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Diffusion of Sn in different purity α-Ti

R.A. Pérez[a], F. Dyment[a,*], M. Behar[b]

[a] Departamento de Materiales, Comisión Nacional de Energía Atómica, Av. del Libertador 8250, 1429 Buenos Aires, Argentina
[b] Instituto de Fisica, Universidad Federal de Río Grande do Sul, Av. Bento Gonçalvez 9500, 91501-970 P. Alegre, Brazil

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Abstract

The diffusion of Sn in the hcp (α) phase of high purity (99.99%) and pure (99.9%) Ti was studied at different temperatures from 873 up to 1100 K. The Rutherford Backscattering Spectrometry (RBS) technique was used to obtain the penetration profiles. The evolution of the diffusion coefficient, D, as a function of temperature follows the prediction of the Arrhenius law. No significant difference between both kinds of Ti samples was observed. Normal diffusion parameters, Q and D_0, close to the self-diffusion ones were obtained.

Keywords: Diffusion; Ti; Sn; RBS; hcp Metals; Ultra-fast diffusion; Enhanced diffusion

1. Introduction

Ti belongs to the IV-B group of the periodic table together with Zr and Hf. All the elements of the IV-B group crystallize in an hcp (α) structure at low temperatures and change to a bcc (β) one at high temperatures. Despite the widespread use of α-Ti and α-Zr in the industry, most of the diffusion studies were initially done in their β-phase. A pronounced curvature was observed in all the Arrhenius plots and this curvature is also observed in other bcc metals. This behavior is considered as an intrinsic property, product of a phonon softening previous to the α/β phase transition (for a wide explanation, see Ref. [1]).

Measurements in an extended temperature range in α-Ti and α-Zr were performed only in the last 15 years, applying techniques that allow the determination of diffusion coefficients below 10^{-17} m^2 s^{-1}. The use of ion beam techniques like Rutherford Backscattering Spectrometry (RBS) and Heavy Ion RBS has allowed the present authors to perform in the last years a systematic study on diffusion of substitutional elements in matrices of the IV B group (for Refs. [2,3]). Self-diffusion in an extended temperature range in low pure α-Ti was measured by Herzig et al. [4]. They also studied the self-diffusion in high purity Ti, together with In, Ga and Al hetero-diffusion in the same material [5].

Some peculiarities in these matrices were observed: α-Zr self-diffusion [6] shows a downward curvature; the hetero-diffusion of the very few substitutional impurities studied in α-Zr follow this curvature, some 3d transition elements (particularly Fe, Co and Ni) are ultra-fast diffusers in both, α-Zr and α-Ti, and in α-Zr, Fe [7] and Co [8] also show downward curvatures.

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* Corresponding author. Fax: +54-11-6772-7362.
E-mail address: dyment@cnea.gov.ar (F. Dyment).

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Essentially two models [9,10] were proposed to explain the behavior described above. Both used a rapid pair formed by a vacancy and a Fe atom in solution as the responsible defect for the enhancement. For a detailed analysis and criticism of these models, see Ref. [11].

In α-Ti an enhancement was observed in the self-diffusion case [4,5], and also in the Al [5] and Ta [12] hetero-diffusion, when matrices with different amount of ultra-fast impurities were used. However, the characteristics of this behavior are different to that observed in α-Zr matrix [3].

This work is a part of a systematic study of the present authors; they had previously performed measurements of diffusion of Sn in less pure α-Ti [13] with the same RBS technique. In the present work the diffusion of Sn in high purity α-Ti was measured together with samples of less pure Ti (the same is used in Ref. [13]) in order to compare them under the same experimental conditions to see if the enhancement observed for self-diffusion and Al and Ta diffusion in α-Ti also proceeds in this case or if the previous result is maintained.

2. Experimental procedure

The measurements were performed on discs of Ti of about 9 mm in diameter and 3 mm thickness, with two different degrees of purity: the high purity one (99.99%) and the less pure-type (99.9%). For a complete list of the impurity content, see Table 1.

