Dilatometric measurements of helium densities in bubbles arising from tritium decay in tantalum

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The swelling rates of the bulk tritides $TaT_{0.42}$ and $TaT_{0.103}$ were measured at room temperature using the technique of strain gauges. Such swelling is expected in tritides because of the decay of tritium to ^{3}He and the subsequent precipitation of gas bubbles. Observations were made for up to 10 months. Almost-linear swelling was found in the first months for both tritides, indicative of a constant ^{3}He density in the bubbles. The slopes of the linear parts of the expansion curves normalized to the T concentration were almost identical in the two cases considered. From this a ^{3}He-to-Ta atom volume ratio, $v_{He}/\Omega \leq 0.52 \pm 0.03$ in the bubbles was derived, which is in good agreement with recent but less direct spectroscopic measurements of ^{4}He densities in bubbles formed after room-temperature implantation into other metals. Corrections for the presence of self-interstitials and their clusters and due to the elastic relaxation of the bubbles were considered. Calculated bubble pressures were in the vicinity of 5 GPa, which is close to the expected threshold pressure for athermal bubble growth.

I. INTRODUCTION

The development of fusion-reactor technology has created increasing interest in the behavior of helium in solids. Helium will be introduced into structural components of fusion reactors by direct α injection and (n,α) reactions, and into tritium storage materials by tritium decay. Since helium is practically insoluble in solids, it strongly tends to precipitate into bubbles. Bubble formation in solids leads to drastic changes in their macroscopic properties: It causes swelling and results in intergranular embrittlement.

Swelling of metal tritides resulting from transmutation of tritium into ^{3}He and the precipitation of this ^{3}He into bubbles has been observed previously.[1,2] At room temperature the formation of bubbles starts from clustering of ^{3}He interstitial atoms: When the number of He interstitials in such a cluster exceeds a certain value (say five) a Frenkel pair is spontaneously formed and the He atoms are trapped in the vacancy.[3] Formation of further Frenkel pairs under continuous He supply will finally result in visible bubbles.

The formation of ^{3}He bubbles was first inferred from NMR work[4,5] and then confirmed by transmission electron microscopy (TEM) for Pd-T,[6] V-T,[7] and Zr-T (Ref. 8) alloys. Also, it was observed that ^{3}He precipitates at dislocations in the form of long, thin cylindrical tubes or strings of bubbles.[9] In young tritides essentially all of the generated ^{3}He remains inside the samples[10–12] and leads to swelling, since the volume decrease occurring upon the decay of the tritium atom is more than compensated by the volume increase associated with the incorporation of an insoluble noble-gas atom into the lattice. Until now, however, the volume change per He atom has not been determined quantitatively.

In the present work, swelling is studied in two selected Ta tritides: (a) an α-phase sample of composition $TaT_{0.103}$ with cubic structure and random tritium distribution and (b) a β-phase sample of composition $TaT_{0.42}$ consisting of domains with an ordered orthorhombic structure. Novel features in the present dilatometric study are (i) the technique of strain gauges[13] was applied and (ii) true platelike bulk samples (rather than evaporated films or compacts as in previous studies[1,2]) were used. The final goal of this paper is the deduction of the He density in the bubbles causing the swelling.

II. EXPERIMENTAL

Rectangular ultrahigh vacuum annealed Ta slabs of size $5\times5\times0.25$ mm^3 were tritium charged to $c=0.103$ and

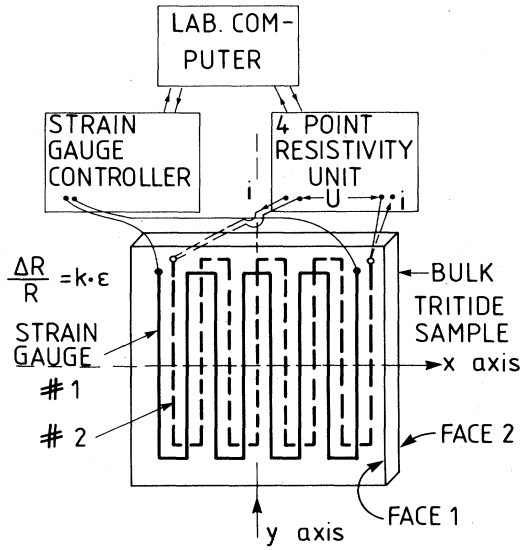

FIG. 1. Schematic illustration of the experimental setup. A radioactive bulk tritide plate with an activity of several Ci's is cemented between two strain gauges. The resistivity changes ΔR were monitored with two independent techniques.

