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Journal of Nuclear Materials 249 (1997) 52–57

journal of nuclear materials

Indium diffusion study in α-titanium

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Received 22 November 1996; accepted 30 May 1997

Abstract

The diffusion of implanted In in α-Ti has been studied in the 823–1073 K temperature range by using the Rutherford backscattering spectrometry (RBS) technique. The measurements show that the diffusion coefficients follow a linear Arrhenius plot: $D(T) = (2.0 \pm 1.3) \times 10^{-6} \exp[-(260 \pm 40)\ \mathrm{kJ/mol}/RT]\ \mathrm{m^2\ s^{-1}}$. The diffusion parameters D_0 and Q are typical of a normal substitutional behavior. Comparison of the present and previous published results of impurity diffusion in α-Ti does not show evidence for mass or size effects in the diffusion mechanism. © 1997 Elsevier Science B.V.

1. Introduction

Close relationships exist between Hf, Zr and Ti. They belong to the group IVB of the periodic table, are highly reactive, transform from bcc (β-phase) to hcp (α-phase) structures and, with the exception of Hf in which the β-phase occurs in a very narrow temperature range, they show a pronounced positive curvature in their Arrhenius plots for diffusion in the bcc phase.

While the self-diffusion and substitutional diffusion behavior in the β-phase was intensively studied [1], the same did not occur for the α-phase. The paucity of the experimental data is basically due to two factors: (a) the rather narrow and low temperature interval studied (due to the limited stability range of the α-phase) and (b) the small expected diffusion coefficients ($D < 10^{-17}\ \mathrm{m^2\ s^{-1}}$), features which have strongly reduced the number of possible analyzing techniques. Self-diffusion in α-Zr [2] and Hf diffusion in α-Zr [3] resulted in downward curved Arrhenius plots. However, this anomalous behavior was attributed to extrinsic effects, basically due to an enhancement of the diffusion by fast-diffusing impurities (such as Fe) forming rapidly diffusing and impurity–vacancy pairs. These impurities have a low solubility and tend to precipitate at lower temperatures, thus explaining the observed downward Arrhenius curvature [4].

The situation is more promising for α-Ti. The solubility of the fast diffusing impurities is roughly one to two orders of magnitude larger than in α-Zr. Then, extrinsic effects as the ones observed for α-Zr are less likely to occur. First self-diffusion measurements have rendered a linear Arrhenius plot [5]. However, the activation energy $Q = 193$ kJ/mol and the pre-exponential factor $D_0 = 1.7 \times 10^{-8}\ \mathrm{m^2\ s^{-1}}$ found in this work were rather low as compared to other hexagonal metals and with the values predicted by the semiempirical rules [6].

More recently, the use of the Rutherford backscattering (RBS) and heavy ions Rutherford backscattering (HIRBS) techniques have allowed to measure the diffusivity of several substitutional elements in α-Ti. Since these techniques have rather good depth resolution, they are quite suitable for measuring shallow penetration profiles as should be the case for α-Ti. It was shown that for all the studied cases the data follow a linear Arrhenius behavior being the Q and D_0 values of the diffusion of Hf [7,8], Au [9], Zr [10], Pb [11] and Sn [12] in α-Ti very close to those expected for substitutional impurity diffusion. More recent self-diffusion data in ultra pure α-Ti single crystals [13] yielded as a result, $D_0 = 1.35 \times 10^{-3}\ \mathrm{m^2\ s^{-1}}$ and $Q = 303$ kJ/mol, parameters that are quite consistent with those

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PII S0022-3115(97)00181-5

obtained for the above mentioned substitutional diffusers and with those predicted by the semiempirical rules.

Despite this overall agreement there are still several open questions. Among them are the following: the diffusion coefficients corresponding to Pb, Au, Hf, Zr and self-diffusion in a-Ti [7–11,13] lay in a very narrow interval, the maximum difference, for a given temperature, being less than one order of magnitude. The exception is Sn [12] which was shown to be a much slower diffusor as compared to the other elements. Therefore, it is interesting to investigate if this is an exceptional case or if there is a possible systematics behind this behavior.

From the above arguments it can be deduced that it is interesting to perform more experiments with other impurities. Among the possible candidates In seems to be a good one. It has a large solubility in α-Ti [14], an atomic radius very similar to the host (In, $r = 0.1663$ nm; Ti, $r = 0.1462$ nm) [15] and a small difference of valences (In, 3: Ti, 4). Then, following the Hume–Rothery rules [16], In is a candidate to diffuse substitutionally in a α-Ti matrix by a vacancy mechanism.