Table 1
Impurity content of the Ti samples

Element	Content (μg/g)	
	lp	hp
Ag	< 10	
Al	< 50	< 5
Co	< 10	
Cu	< 30	< 3
Fe	< 150	< 4
K	< 10	
Li	< 10	
Mg	< 10	
Mn	< 10	
Mo	< 10	
Na	< 10	
Ni	< 50	< 0.2
Pb	< 20	< 0.2
Si	< 50	< 0.3
Ta	< 10	
Zr	< 10	
O	< 800	< 300
N	< 35	< 12

hp: high purity Ti. lp: less pure Ti.

The samples were mechanically polished and subjected to three annealing cycles of 1 h at 1473 K followed by 10 days at 1133 K in an argon atmosphere. This procedure led to samples with at most three to four large grains. Subsequently the samples were mechanically and chemically polished again in order to obtain very flat surfaces. After that a new annealing treatment for 1 day at 1123 K was done in order to remove the stress originated in this process.

Sn was implanted in the specimens using a 400 kV ion implanter. The implantation energy was 50 keV and the implanted fluency was 5×10^{15} atoms cm^{-2}. The corresponding initial Sn peak concentration before the diffusion annealings was 4 at.%.

The diffusion annealings were performed in sealed quartz tubes under high purity argon. To prevent reactions between Ti and quartz, the samples were wrapped into Ta foils. The diffusion temperatures were controlled within ± 1 K. Corrections for heat-up and cooling times were made whenever the total annealing time was less than 7200 s.

Quantitative RBS analysis was performed with 3 MeV He^+ ions of the Tandetrom accelerator of the Instituto de Fisica, Universidad Federal de Rio Grande do Sul, (IF-UFRGS), Porto Alegre, Brazil, on all the “as coated” specimens and after the diffusion anneals. The backscattered particles were energy analyzed with Si surface-barrier detectors at a scattering angle of 170°. The measured energy spectra were evaluated to yield diffusion profiles using a specially developed computer program. More details of this program and its successful application in previous studies are contained in Ref. [14].

3. Results

The diffusion coefficient of Sn in high purity α-Ti was measured at six temperatures in the range of 873–1100 K, and at three temperatures, in the samples of less pure α-Ti. The experimental diffusion

