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Helium depth profiling in tantalum after ion implantation and high-temperature annealing

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Abstract

We have studied the depth profiles of ^{3}He implanted into tantalum with concentrations ranging between 500 and 2500 at. ppm. We used the ^{3}He nuclear reaction analysis based on the ^{3}He(d,p)^{4}He 'resonant' reaction which yields a specific signal, independent of the Ta host. Excitation curves were obtained by measuring the 13-MeV proton yield as a function of the incident deuteron energy for as-implanted and annealed Ta samples. These curves are ^{3}He depth profiles convoluted with the reaction cross-section. The as-implanted depth profile is approximated by a Gaussian curve which is fitted to match the experimental excitation curve. The same process is used for data on annealed samples at high-temperatures from 1000 K to 1773 K. Diffusion constant data are deduced from the depth profile standard deviations of the same sample at two consecutive annealing temperatures. The small diffusion constant values found are consistent with helium trapping at vacancies or vacancy clusters.

1. Introduction

The behaviour of helium in heavy metals plays a major role in the ageing of materials, in particular when they are used in controlled fusion reactors exposed to 3.5-MeV α particle irradiations [1]. Helium atoms are known to have a very low solubility in metals and to agglomerate into bubbles which can have a detrimental effect on mechanical properties. Ion implantation is currently used to simulate ageing in an accelerated manner. Some of the key parameters are helium diffusion constants and activation energies of the processes involved in implanted helium atom migration at high-temperatures. However, such data are difficult to obtain [2] due to the small helium atomic mass and number, especially in heavy metal hosts which preclude the use of conventional X-ray scattering and Rutherford backscattering techniques (RBS) [3].

We therefore used the ^{3}He nuclear reaction analysis (NRA) based on the ^{3}He(d,p)^{4}He 'resonant' reaction [4,5] which yields a specific signal, regardless of the host, in order to study ^{3}He thermally activated diffusion after ^{3}He ion implantation in tantalum. Results can easily be transferred to ^{4}He with a simple isotopic diffusion constant correction. This technique has already been used in other materials [6,7] but experimental data about Ta are not available in the literature and are scarce for other bcc metals [8] compared to the fcc ones obtained mainly with thermal desorption spectroscopy [9–14].

The purpose of the present work was to measure ^{3}He diffusion constants in Ta. A simple diffusion model was assumed and experimental data were fitted with a specifically developed computer code in order to extract helium depth profiles. Resulting fits are in good agreement with experimental data.

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2. Experimental procedure

Polycrystalline tantalum foils (25-μm thick) provided by Goodfellow were first implanted under secondary vacuum with ^{3}He ions at 3.4 and 4.0 MeV on either the CEA/DIF 4-MV or the 7-MV tandem Van de Graaff accelerator (Table 1). The ion beam was swept over the sample surface (1 cm^2) in order to obtain homogeneous implantations. Implantation characteristics calculated with the SRIM 2000 code [15] are displayed in Table 1 together with the irradiation and annealing conditions. Two samples have been implanted with different helium concentrations ρ_{He} between 10^{19} and 10^{20} cm^{-3} ($\rho_{\mathrm{He}} = \varphi_{\mathrm{He}}/2\Delta R_{\mathrm{p}}$ with φ_{He} being the ^{3}He fluence and ΔR_{p} the longitudinal projected range straggling) or c_{He} between 500 and 2500 at. ppm ($c_{\mathrm{He}} = \rho_{\mathrm{He}}/\rho_{\mathrm{Ta}}$ where $\rho_{\mathrm{Ta}} = 5.52 \times 10^{22}$ at cm^{-3} is the Ta density) (Table 1). In order to control the implantation process, temperatures were measured using a Pt resistance thermometer welded on the samples. With a 500 nA cm^{-2} helium beam current density at 3.5-MeV, a 400 K maximum temperature was reached in less than one minute, this temperature being far below the Ta melting temperature ($T_{\mathrm{m}} = 3269$ K). Therefore no ^{3}He diffusion is expected to occur during irradiation under these conditions ($\approx 0.12\ T_{\mathrm{m}}$).