Therefore, in the present work we have studied the In diffusion behavior in the α-Ti matrix by using the Rutherford backscattering technique. This technique with its fine depth resolution, is particularly suited for studies such as the present one, where due to the expected small D values, the diffusion depths are going to be restricted for reasonable annealing times to some tens of nm.

2. Experimental procedure and data analysis

Six samples of polycrystalline α-Ti were used in the present work. The 99.9% pure Ti impurity contents is described in Table 1. The samples were discs of about 9 mm diameter, and 3 mm thickness prepared as described in Ref. [10]. In this way, few and large textured grains free of residual stresses were obtained.

Further, the specimens were In implanted using the 400 kV ion implanter of the Instituto de Fisica, Universidade Federal do Rio Grande do Sul (IF-UFRGS). The implantation energy was 40 keV and the implanted fluence $\Phi = 5 \times 10^5$ at/cm^2. In this way we have obtained an In peak concentration $C_p \cong 5$ at.%, well below the maximum solid solubility of In in α-Ti which is about 10 at.% [14]. All the implantations were performed in a vacuum better than 10^{-10} bar.

Table 1
Impurity content of the α-Ti samples [a]

Element	Content (μg/g)
Al	< 50
Cu	< 30
Fe	< 150
Ni	< 50
Pb	< 20
Si	< 50
O	< 800
N	< 35

[a] Impurities at a level lower than 10 μg/g are not quoted in the present table.

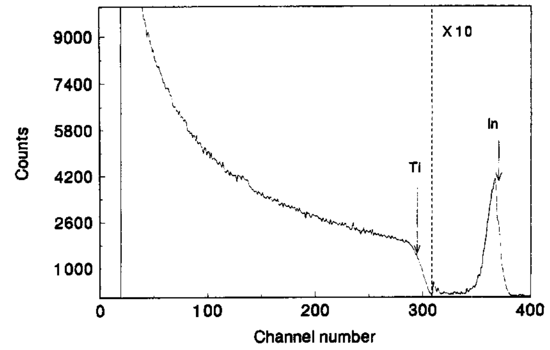

Fig. 1. Typical RBS spectrum for In as implanted in an α-Ti matrix.

Each sample was submitted to several isothermal annealings (within ±1 K) for different periods of time. In order to avoid possible contaminations during the annealings, the samples were wrapped with tantalum foils and annealed in a dynamic vacuum better than 10^{-10} bar. Corrections for heat-up and cooling times were made whenever the total annealing time was < 7200 s.

The In depth profiles were determined using the RBS technique through a 800 keV He^{2+} beam from the IF-UFRGS ion implanter. The backscattered α particles were detected by a Si surface-barrier detector at a scattering angle of 165°. The electronic resolution of the system was better than 13 keV which implies a depth resolution of around 10 nm. The energy-to-depth conversion was done using the He^{2+} electronic stopping power as given by the subroutine RSTOP of the Monte Carlo TRIM program (version 1995) [17]. A typical RBS spectrum from a non-annealed sample is shown in Fig. 1.

In order to minimize possible effects of α radiation damage a fresh area was used after each annealing. However, previous experiments [9,12] and our present observations have shown that the α-beam does not produce any noticeable effect on the diffusion process.

The In part of the RBS spectrum shows, after the implantation process, a Gaussian shape (see full line in Fig. 2a). Then, we have performed the same data analysis as described in Ref. [12]. As a consequence we have obtained the following expression for the diffusion coefficient D:

$$D = \frac{p - p_0}{4 p p_0 t}, \tag{1}$$

where p is the slope of the penetration profile [$\log C(x)$ vs. (x^2)] corresponding to the annealing time, t, and p_0 is a parametric slope defined in Ref. [12].

It can be shown [12] that if n isothermal annealings are performed, then the mean $\overline{D}$ value of the diffusion coefficient for a given temperature is represented by the expression

$$\overline{D} = \frac{1}{n}\sum_{i=0}^{n}\sum_{j<i}\frac{p_i - p_j}{4p_i p_j(t_i - t_j)}, \qquad (2)$$

where p has been replaced by p_i, p_0 by p_j and t by $(t_i - t_j)$, with $j < i$.

The main error in the estimation of the diffusion coefficients basically arises from the reported uncertainties in the He stopping power which are estimated to be of the order of 5%. Then the uncertainties attributed to the diffusion coefficients are of the order of 20%.