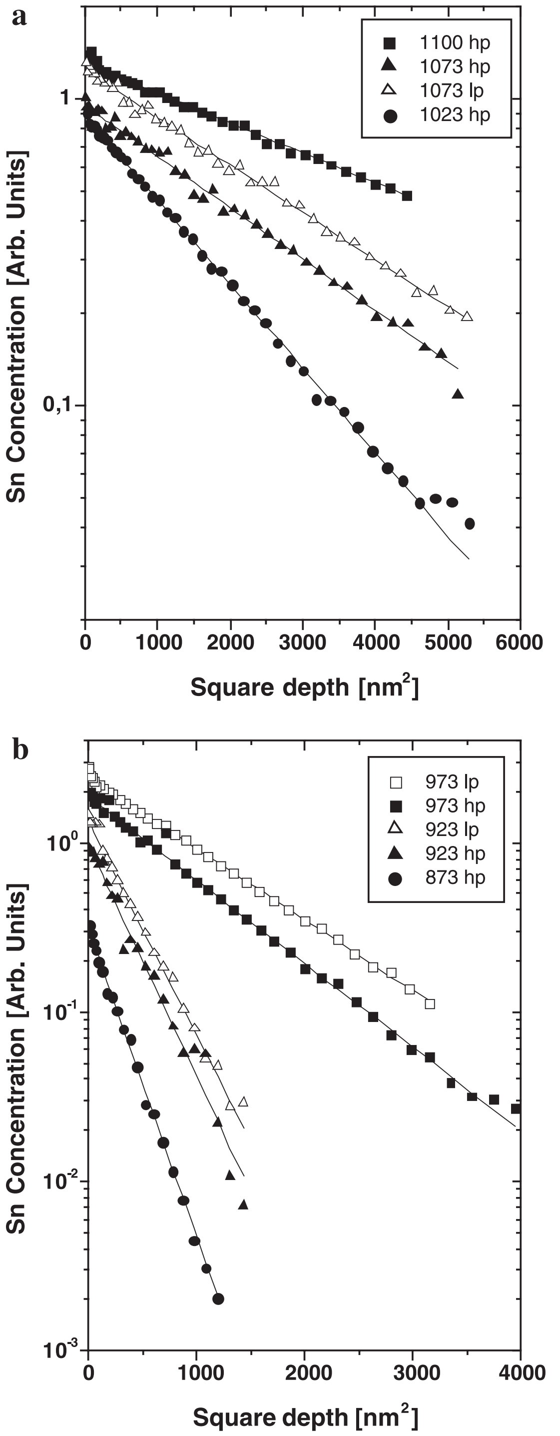

Fig. 1. Diffusion profiles of the measurements shown in Table 2. lp means less pure samples (open symbols) and hp means high purity material (close symbols).

Table 2
Diffusion coefficients of Sn in α-Ti

Temperature (K)	Time (10^4 s)	D ($m^2\ s^{-1}$)	
		High pure	Less pure
1100	0.36	$(3.1 \pm 0.6) \times 10^{-19}$	–
1073	0.54	$(1.2 \pm 0.2) \times 10^{-19}$	$(1.3 \pm 0.2) \times 10^{-19}$
1023	1.8	$(2.2 \pm 0.2) \times 10^{-20}$	–
973	12.96	$(1.7 \pm 0.3) \times 10^{-21}$	$(2.0 \pm 0.3) \times 10^{-21}$
923	34.56	$(2.3 \pm 0.4) \times 10^{-22}$	$(2.5 \pm 0.5) \times 10^{-22}$
873	259	$(2.3 \pm 0.4) \times 10^{-23}$	–

conditions correspond to an infinitely thin source diffusing into a semi-infinite sample; the penetration profiles obtained conform well to the thin film solution of the diffusion equation:

$$C(x,t) = \frac{M}{\sqrt{\pi D t}} \exp\left(\frac{-x^2}{4Dt}\right) \tag{1}$$

where $C(x,t)$ is the Sn concentration at depth x, after a diffusion annealing time t; D is the diffusion coefficient of Sn in α-Ti and M is the initial amount of Sn implanted in the samples. The measured penetration profiles are shown in Fig. 1. The individual D values are mainly affected by two sources of uncertainties: (a) the statistical nature of the collected RBS data and (b) the reported uncertainties in the stopping power of the alpha particles. We estimate the total error around 20%.

The final results of the diffusion coefficients for both α-Ti samples, with different purity, are listed in Table 2 and, as a function of the temperature, shown in Fig. 2. As can be observed the diffusion coefficients obtained for the high purity α-Ti follows the Arrhenius law fitted by:

$$D(T) = (4 \pm 2) \times 10^{-3} \exp\left(\frac{-(340 \pm 10)\ \mathrm{kJ/mol}}{kT}\right)\ \mathrm{m^2\ s^{-1}} \tag{2}$$

The full line in Fig. 2 corresponds to a least square fit using only data of high purity samples, the same that were used to obtain the values of Eq. (2). The

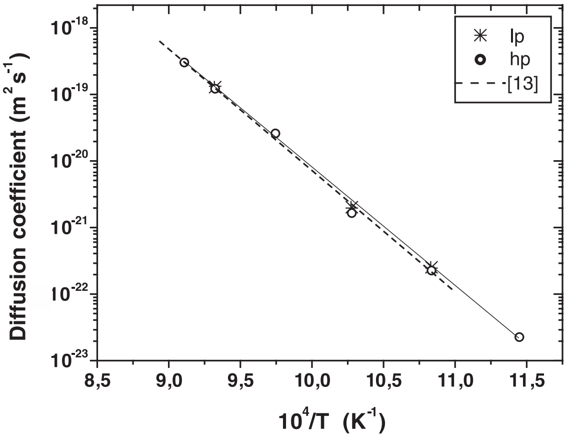

Fig. 2. Arrhenius plots. Circles: Sn diffusion in high purity α-Ti. Full line: least squares fit. Cross symbol: Sn diffusion in less pure α-Ti. Dashed line: Arrhenius line obtained in Ref. [13].

dashed line corresponds to the previous measurements in less pure Ti samples [13].

4. Discussion

Comparing the diffusion coefficients measured in both kinds of samples in all the three temperatures almost the same values were obtained inside the experimental error. This behavior is different to the one observed in α-Ti self-diffusion [5], Al [5] and Ta [12] diffusion in α-Ti, where an enhancement in the diffusion process was observed.

