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The effect of the solute atomic size on the swelling of vanadium alloys

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Abstract

Addition of impurities to vanadium can substantially enhance its swelling. However, the swelling is accelerated only by 'undersized' and not by 'oversized' impurities. In this report we propose a mechanism of swelling acceleration in vanadium, which is based on the impurity effect on the elastic interaction of dislocations with point defects. It is shown that the segregation of impurity atoms at dislocations modifies the dislocation bias, the sign of the bias correction being opposite to that of the impurity misfit. Such bias modification should affect the swelling in qualitative agreement with the existing experimental observations for vanadium alloys. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Addition of solutes to structural materials can substantially modify their swelling behavior. For example, the addition of approximately 1 wt% Si noticeably decreases the swelling of Fe–Cr–Ni alloys, whereas 0.2 wt% Si sharply increases the swelling [1]. The most pronounced effect of impurity on swelling was observed during irradiation of vanadium alloyed with iron [2] or chromium [3]. Although pure vanadium, like all bcc metals, exhibits very low swelling as compared to austenitic stainless steels, addition of 5–10 wt% of solutes can increase the swelling rate of vanadium by two orders of magnitude, making it comparable to or even higher than that in fcc metals. One of the most striking features of the vanadium swelling acceleration by solutes is related to the effect of solute atomic size misfit. It has been demonstrated that swelling is accelerated only by 'undersized' solutes (Fe,Si,Cr), whereas those 'oversized' (Mo,W) do not modify the swelling rate [4].

The microstructural reasons for the effect of swelling acceleration by undersized solutes is not yet firmly established. As demonstrated by high-voltage electron microscopy [5], the dislocation evolution is not sufficiently modified in order to explain such enormous differences in swelling rate. An alternative possibility can be related to solute segregation at dislocations. As demonstrated by TEM [2], the onset of enhanced swelling in V–5%Fe is preceded by solute accumulation at dislocation lines and therefore it seems reasonable to assume that the reason for the swelling enhancement is related to modification of dislocation bias for interstitial absorption by these solute atmospheres.

The only analytical model devoted to the study of the modification of point defect absorption rate at dislocations [6] is based on the inverse Kirkendal effect accompanying solute segregation. It was demonstrated there, however, that this effect can only diminish dislocation bias and thus cannot explain the acceleration of swelling observed in Refs. [2,3].

In this work we propose another mechanism for dislocation bias modification by solute atmosphere. This mechanism is based on the fact that the primary reason for dislocation bias is the elastic interaction of dislocations with point defects [7]. In the cases when solute noticeably modifies the swelling behavior of a host material, the size of solute atoms is noticeably different

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from that of the host material atoms and thus solute segregation at dislocations should be accompanied by changes of the dislocation stress fields and, consequently, of dislocation bias factors for vacancies and interstitials.

2. Modification of dislocation stress field by solute atmosphere

Let us assume that the average concentration of impurity in material is $C_{g\infty} \ll 1$ and spatial variations of solute concentration are due only to the formation of solute atmospheres around dislocations. Then the solute concentration near a dislocation (i.e. in the cylindrical 'influence cell' V_d around the dislocation with the cell radius $R_\mathrm{d} \simeq (\pi\rho_\mathrm{d})^{-1/2}$, where ρ_d is the dislocation density) can be described as

$$C_g(\mathbf{r}) = C_{g\infty}\Psi(\mathbf{r}), \tag{1}$$

where

$$\Psi(\mathbf{r}) = \frac{\exp(\beta U_g)}{\rho_\mathrm{d}\int_{V_\mathrm{d}} \exp(\beta U_g)\,\mathrm{d}\mathbf{r}'}, \tag{2}$$

U_g is the energy of the solute interaction with dislocation, $\beta = 1/kT$ and kT has its usual meaning.