TABLE I. List of experimental results [with the assumptions: $\Omega_0 = 18.0143 \times 10^{-30}$ m^3; $(\Delta v/\Omega_0)_H = 0.1589$; $(\Delta v/\Omega)_I = 1$].

	$10^{30} \times \Omega$ (m^3)	$(\Delta v/\Omega)_T$	$(\Delta v/\Omega)_{T \to He}$	(v_{He}/Ω)	$10^{30} \times v_{He}$ (m^3)	p (GPa)
$TaT_{0.103}$	18.31	0.156	0.37	0.53	9.6	5.3
$TaT_{0.42}$	19.22	0.149	0.37	0.52	10.0	4.7

$c = 0.42$ (T/M) in the Jülich tritium facility[14,15] at temperatures around 500 °C. Approximately 1 week after production, two 3-mm gauge length strain gauges were bonded to the two faces as shown in Fig. 1 using a special cement. [Strain gauges of type 3/120 LY11 by Hottinger Baldwin Measurements, Inc. (HBM) were applied using the cement X-60 (HBM).] The first strain gauge was monitored with a commercial ac Wheatstone bridge; for the second a sensitive four-point resistivity technique was used. Thus, two independent sensors and measurement techniques were used. We have estimated that strain changes as low as 1×10^{-6} could be observed. In view of this precision, the apparent fluctuations in the data (Figs. 2 and 3) may safely be ascribed to physical effects occurring either in the specimen or in the metal-gauge bond and not to measurement errors. This is underscored by the fact that there is very little scatter between successive measurements taken at intervals of 1 or 2 days.

The strains on the two faces $\epsilon = (\Delta L/L)$ were obtained from the relative resistivity change via the relation

$$\Delta R/R = k\epsilon \,, \tag{1}$$

where k is the strain sensitivity ($k \approx 2.0$), which is known within 1%. For isotropic swelling the relative volume change in the present geometry (Fig. 1) follows from

$$\Delta V/V = 3\epsilon \,. \tag{2}$$

It is conceivable that the cement between the tritide and the embedding material of the strain gauge may have suffered some radiation damage from the continuous irradiation with low-energy electrons and soft bremsstrahlung x-rays. This was checked by comparison of the resistivity changes of the strain gauges on the two faces of the sample. The specimens were periodically checked with a sensitive tritium counter for possible loss of tritium. The measured losses were much too insignificant to affect the present data.

III. RESULTS

A. Specimen $TaT_{0.42}$

In Fig. 2, the strain ϵ is plotted versus time. Unfortunately, one strain gauge on one face later turned out to be defective; thus the data in Fig. 2 were taken with only one gauge. Up to ~ 100 days the expansion increased linearly with time. Then, the expansion rate decreased somewhat. In Table I the numerical value of the initial slope is given.

B. Specimen $TaT_{0.103}$

Here both strain gauges worked properly and gave similar quantitative results. Figure 3 shows the average strain versus time obtained from these two independent measurements. Again, a quasilinear expansion with time was observed. The swelling rate in intervals of a few days was seen to range from zero (or even negative values) to a maximum value. After smoothing of the data, a slight curvature of the swelling curve can be recognized. For numerical values of the slope see Table I.

For safety reasons neither one of the present samples could be prepared for transmission electron microscopy to study the He bubble morphology. We refer however in this context to other recent TEM studies.[6–9]

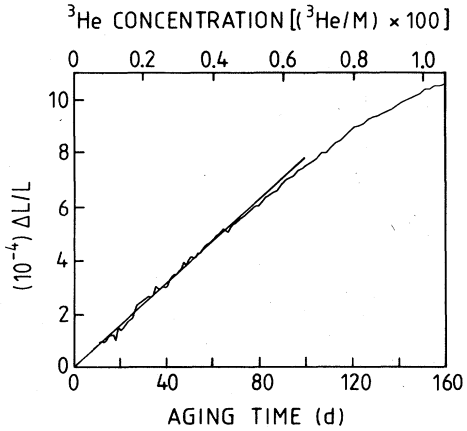

FIG. 2. Strain vs time for the $TaT_{0.42}$ sample. The straight line through the data points in the quasilinear regime represents the best fit.