The samples were then analysed by the resonant nuclear reaction ^{3}He(d,p)^{4}He [5] at the 7 MV tandem accelerator. The cross-section of this reaction (Fig. 1) has a broad peak at a deuteron energy around 430 keV with a full-width at half maximum around 350 keV at a detection angle of 86° [4]. An aluminium screen (120-μm thick) was set on the surface barrier detector in order to stop the backscattered deuterons, and the protons and α particles due to the deuteron-induced reactions on surface contaminants (C, N, O), at much lower energy than the 13-MeV protons of the ^{3}He(d,p) reaction. Excitation curves were obtained by measuring the proton yield (I_0) as a function of the incident deuteron energy (E_0) at a detection angle of 160°. The deuteron beam was swept over the sample surface (1 cm^2) in order to obtain a large representative proton count rate. All samples were covered with an aluminium sheet (10-μm thick) because 1.4 MeV is the lowest available energy on the tandem. An energy straggling overestimation at 10-μm depth in Ta is around 40 keV according to Bohr's approximation. The incident deuteron energy (E_0) was varied from 1.7 to 2.15 MeV by 25 or 50 keV steps, to record the complete energy profile. The measured proton yield (I_0) was normalised to the beam current density and measuring time. The beam current density measured with a Faraday cup was about 400 nA cm^{-2}. Measurements lasted 100–900 s, according to helium concentration, in order to obtain a reasonable number of counts (≈1000) at the curve maximum yield. Under these irradiation conditions we estimated irradiation temperatures at several beam energies, taking black body losses into account and neglecting thermal conduction losses. These temperatures do not exceed 600 K; they are overestimated compared with exact irradiation temperatures, but are still smaller than 0.2 T_{m}.

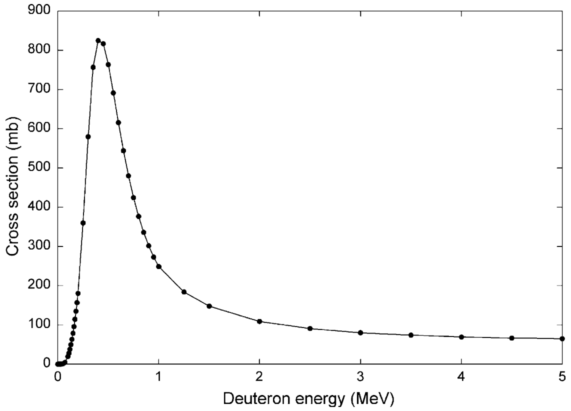

Fig. 1. Total cross-section of the ^{3}He(d,p)^{4}He nuclear reaction versus the deuteron energy [16].

Samples were then isochronously annealed at high-temperatures for 4 hours in various low-thermal inertia secondary vacuum furnaces according to the desired temperatures ranging from 1000 K (0.31 T_{m}) to 1773 K

Table 1

Characteristics of ^{3}He implantations and annealing ($t = 4$ h except for TaHe3013 $t = 4$ d) of Ta samples. E_{He} is the ^{3}He ion energy, I_{He} is the beam current density, R_{p} is the mean projected range, ΔR_{p} is the longitudinal projected range straggling computed with the SRIM 2000 code [15], φ_{He} is the ion fluence, ρ_{He} and c_{He} are the ^{3}He atom concentrations and T/T_{m} is the reduced annealing temperature (T) to the Ta melting temperature ($T_{\mathrm{m}} = 3269$ K)

Samples	E_{He} (MeV)	I_{He} (nA/cm^2)	R_{p} (μm)	ΔR_{p} (μm)	φ_{He} (cm^{-2})	ρ_{He} (cm^{-3})	c_{He} (at. ppm)	T/T_{m}
TaHe3002 (4 MV), He charge = 1	3.4	200	6	0.48	1.30×10^{16}	1.35×10^{20}	2500	0.31(R1), 0.42(R2), 0.54(R3)
TaHe3013 (7 MV), He charge = 2	4	280	7.4	0.54	3.14×10^{15}	2.91×10^{19}	529	0.39(R1)

(0.54 T_m). One sample was annealed 4 days at 1273 K. A SIMS surface analysis of a reference annealed sample exhibits an oxide surface layer (0.5-μm thick) which is negligible with respect to ^{3}He mean projected ranges R_p (Table 1). The annealed samples were then analysed a second time with deuterons.

3. Excitation curve modelling

In order to determine diffusion constants, it is necessary to extract helium depth profiles in the sample from as-implanted and annealed sample data. The measured excitation curves $I_0(E_0)$ are ^{3}He depth profiles $\rho(x)$ convoluted with the ^{3}He(d,p)^{4}He reaction cross-section σ [4,16].