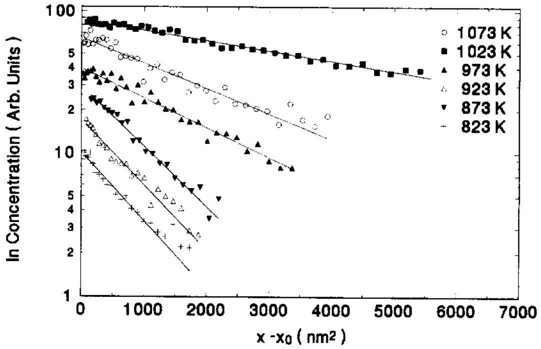

Fig. 3. Penetration profiles corresponding to the last annealing for all the samples.

3. Results

In the present work we have used six different samples. Each of these samples was submitted to several isothermal annealings in the 823–1073 K temperature range. The corresponding annealing times were varied between 1800 and 206.6 × 10^4 s. In most of the cases, the results obtained after the first annealing time were disregarded for two main reasons: (a) the time was too short to obtain a reliable diffusion coefficient, (b) usually a rearrangement of the implanted material occurs. This phenomena is noticeable by a slight displacement of the maximum concentration peak (less than 2 nm toward the surface) and a small amount of In evaporation (less than 15% for the higher temperatures). In addition, when a similar behavior was observed in the Pb diffusion studies, the obtained diffusivity values after the first annealing were one order of magnitude higher than the ones obtained after the equilibrium was reached.

It should be stressed that this first annealing was enough to recover the damage produced by the ion implantation process. In fact, in a previous experiment [9] it was shown that the implantation damage is recovered at temperatures as low as 823 K when the sample is annealed for 1.8 × 10^4 s. This feature is in agreement with the data reported by Hasegawa et al. [18] which demonstrated that irradiated Ti completely recovers at 400°C. Moreover some present exploratory channeling experiments (not shown here) have confirmed that in all cases, the damage induced by the implantation process has recovered after the first short annealing time.

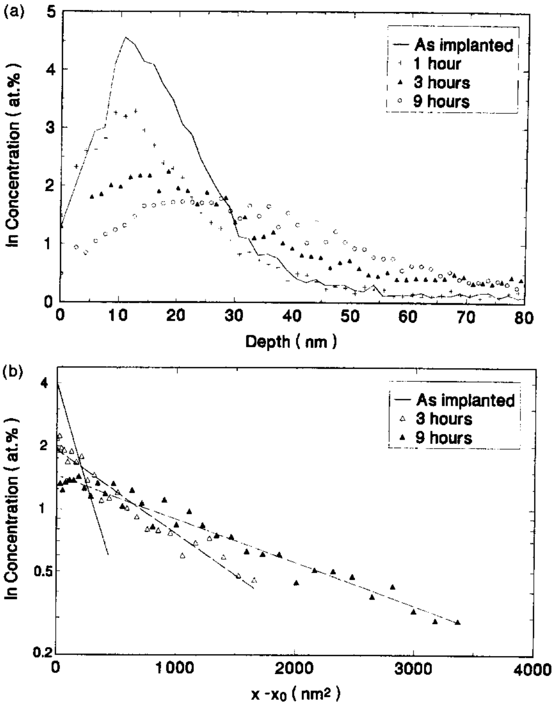

Fig. 2. (a) In part of the RBS spectra of sample 4 for several diffusion annealing times at 973 K. (b) Penetration profiles corresponding to the RBS spectra of (a).

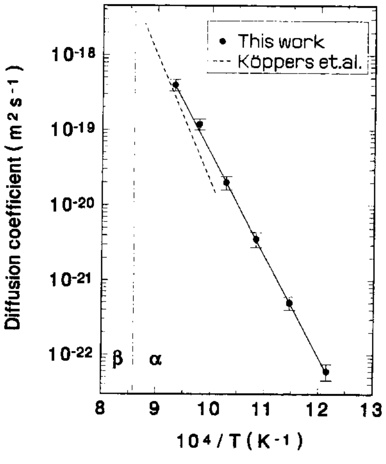

Fig. 4. Arrhenius plot of In diffusion in α-Ti. The full line is a least square fit of the measured data. The dashed line corresponds to the data of Ref. [13] (see text).

