adda reports a try made in order to get ^{235}U diffusion profiles trough the measurement of the trace density left in an autoradiography by the γ activity of fission products after the samples were neutron irradiated. The technique was discarded since he could not achieve reproducible results. This attracted the attention on measurements made with the technique, such as the U self-diffusion in [5], or the only measurement reported for U diffusion in γ-Fe [10], etc.

U diffusion in other metals compared with self-diffusion

For the other early measurements listed in Table 1 no new data using α-spectrometry is available. In Fig. 9 to Fig. 11 a comparison between U and self-diffusion in each material base is shown; despite some elements having several self-diffusion measurements, we take the newest available in the literature and/or an average of them, (for bcc metals the re-assessment performed by Newman [34] is taken).
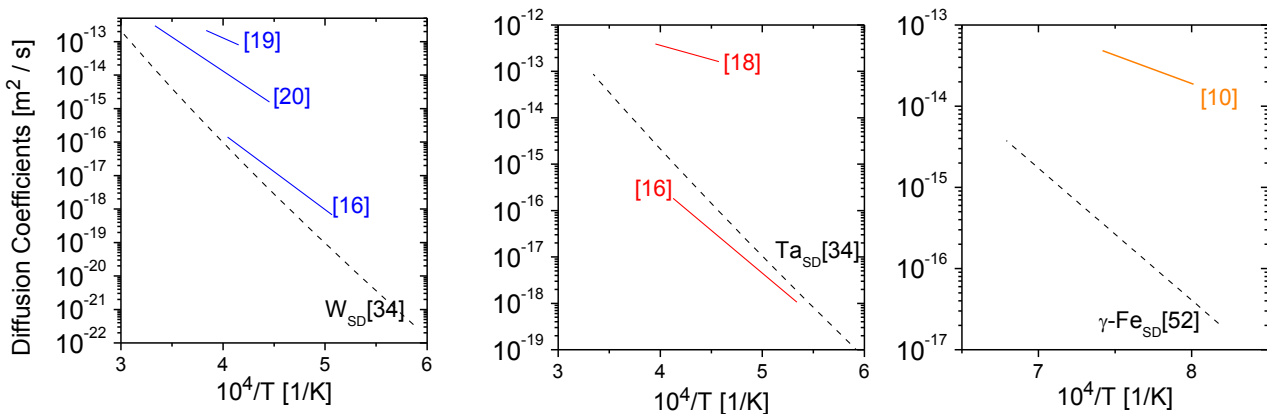

Figure 9: U diffusion in W. W_{SD} dashed line.   b) U diffusion in Ta. Ta_{SD} dashed line   c) U diffusion in γ-Fe. SD in dashed line

Ta and W present a similar behaviour than Nb and Mo already discussed: lower Q values than the self-diffusion [34] and differences in D of around 4 orders of magnitude between [16] and [18]. On the other hand, in both matrices Q values for U diffusion are also lower than ΔH^F_V. In any case new measurements with sub-micrometric techniques, in order to clarify these results and extending the data to the low temperatures regime, are highly desirable.

There is only one measurement of U diffusion in γ-Fe [10] in which Q is also lower than self-diffusion and ΔH^F_V, with D values several orders of magnitude higher than γ-Fe self diffusion ones [51-52], besides the technique used, fission fragment radiography, is the one which Adda found no reproducible [4]. All those elements: Nb, Mo, Ta, W and γ-Fe have at least one measurement with those characteristics; this behaviour is the same observed in the α-Ti matrix, so the possible influence of short circuits and/or impurities must not be disregarded.