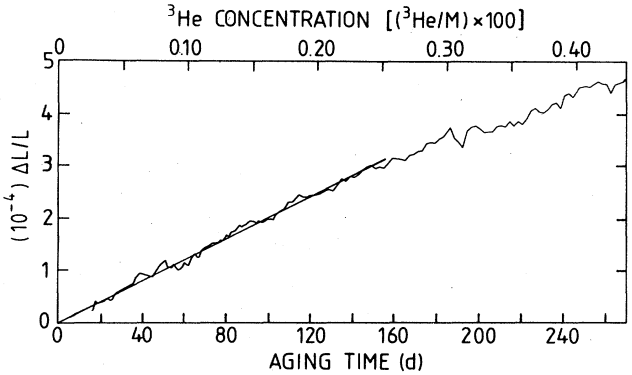

FIG. 3. Strain vs time for the $TaT_{0.103}$ sample. Straight line, best fit through data points in the quasilinear regime.

IV. DISCUSSION

In the following we discuss the linear portions of the strain-versus-time curves and deduce the volume per He atom in a bubble. First, however, it is useful to consider low-temperature ^{3}He precipitation in some detail in the light of current theoretical understanding.

For high ^{3}He production rates and/or low temperatures (as in the case of T decay in tritides at room temperature), diffusion controlled clustering of thermal vacancies is too slow to contribute to the formation of He bubbles. In this case, the first stage of He precipitation is clustering of He interstitial atoms. At a certain number of clustered He interstitials (about 5 to 7) the stored energy in such a cluster is sufficiently high to allow relaxation of the cluster by the spontaneous formation of a Frenkel pair (self-trapping mechanism).[3] When further He is trapped by such a defect, further metal self-interstitials (SIA's) (remaining close to the He-vacancy cluster) will be ejected to increase the (free) space available for the He. In a later stage emission of SIA clusters, in particular dislocation loops,[16,17] by over-pressurized bubbles is expected to be energetically more favorable than the emission of SIA's, because the binding energy of the SIA's to their cluster is saved in this process. Independent of the details of this process,[18] it seems clear, however, that low-temperature bubble formation is associated with the formation of SIA-type defect clusters. What is seen in dilatometric measurements is the volume change occurring in forming such defect configurations.

Assuming no leakage of tritium and ^{3}He from the sample, an initial (atomic) tritium concentration $c_{T,O}$ results in an increasing (atomic) He concentration:

$$c_{He}=c_{T,O}-c_T=c_{T,O}[1-\exp(-\lambda t)] , \tag{3}$$

where $\lambda=0.1779\times10^{-8}$ s^{-1} is the tritium decay constant ($T_{1/2}\approx12.33$ y). In linear elasticity, the total relative volume change, $\Delta V/V$, is given by the ratio of the average volume change per decay event and host-atom volume, $(\Delta v/\Omega)_{T\to He}$, times the He concentration, c_{He}:

$$\frac{\Delta V}{V}=c_{He}\left[\frac{\Delta v}{\Omega}\right]_{T\to He} =c_{T,O}[1-\exp(-\lambda t)]\left[\frac{\Delta v}{\Omega}\right]_{T\to He} , \tag{4}$$

which for $\lambda t\ll1$ becomes

$$\frac{\Delta V}{V}=c_{T,O}\lambda t\Delta v_{T\to He}/\Omega . \tag{5}$$

Accordingly, from the linear part of the expansion curves a time-independent volume change per decay event is found as given in Table I.

The total relative volume change $\Delta V/V$ is given by the difference between relative volume changes associated with the formation of He-Frenkel pair configurations $(\Delta V/V)_{He\text{-}F}$, and the decay of tritium $(\Delta V/V)_T$,

$$\Delta V/V=(\Delta V/V)_{He\text{-}F}-(\Delta V/V)_T =c_{He}(\Delta v_{He\text{-}F}/\Omega-\Delta v_T/\Omega) , \tag{6}$$

where $\Delta v_{He\text{-}F}$ and Δv_T are the volume changes per He and tritium atom, respectively.