Table 2
Summary of the results of the present experiment

No.	Temperature (K)	Annealing time (10^4 s)	D_i ($m^2 s^{-1}$)	$\bar{D}$ ($m^2 s^{-1}$)
1	823	4.32	NO	
		206.6	5.1×10^{-23}	$(5.1 \pm 1.5)\ 10^{-23}$
2	873	1.44	NO	
		5.76	4.7×10^{-22}	
		40.32	5.0×10^{-22}	
			5.4×10^{-22}	$(5.0 \pm 1.0)\ 10^{-22}$
3	923	0.36	NO	
		1.44	3.7×10^{-21}	
			3.6×10^{-21}	
		5.76	3.6×10^{-21}	$(3.6 \pm 0.8)\ 10^{-21}$
4	973	0.36	NO	
			1.8×10^{-20}	
		1.08	2.2×10^{-20}	
			1.8×10^{-20}	
		2.34	2.0×10^{-20}	
			2.0×10^{-20}	$(2.0 \pm 0.4)\ 10^{-20}$
5	1023	0.36	9.5×10^{-20}	
			1.2×10^{-19}	
		1.08	1.3×10^{-19}	$(1.2 \pm 0.2)\ 10^{-19}$
6	1073	0.18	4.0×10^{-19}	$(4.0 \pm 0.7)\ 10^{-19}$

D_i are the diffusion coefficients. $\bar{D}$ are the mean diffusion values (see text), obtained for each annealing time.
NO: Annealing time was too short in order to get the available D value.

The temperatures and the corresponding annealing times used in the present study are quoted in Table 2. Representative In depth profiles before and after the annealings are shown in Fig. 2a and the corresponding penetration profiles [$\ln C(x)$] vs. $(x - x_0)$] are displayed in Fig. 2b. In addition, in Fig. 3 we show the penetration profiles corresponding to each annealing temperature. As can be observed in all the cases we have obtained straight penetration profiles, so, the corresponding diffusion coefficients were deduced according to the equations derived in Section 2.

In Table 2 are listed the diffusivities D obtained for each temperature and for each individual annealing time. In addition we quote the mean diffusion value $\bar{D}$ obtained for each annealing temperature. The corresponding Arrhenius plot is shown in Fig. 4. As can be observed, the experimental points follows an Arrhenius law

$$D = D_0 e^{-Q/RT},$$

where a least square fit (represented by the straight line) yields the following diffusion parameters:

$$D_0 = (2.0 \pm 1.3) \times 10^6\ m^2\ s^{-1}\ \text{and}$$

$$Q = (260 \pm 40)\ kJ/mol.$$

These parameters are (as will be discussed in the next section) consistent with a substitutional diffusion mechanism.

4. Discussion

It is generally believed that the vacancy mechanism is operative for self-diffusion and also for substitutional impurity-diffusion. At T_m the diffusion coefficients of impurity atoms are expected to differ in not more than about one order of magnitude from those of the self-diffusion. More precisely, the diffusion parameters have values which suggest that the same mechanism operates for both solute and self-diffusion:

$$0.1 \le D_0^{imp}/D_0^{self} \le 10 \text{ and } 0.75 \le Q_{imp}/Q_{self} \le 1.2. \quad (3)$$

The present study indicates that the diffusion of In in α-Ti follows a linear Arrhenius plot. This behavior is similar to those observed for Pb [11], Au [9], Hf [7,8], Sn [12], Zr [10], and the self-diffusion studies performed by Herzig et al. [5,13]. A summary of the present and previously published data is presented in Table 3 where the pre-exponential factors D_0 and the corresponding activation energies Q obtained for each case are quoted. In addition, we have included recently published Au [19], Al, Ga and In [13] in α-Ti diffusion data reported by Taguchi and Iijima [19] and Köppers et al. [13], respectively.

Table 3
Summary of the present and previous published results concerning substitutional data in α-Ti

Diffuser	Technique [a]	D_0 ($m^2 s^{-1}$)	Q (kJ/mol)	Ref.
SD	IBSy	1.7×10^{-8}	193	[5]
	IBS	5.9×10^{-3}	303	[13]
Pb	RBS + HIRBS	5.0×10^{-6}	260	[11]
Au	RBS	1.9×10^{-5}	260	[9]
	E.M.	2.5×10^{-8}	188	[20]
Hf [b]	RBS + HIRBS	2.3×10^{-5}	270	[7,8]
Sn	RBS	4.0×10^{-3}	338	[12]
In	RBS	2.0×10^{-6}	260	this work
	SIMS	3.1×10^{-3}	330	[13]
Zr	RBS + HIRBS	4.3×10^{-3}	304	[10]
Ga	SIMS	2.1×10^{-3}	295	[13]
Al	SIMS	6.6×10^{-3}	330	[13]

[a] IBS: ion beam sputtering, RBS: Rutherford backscattering spectrometry. HIRBS: heavy ions RBS, E.M.: electron microprobe.
[b] The quoted values are results of the combined [7,8] reported diffusion data.