We neglected I_0 angular variations because the cross-section σ is almost constant versus the detection angle at the considered energies [4]. Thus, I_0 can be written as

$$I_0(E_0) = \int_0^{x_0} \sigma(E(x))\rho(x)\,\mathrm{d}x, \tag{1}$$

where x_0 is the thickness at which all the incident deuteron energy is absorbed, and the energy $E(x)$ represents the deuteron beam energy at a depth x in the sample as given by the SRIM 2000 code [15], which includes an electronic and a nuclear contribution [4].

In order to fit our experimental results, we assumed that helium depth profiles $\rho(x)$ in as-implanted samples can be approximated by Gaussian curves, thus neglecting the distribution higher-order moments [15,17]:

$$\rho(x) = \frac{A}{s}\exp\left[-\frac{(x-x_c)^2}{2s^2}\right], \tag{2}$$

where A is a normalization constant proportional to the helium content, s the standard deviation and x_c the depth distribution centroid.

For the as-implanted samples, s should be equal to the longitudinal projected range straggling (ΔR_p) and x_c to the mean projected range (R_p), both estimated by the SRIM 2000 code [15]. However, all three parameters of the depth distribution were fitted by using the SRIM 2000 calculations as input data. During annealing, the time-dependent depth distribution is assumed to follow the classical Fick's second law, given by

$$\frac{\partial\rho}{\partial t} = D(T)\frac{\partial^2\rho}{\partial x^2}, \tag{3}$$

where $D(T)$ is the sample helium diffusion constant depending on temperature.

The solution of this equation is a Gaussian function because the as-implanted ($t = 0$) sample depth profile is assumed to be a Gaussian distribution centered at a few micron depth, sufficiently far from surface sinks with $R_p/\Delta R_p \approx 10$. Fick's solution $\rho_i(x,t)$ of Eq. (3) with the Gaussian assumption at $t = 0$ can be written as [17,18]

$$\rho_i(x,t) = \frac{A_i}{s_i}\exp\left[-\frac{(x-x_c)^2}{2s_i^2}\right] \tag{4}$$

with a standard deviation s_i which can be written as [17,18]

$$s_i^2 = s_{i-1}^2 + 2D_i t, \tag{5}$$

where D_i is the diffusion constant at an annealing temperature T_i, t the annealing time ($t = 4$ h for all annealing except for TaHe3013R1 $t = 4$ d), and s_{i-1} the standard deviation at annealing temperature T_{i-1}.

For a given annealed sample, the parameters of the corresponding as-implanted sample depth distribution were used as initial parameters values to fit experimental data iteratively. As a first physical assumption, x_c was supposed not to vary during annealing. Since it was not possible to fit the data with x_c constant, all three parameters of the depth distribution were fitted to match the experimental excitation curves by minimizing a least-squares difference error function. To that purpose, a specific computer program (AGEING) was developed in a PV-wave/GUI environment. This computer code was already used to process the ^{3}He excitation curves in britholite [19].

4. Results and discussion

Experimental and fitted excitation curves for the two samples (Table 1) are displayed in Fig. 2. The good quality of the fits (±3% relative error per data point) of the experimental ^{3}He excitation curves justifies the choice of a Gaussian expression for the helium depth profile $\rho(x)$ together with the assumed diffusion model. Fitted parameters for these samples are given in Table 2. For the as-implanted samples, the projected range (x_c) is in reasonable agreement with the SRIM 2000 calculations (Table 1) [15] and the normalization constant (A) agrees with the helium content. For the annealed samples, the variation of the x_c parameter (±5%) is not considered to be significant. In contrast, an increase of s larger than the average error of 4% is observed upon annealing, as expected within a diffusion model (Table 2). Using the fitted parameters s, we can calculate the diffusion constants at the corresponding temperatures from Eq. (5) (Table 2). Small values ranging between 5×10^{-16} and 3×10^{-14} cm^2 s^{-1} are found. However, no reliable activation energy value can be deduced from these data within estimated experimental errors on D (±60%). In order to obtain ^{4}He diffusion constants, an $M^{-1/2}$ isotopic correction is necessary, where M is the atomic mass [18], i.e. it leads to a 15.5% correction.