To deduce the volume per He atom in a He-vacancy cluster or bubble v_{He}, from $(\Delta V/V)_{He\text{-}F}$, the contribution of the Ta SIA's in the He-Frenkel pair configuration to $(\Delta V/V)_{He\text{-}F}$ must be considered. For negligible elastic relaxation of the He-vacancy clusters or bubbles $(\Delta V/V)_{He\text{-}F}$ is completely determined by the volume change resulting from the transfer of host atoms from there to interstitial positions (SIA), already existing SIA clusters, dislocations, grain boundaries, and surfaces:

$$(\Delta V/V)_{He\text{-}F}\approx c_V\Delta\tilde{v}_I/\Omega , \tag{7}$$

where $\Delta\tilde{v}_I$ is the volume change per transferred SIA and c_V is the total vacancy concentration contained in bubbles. A relation between c_V and the total atomic concentration of He contained in bubbles c^B_{He}, is obtained by equating the total volume available for this He with that of the vacancies:

$$c_V\Omega=c^B_{He}v_{He} . \tag{8}$$

Using this in Eq. (7) and assuming that essentially all the ^{3}He produced is contained in bubbles, $c^B_{He}\approx c_{He}$, we obtain

$$\frac{\Delta V}{V}\approx c_{T,O}\lambda t\left[\left[\frac{v_{He}}{\Omega}\right]\left[\frac{\Delta\tilde{v}_I}{\Omega}\right]-\left[\frac{\Delta v_T}{\Omega}\right]\right] . \tag{9}$$

Thus, if $(\Delta v/\Omega)_T$ and $(\Delta\tilde{v}/\Omega)_I$ are known (v_{He}/Ω) can be calculated from the measured initial swelling rate. Neglecting isotopic differences we use for $(\Delta v/\Omega)_T$ the value for the dilute hydride, $(\Delta v/\Omega_0)_H=0.1589$,[13] corrected for the lattice expansion due to the actual T content. The value of $(\Delta\tilde{v}/\Omega)_I$ is expected to lie between the corresponding values (relaxation volume) for single SIA's and SIA's clustered in large dislocation loops or transferred to network dislocations, grain boundaries, and surfaces. In the latter case $(\Delta\tilde{v}/\Omega)_I\to1$; whereas the value of $(\Delta\tilde{v}/\Omega)_I$ for isolated Ta-SIA's is not known. Measurements on α-Fe and Mo (Ref. 19) indicate that this value is only slightly above 1 (around 1.1) for bcc metals. Thus, the actual value of (v_{He}/Ω) should be close to the upper bound obtained by using $(\Delta\tilde{v}/\Omega)_I=1$ in Eq. (9).

The effect of an excess of the relaxation volume per SIA $\Delta\tilde{v}_I$, with respect to the atomic volume Ω, is, at least partly, compensated when some of the He is trapped at previously generated SIA's or dislocation loops. An upper bound estimate of this effect is obtained by assuming that the total excess volume $c_I(\Delta\tilde{v}_I-\Omega)$ is filled up with ^{3}He of the same density as in bubbles and without elastic relaxation. In this case, the total ^{3}He concentration trapped at SIA's and dislocation loops, c^D_{He}, would not contribute at all to swelling but would have to be subtracted from c_{He} to get the total He concentration in bubbles c^B_{He} controlling swelling. Equating, as before, the total volume available for He at dislocations $c^D_{He}v_{He}$ with the total excess volume $c_I(\Delta\tilde{v}_I-\Omega)$ we find

$$c^B_{He}\approx c_{He}\Omega/\Delta\tilde{v}_I . \tag{10}$$

Hence, $\Delta\tilde{v}_I/\Omega$ would be canceled in Eqs. (7) and (9) yielding a result expected for complete filling of all available "free space" with He.

The upper bounds of v_{He}/Ω for the two investigated tritides given in Table I agree surprisingly well. In calculating v_{He} from this quantity we have accounted for the lattice expansion in the volume available for a Ta atom Ω, due to the different tritium contents.

Applying a recently developed high-density equation of state for ^{3}He,[17] we obtain the pressure associated with v_{He}. In both cases, we find pressures of about 5 GPa.