In other group, Mg and V show Q values lower than self-diffusion, but higher than $\Delta H^F{}_V$, being uranium D values around 4 orders of magnitude lower than the self-diffusion ones for Mg [53] and around 2 orders for V [34].
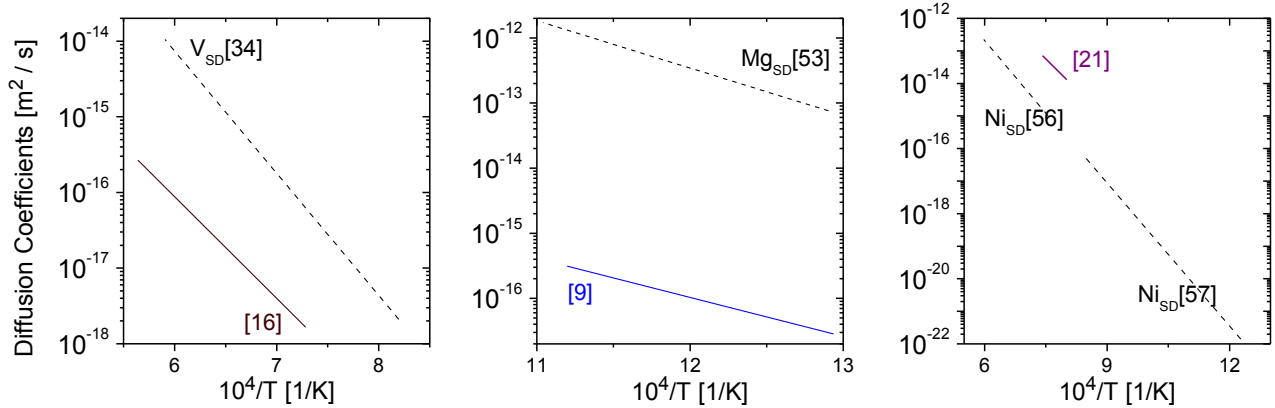

Figure 10: U diffusion in V. V_{SD} dashed line   b) U diffusion in Mg. Mg_{SD} dashed line   c) U diffusion in Ni. Ni_{SD} dashed line.

Self diffusion in β-Zr [54] and β-Ti [55] has curved Arrhenius plots due to Q dependence on temperature as shown in Fig. 11 a) and b). This dependence is originated in the phonon softening of the mode $LA_{2/3}$ <111>, an intrinsic characteristic of bcc structures that diminish the energy required to move a vacancy when the temperature goes down until it reaches $T_{\alpha/\beta}$. U diffusion in both matrices has one measurement in which the curvature is also observed for β-Zr [14] and for β-Ti [12], in both cases those measurements can be described as the expected behaviour for a substitutional diffuser in a metallic matrix. Although measurements by means of residual activity [13, 11] and fragment fission radiographies [10] give origin to higher D values, the curvature was not observed.
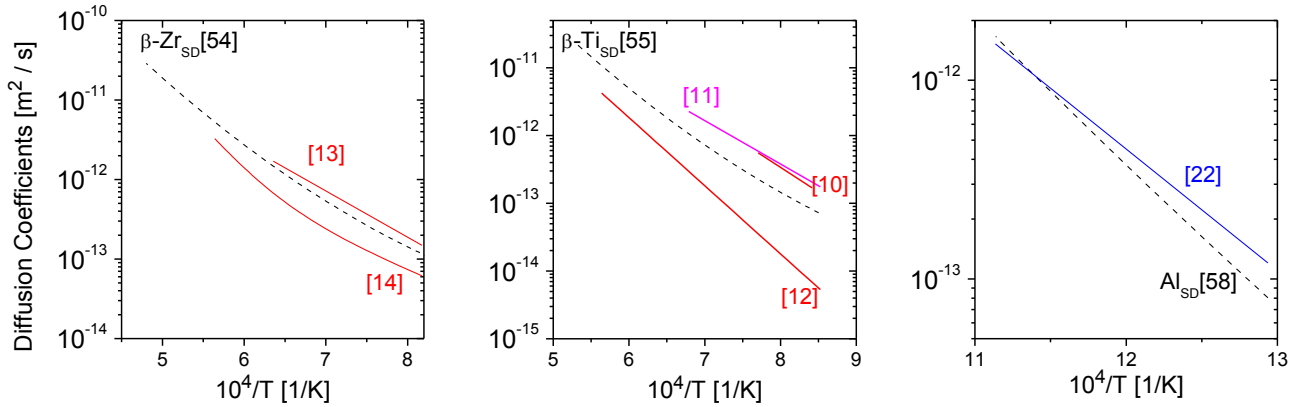