This lack of enhancement is reinforced when we compare the previous results for Sn diffusion in less pure α-Ti [13] (dashed line in Fig. 2), with the present ones performed in high purity α-Ti (full line). The two lines almost superpose.

On the other hand, measurements in the so-called commercial samples of Ti (samples with a high impurity content, in particular 0.05 at.% of Fe) were also performed [13]. With this amount of Fe, above its limit of solubility in α-Ti [15], the enhancement proceeds with the characteristics observed in the other substitutional diffusers, i.e.:

- lower Q and D_0 values than the corresponding to the purest samples (see Table 3);
- the higher enhancement corresponds to the lower temperature.

When the diffusion of Zr [16], Hf [17,18], Au [19], Pb [20], In [21] and Sn [13] in less pure α-Ti was studied, the Arrhenius law was always obeyed, but some scatter was observed among the diffusion parameters (see Table 3). This scatter is reflected by the cross-link among the different lines in Fig. 2 in Ref. [2].

On the other hand, when the diffusion studies were performed in high purity α-Ti, a more regular behaviour was observed, as reflected in the diffusion parameters shown in Table 3. All the activation enthalpies, Q, lie between 295 and 340 kJ/mol and the pre-exponential factors, D_0, are of the order of magnitude of 10^{-3} m^2 s^{-1}.

Let us now note that the diffusion parameters obtained for Sn diffusion in less pure α-Ti [13]: $Q = 338$ kJ/mol and $D_0 = 4 \times 10^{-3}$ m^2 s^{-1}, align

Table 3
Diffusion parameters for substitutional elements in α-Ti

Diffuser	Reference	Less Pure Ti		High purity Ti	
		Q (kJ mol^{-1})	D_0 (10^{-3} m^2 s^{-1})	Q (kJ mol^{-1})	D_0 (10^{-3} m^2 s^{-1})
Self-diffusion	[4,5]	193	1.7×10^{-5}	303	1.4
Zr	[16]	304	4	–	–
Hf	[17,18]	270	2.3×10^{-2}	–	–
Au	[19]	260	1.9×10^{-2}	–	–
Sn	[13][a]	338	4	340	5
Ta	[12]	–	–	318	1
In	[5,21]	260	2×10^{-3}	329	3.1
Al	[5]	–	–	329	6.6
Ga	[5]	–	–	295	2.1
Ga	[22]	–	–	308	2.5

[a] This work.

perfectly well with the values expected for diffusion in high purity material (as a matter of fact, they are the same parameters than the obtained in this work, according to the experimental error). So, it was possible to expect this lack of enhancement.

An interesting case would be the study of diffusion of Zr in high purity α-Ti in order to test this idea. In fact the diffusion parameters obtained in Ref. [16], measured in specimens with an impurity content similar to the present less pure Ti, are very close to those obtained for self-diffusion in high purity α-Ti (see Table 3). So, it is presumable that no enhancement would be observable as in the present case of Sn diffusion.

The lack of enhancement observed between samples with 4 and 150 μg/g of Fe in the present work does not support the idea of an enhancement solely due to the vacancy mobility induced by the association with Fe atom in solid solution. The need of a higher amount of Fe, above its limit of solubility in α-Ti, in order to enhance the diffusion process in the particular case of Sn, shows that the total amount of Fe must be taken into account in order to explain the enhancement process and that the enhancement mechanism should consider a cluster that includes the diffuser atom as well as the vacancy and the Fe impurity.

5. Conclusions

Diffusion of Sn in high purity α-Ti was measured in the range of 873–1100 K. Normal diffusion parameters Q and D_0, close to the self-diffusion ones, were obtained.

At three different temperatures, measurements in less pure Ti were also performed for comparison. There is no significant difference between the diffusion coefficients obtained in high purity and less pure α-Ti samples. This behavior is opposite to the observed in other substitutional diffusers in which the increment in the amount of Fe from 1–4 to around 100 μg/g enhances the diffusion process; in the present case, amounts of Fe above its solid solubility in α-Ti are required in order to produce such enhancement.

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