Using the above pressure values we may estimate the correction associated with the elastic relaxation of the bubbles. Since the average dilatation in a bubble-containing sample would vanish only "image corrections" associated with the presence of a free sample surface[20] have to be considered. In the linear isotropic elastic continuum approximation the correction for spherical bubbles is

$$\frac{\delta v_{He}}{v_{He}} = -\frac{3}{2}\frac{1-2\nu}{1+2\nu}\frac{\hat{p}}{\mu} , \tag{11}$$

where ν is Poisson's ratio, μ the average shear modulus, and $\hat{p}$ is the pressure reduced by the stress due to the surface tension. Neglecting the surface tension effect and using $\nu=\frac{1}{3}$ and $\mu=70$ GPa we only find a correction of -3%.

Assuming the presence of single SIA's (or small SIA clusters) with $(\Delta\tilde{v}/\Omega)_I \approx 1.1$, rather than dislocation loops with $(\Delta\tilde{v}/\Omega)_I = 1$, we must consider a total reduction of the value of v_{He} obtained from Eq. (8) by about 13%. Using the high-density equation of state for He,[17] this corresponds to a pressure increase of about 50%. Hence, we expect pressures between 5 and 8 GPa.

Let us examine now whether these values are compatible with the current understanding of athermal He bubble growth. A necessary condition for the emission of a SIA-type metal defect by He-vacancy cluster or He bubble is that the decrease of the free energy of the He-vacancy cluster associated with such a process must at least be equal to (or larger than) the formation free energy of the SIA defect. This condition was discussed in detail recently for dislocation loop punching by small bubbles down to sizes of about 1 nm in diameter:[17]

$$p \gtrsim (2\gamma+\mu b)/r . \tag{12}$$

Here γ is the specific surface free energy of the metal, b is the magnitude of the Burgers vector of the dislocation loop and r is the radius of the bubble. An additional condition is that the force between the bubble and the dislocation loop must be repulsive over the whole dissociation path. This results in[18]

$$p \gtrsim 2\gamma/r+\mu/4\pi . \tag{13}$$

Conditions (12) and (13) are operative for $r \lesssim 4\pi b$ and $r \gtrsim 4\pi b$, respectively. Hence, the threshold pressure for loop punching will first decrease with increasing loop size but it will finally converge to a constant value around $\mu/4\pi$ (about half the theoretical shear strength). In our case, $p \gtrsim \mu/4\pi \approx 5.6$ GPa in agreement with the pressure range deduced from the swelling curves.

A pressure and density decrease during growth should be reflected in an increasing swelling rate. The expected time dependence of the latter is, however, so weak (due to the weak dependences of the density $n_{He}=1/v_{He}$ on the pressure $p \propto n_{He}^3$, and the radius r of the bubble on its volume $V \propto r^3$) that it is not surprising that we did not observe it in our experiment. Assuming condition (12), $p \propto n_{He}^3$, all He located in bubbles and a constant bubble density, we obtain the strongest time dependence to be $v_{He} \propto t^{1/8}$. The resulting increase in the swelling rate (9% in double the time) could be completely masked by other effects.

It is worth noting that the pressure ranges deduced from our swelling curves are in the vicinity of those determined by electron loss spectroscopy for He,[21,22] Ne, Ar, and Xe bubbles[23] and in addition by electron diffraction for Ne, Ar, and Xe bubbles[23] formed in Al after implantation at room temperature (around 4 GPa). This suggests that in all cases the same athermal bubble growth process occurs.

V. CONCLUSIONS

(1) The swelling of two selected Ta tritides was found to increase almost linearly with time.

(2) The resulting slopes normalized to T concentration were almost identical and yielded a ^{3}He-to-Ta atom volume (v_{He}/Ω) of (0.52 ± 0.03).

(3) The reciprocal of that value, the ^{3}He density in the highly pressurized ^{3}He bubbles, is in good agreement with less direct measurements of densities in high-pressure ^{4}He bubbles occurring after room-temperature ^{4}He implantation.

(4) Corrections were considered for the distribution of SIA's and for the elastic relaxation of the bubbles but were not found to change the above result significantly.

(5) Converting our experimentally determined densities to pressures using a high-density equation of state we obtained pressures of about 5 GPA of ^{3}He in our 1—2-nm diameter bubbles.

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