Figure 11: U diffusion in β-Zr. SD dashed line   b) U diffusion in β-Ti. SD dashed line   c) U diffusion in Al. Al_{SD} dashed line

Ni is an intermediate case. When compared with Ni self-diffusion [56, 57], U diffusion [21] measured in a short temperature range, is only 1 order of magnitude larger; besides activation enthalpies are congruent, 278 and 236.1 kJ/mol respectively, both higher than $\Delta H^F{}_V$ = 172 kJ/mol [3] for Ni. This behaviour is compatible with U being a substitutional diffuser.

Finally, for Al U and self-diffusion [58] data are in the same order of magnitude, like the data achieved by means of α-spectrometry in α-Ti, α-Zr and Nb that can be called the "normal" behaviour for U diffusion, being Q = 117.2 kJ/mol higher than $\Delta H^F{}_V$ = 64-74 kJ/mol [3] for pure Al.

In Fig. 12 log[D] vs [T_m/T] ($T_{m\alpha}$ was used for α-Ti and α-Zr) is shown for all new measurements with α-spectrometry together with Al and Ni, the only early works where U fulfil the semi-empirical rules to qualify as substitutional diffuser in the base material. Even though the number of element is not so high (6), the homogeneity among U diffusion in these metals is noticeable when compared to the large dispersion observed in Fig. 1.
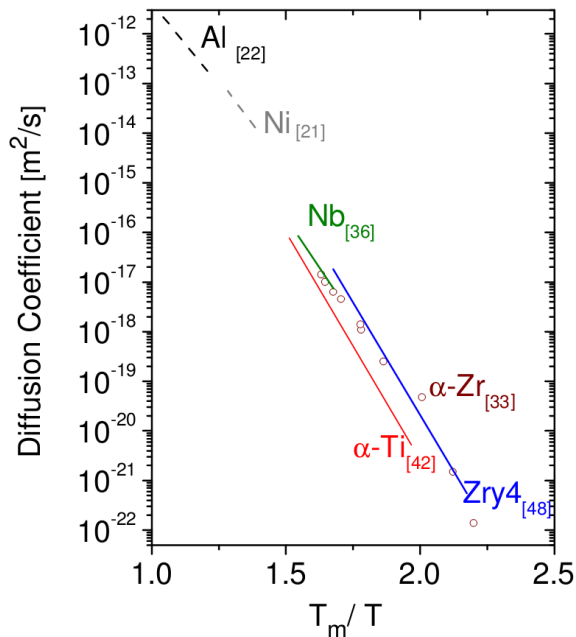
Figure 12: α-spectrometry data

Summary

New data for U diffusion at infinite dilution in metals measured with a sub-micrometric technique, the α-spectrometry, were compared with early works compiled in Diffusion Handbooks [1] and [2].

α-spectrometry reveals as a suitable technique in order to extend the range of measurements to lower temperatures, together with the ability to avoid the effect of short circuits and boundaries on diffusion, if samples of large enough grain size (at least 2 orders of magnitude larger than $\sqrt{4Dt}$) are used in the experiments.

α-spectrometry measurements in α-Ti, α-Zr, Zry-4 and Nb have a similar behaviour than self-diffusion in the material base, D values are within one order of magnitude with similar Q and D_0 diffusion parameters, when available. U substitutional diffusion via vacancy mechanism is compatible with those data.

A significant part of the early data seems to be affected by short circuits, boundaries and/or impurities probably due to the characteristics of the experimental techniques used.

Attention is called upon data in which Q for U diffusion is lower than for self-diffusion and ΔH^F_V of the base material.

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