An inspection of Table 3 shows several interesting features. Firstly, with exception of Au data reported in Ref. [19], and the first self-diffusion study [5], all the other activation energies lie in the 260–340 kJ/mol energy range and the D_0 pre-factors in the 5×10^{-6}–2.1×10^{-3} m^2 s^{-1} interval. We can disregard the first self-diffusional result, since as later recognized by the same group [20], the reported Q value was eventually influenced by a Fe-vacancy controlled process. In fact a very recent measurement performed in ultrapure α-Ti single crystals have given as a result $Q = 303$ kJ/mol and $D_0 = 5.9 \times 10^{-3}$ m^2 s^{-1} [13] confirming in this way the previous assumptions.

The experiments performed by Taguchi and Iijima [19] were done using non-high purity α-Ti samples. They extrapolated the Au diffusion coefficients at infinite dilution from the concentration dependence of the interdiffusion coefficients, measured in the binary solid-solution system. Their diffusion parameters $D_0 = 2.5 \times 10^{-8}$ m^2 s^{-1} and $Q = 188$ kJ/mol are lower than the ones obtained by dos Santos et al. [9] for Au diffusion in α-Ti samples of higher purity, see Table 2. We attribute this difference to the impurity content of the α-Ti samples used in the experiment of Ref. [19]. In fact it was observed in a previous work [12] that the measured D values of Sn in commercial α-Ti were considerably larger than the corresponding ones obtained in α-Ti samples of higher purity. This effect could be responsible for the rather high D values obtained by Taguchi et al. [19] as compared with those obtained by dos Santos et al. [9]. Secondly, it can be observed that for all the studied elements the corresponding diffusion coefficients (at the same temperature) are inside a narrow region of less than one order of magnitude (see Fig. 5). The exception is Sn which has shown to be a much slower diffusor, consequently it has (up to the present) the highest observed activation energy ($Q = 338$ kJ/mol). On the other side, In which has a similar mass and atomic radius as compared with Sn is characterized by diffusion coefficients which are inside the same narrow region as the ones corresponding to the other substitutional diffusers. Moreover, an inspection of Fig. 5 does not show indications of mass or size effects on the diffusional behavior of the substitutional elements in α-Ti.

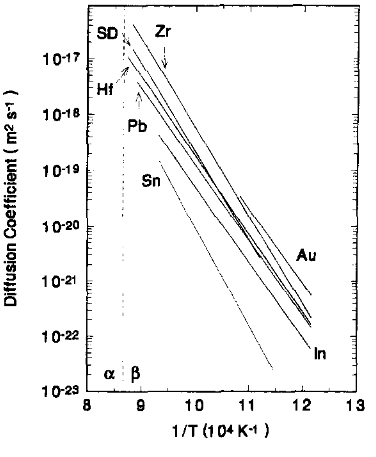

Fig. 5. Arrhenius plots for different elements diffusing in α-Ti, SD represents the self-diffusion data of Ref. [13].

In the recent DIMAT-96 conference, in addition to the self-diffusion parameters Al, Ga and In solute diffusion in α-Ti data [13] (IIIA group) were reported. The measurements were performed in a short temperature interval ($993 < T < 1141$ K) near the $\alpha \Leftrightarrow \beta$ transition temperature. Linear Arrhenius plots were observed in all the cases. In addition it was shown that there is a fair correlation between the diffusion coefficients of the different elements and the corresponding atomic size sequence. However, it should be stated that this correlation is strictly followed by In, Ga and Al, being the self-diffusion data out of place in this sequence (see fig. 9 and table 1 in Ref. [13]). As can be observed the results of Köppers et al. [13] are at variance with our observations. This shows that, in the best case, simple relations between radius size and diffusion coefficients are limited to some elements, in this case, to those that belong to the IIIA group. On the other hand, that relation is not obeyed by the IVB group elements Ti, Zr and Hf as shown by our data.