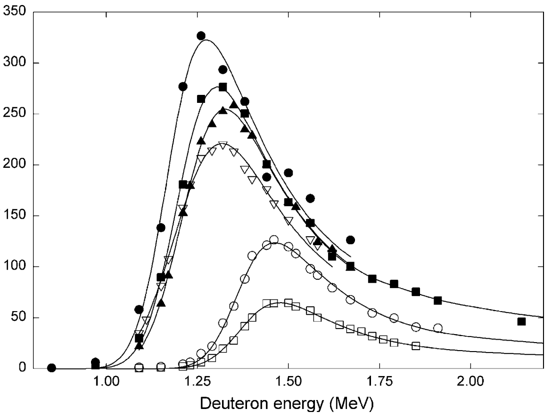

Fig. 2. Experimental excitation curves of the ^{3}He(d,p)^{4}He reaction in two Ta samples. 13-MeV proton normalized yield (I_0) versus deuteron incident energy (E_0) for as-implanted TaHe3002NR (full circles) and TaHe3013NR (open circles) and annealed samples (Table 1): TaHe3002R1 (1000 K, full squares), TaHe3002R2 (1373 K, full triangles), TaHe3002R3 (1773 K, open triangles), TaHe3013R1 (1273 K, open squares). Solid lines are fitted curves using the optimised parameters of the Gaussian ^{3}He depth profiles given in Table 2.

After room temperature ion implantations, all helium atoms are generally considered to be trapped at the nearby vacancies of the damage profile, in substitutional positions of the host [6,7,10,11]. Around 300 Ta atoms are displaced per incoming 3.5-MeV ^{3}He ion according to a SRIM 2000 simulation [15]. This trapping can account for the small diffusion constant values found here, as it was observed in the case of helium-implanted Nb [8]. Similar small values were found by Lewis et al. [6,7], by using the same NRA technique, in polycrystalline samples of stainless steel, α-Fe, Ni and α-Zr implanted with ^{3}He ions at annealing temperatures ranging between 300 and 973 K ($\leqslant 0.5\ T_m$). Effective diffusion constants ranging from 10^{-16} to 10^{-14} cm^2 s^{-1} were obtained in these cases at temperatures larger than 700 K [6]. Moreover, in the present high-temperature annealing range ($>0.3\ T_m$), helium–vacancy (He–V) clusters likely form bubbles [20]. More data at higher temperatures would be needed to implement these results.

The present data are probably effective values averaging out the grain-boundary and intra-granular processes. More reliable measurements would certainly be obtained in large grain polycrystalline samples and single crystals. In addition, ion implantations at smaller depths would increase the measurement accuracy through the use of the recoiling α particle spectrum of the ^{3}He(d,p)^{4}He reaction (like in Refs. [6,7]) instead of the emitted 13-MeV proton spectrum.

5. Conclusions

We have used the ^{3}He(d,p)^{4}He resonant nuclear reaction to study the helium migration in tantalum after ^{3}He ion implantation followed by successive isochronal thermal annealing from 1000 K (0.31 T_m) to 1773 K (0.54 T_m). The experimental excitation curves of the as-implanted and annealed samples are analysed with a classical diffusion approach based on the Fick's equation and a Gaussian ^{3}He depth profile. The diffusion constants are then deduced from the standard deviations of the depth profiles fitted to experimental data for two samples annealed at increasing temperatures.

Small diffusion constant values ranging between 5×10^{-16} and 3×10^{-14} cm^2 s^{-1} are obtained for these samples annealed at temperatures from 1000 to 1773 K. These small values hint to strong helium trapping by vacancies and He–V cluster formation. We emphasize that the interest of this technique lies in comparing measurements at different annealing temperatures on the same sample and in deducing effective diffusion constant data at these temperatures.

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Table 2
Parameters obtained from the fits of the Gaussian ^{3}He depth profiles for samples TaHe3002 and TaHe3013 (Table 1)

Samples	A (arb. u.)	x_c (μm)	s (μm)	D (cm^2 s^{-1})
TaHe3002NR as-implanted	0.16	5.05	0.28 ± 0.01	
TaHe3002R1, 1000 K, 4 h	0.14	5.25	0.32 ± 0.01	$(9.45 \pm 5.67) \times 10^{-15}$
TaHe3002R2, 1373 K, 4 h	0.13	5.35	0.38 ± 0.01	$(1.48 \pm 0.89) \times 10^{-14}$
TaHe3002R3, 1773 K, 4 h	0.12	5.20	0.48 ± 0.01	$(3.02 \pm 1.81) \times 10^{-14}$
TaHe3013NR as-implanted	0.06	6.40	0.30 ± 0.01	
TaHe3013R1, 1273 K, 4 d	0.03	6.47	0.36 ± 0.01	$(5.3 \pm 3.18) \times 10^{-16}$

A is the normalization constant, x_c is the centroid, s is the standard deviation, and D is the diffusion constant.

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