In Fig. 5 are represented the Arrhenius plots corresponding to the present and Ref. [13] works. As can be observed the agreement between both sets of data is fairly good. For the highest common temperature the difference between both diffusion coefficients is less than 20%, increasing this difference for lower temperatures (being a factor of 2 for the lowest common one). At present we do not have an explanation for this behavior. The authors of Ref. [13] have used ultrapure α-Ti samples. Therefore it could be possible that the amount of impurities present in the samples can influence the In diffusional behavior. However, at the present it is not clear if the difference of impurity contents in pure (as in the present case) and ultrapure samples is large enough to play a significant role in the diffusional behavior in α-Ti. As can be observed this question remains as an open one, and further experiments should be performed in order to clarify this point.

5. Conclusions

We can summarize the results of the present work as follows: The present study indicates that In diffuses in α-Ti following a linear Arrhenius plot in the 873–1071 K temperature range. The measurements yield an activation energy Q and pre-exponential D_0 factor that are expected for a normal substitutional diffusion behavior. In addition the present results are in good agreement with previous ones obtained from self-diffusion and impurity diffusion data. The diffusion coefficients of all of them (with exception of Sn) at the same temperatures are within a very narrow range of less than one order of magnitude. It should be also stated that a comparison of our present and previously published data does not render any evidence for size or mass effects on the substitutional diffusion process in α-Ti. Finally, we want to emphasize that it is not clear what is the influence of the impurities on the diffusional process when pure or ultrapure a-Ti samples are used. We believe that more work should be done in order to further clarify this point.

Acknowledgements

This work was partially supported by Fundacion Antorchas, CONICET and Proyecto Multinacional OEA-CNEA.

References

[1] Chr. Herzig, Def. Diff. Forum 95–98 (1993) 203.
[2] J. Horvath, F. Dyment, H.J. Mehrer, J. Nucl. Mater. 126 (1984) 206.
[3] G.M. Hood, H. Zou, R.J. Schultz, J.A. Roy, J.A. Jackman, J. Nucl. Mater. 189 (1992) 226.
[4] G.M. Hood, Def. Diff. Forum 95–98 (1993) 755.
[5] Chr. Herzig, R. Willecke, K. Vieregge, Philos. Mag. A63 (1991) 949.
[6] A.D. Le Claire, in: Diffusion in Body Centered Cubic Metals (ASM, Metals Park, OH, 1956).
[7] M. Behar, F. Dyment, R. Pérez, J.H.R. dos Santos, R.L. Maltez, E.J. Savino, Philos. Mag. A63 (1991) 967.
[8] R. Pérez, F. Dyment, G.G. Bermudez, H. Somacal, D. Abriola, J. Nucl. Mater. 207 (1993) 221.
[9] J.H.R. dos Santos, P.F.P. Fichtner, M. Behar, R.A. Pérez, F. Dyment, Appl. Phys. A58 (1994) 453.
[10] R. Pérez, F. Dyment, Hj. Matzke, G. Linker, H. Dehers, J. Nucl. Mater. 217 (1994) 48.
[11] M. Mirassou, R. Pérez, F. Dyment, J.H.R. dos Santos, M. Behar, Scri. Metall. Mater. 34 (1996) 1537.
[12] R. Pérez, M. Behar., F. Dyment, Philos. Mag. A, in press.
[13] M. Köppers, D. Derdau, M. Friesel, Chr. Herzig, Def. Diff. Forum, in press.
[14] J.L. Murray, Phase Diagrams of Binary Titanium Alloys, (ASM International, Metals Park, OH, 1987).
[15] W.B. Pearson, The Crystal Chemistry and Physics of Metals and Alloys (Wiley Interscience, New York, 1972) ch. 4.
[16] W. Hume-Rothery, G.M. Malbott, K.M. Channel-Evans, Philos. Trans. R. Soc. A223 (1934) 1.
[17] J.P. Biersack, L.G. Haggmark, Nucl. Instrum. Methods 174 (1980) 257.
[18] M. Hasegawa, S. Koibe, M. Hirabayashi, Y., Higashigachi, E. Kuramoto, K. Kitagima, in: Point Defects and Defect Interactions in Metals, eds. J.I. Takamura, M. Doyama and M. Kiritini (North-Holland, Amsterdam, 1982) p. 695.
[19] O. Taguchi, Y. Iijima, Philos. Mag. A72 (1995) 1649.
[20] M. Köppers, Chr. Herzig, U. Södervall, A. Lodding, Def. Diff. Forum 95–98 (1993) 203.