A particular spatial dependence of U_g depends on the solute distribution near the dislocation, in particular whether precipitation of the solute in dislocation core occurs. Below we assume that U_g is determined by elastic interaction of solute atoms with the trace of the dislocation stress field (Cottrell atmosphere), so that U_g is equal to [8]

$$U_g = -kTe_g\frac{R_0\sin\theta}{r}, \tag{3}$$

where e_g is the solute atom dilatation, r and θ are cylindrical coordinates related to the chosen dislocation and R_0 is the radius of point defect elastic interaction with the dislocation strain field,

$$R_0 = \frac{(1-2\nu)}{2\pi(1-\nu)}\gamma b, \tag{4}$$

where $\gamma = \beta K\Omega$, K is the bulk modulus of the material, Ω the atomic volume of the host material and b the value of the dislocation Burgers vector. In structural materials at typical irradiation temperatures of $T \sim 600$–800 K the value of γ is of the order of 10.

Solute atoms create in the surrounding material stress fields with the trace $\sigma_{g0}(\mathbf{r},\mathbf{r}') = 3K\Omega e_g\delta(\mathbf{r}\text{-}\mathbf{r}')$, where $\mathbf{r}$ is the observation point, $\mathbf{r}'$ the position of a solute atom, and δ the Dirac's delta function [9]. The trace of the total stress field, $\sigma_g(\mathbf{r})$, created by solute atoms in the vicinity of the dislocation is obtained by integration of σ_{g0} over the material volume, $\sigma_g(\mathbf{r}) = 3Ke_gC_g(\mathbf{r})$. The energy U_α of point defect interaction with the united stress field of the dislocation and the solute atmosphere is then equal to

$$U_\alpha = -kTe_\alpha\left(\frac{R_0\sin\theta}{r} + \gamma e_g C_{g\infty}\Psi\right), \tag{5}$$

where e_α is the point defect dilatation ($\alpha = i$ for interstitials and $\alpha = v$ for vacancies).

When the solute misfit is small, $\gamma|e_g| \ll 1$, the elastic interaction of the solute with dislocation is weak everywhere in the matrix up to the dislocation core radius r_0. Then $\Psi \simeq 1 + \beta U_g$ and

$$U_\alpha \simeq -kTe_\alpha(1 - \gamma C_{g\infty}e_g^2)\frac{R_0\sin\theta}{r}. \tag{6}$$

Thus, independent of the sign of the solute volume misfit, the primary effect of the solute in this case is the weakening of the dislocation stress field. On the contrary, when the elastic interaction of solute atoms with a dislocation is sufficiently strong at least near the dislocation core ($|e_g|R_0/r_0 \geqslant 1$), Eq. (1) predicts the segregation of the solute in the regions of local material compression ($e_g < 0$) or tension ($e_g > 0$) near dislocations and noticeable depletion of solute in the material matrix. Correspondingly, the angular dependence of U_α becomes strongly asymmetric.

3. Diffusion problem for point defects

The concentration C_α of α-type point defects in a cell around a dislocation is determined by the diffusion equation

$$\nabla^2 C_\alpha + \beta\nabla(C_\alpha\nabla U_\alpha) = 0, \tag{7}$$

with the boundary conditions that the concentration vanishes at the dislocation core radius and is maintained at a certain constant level $C_{\alpha\infty}$ at the outer boundary of the cell. It is convenient to look for the solution of Eq. (7) in the form [7]

$$C_\alpha(\mathbf{r}) = C_{\alpha\infty}\mathrm{e}^{-\beta U_\alpha/2}w_\alpha, \tag{8}$$

where w_α satisfies the boundary value problem

$$\nabla^2 w_\alpha + \left(\beta\,\nabla^2 U_\alpha - \frac{\beta^2}{4}(\nabla U_\alpha)^2\right)w_\alpha = 0, \tag{9}$$

$$w_\alpha(r = R_\mathrm{d}) = 1, \tag{10}$$

$$w_\alpha(r = r_0) = 0, \tag{11}$$

where we have assumed that at the outer cell boundary $\beta U_\alpha \ll 1$. Then the dislocation bias factor Z_α for α-type point defects is given by [10]:

$$Z_\alpha = -r_0\int_0^{2\pi}\left(\nabla w_\alpha + \frac{1}{2}\beta w_\alpha\nabla U_\alpha\right)\mathrm{e}^{-\beta U_\alpha/2}\,\mathrm{d}\theta. \tag{12}$$

Using the bias factors for vacancies and interstitials, one can obtain one of the main factors that determine the swelling behavior of materials [11], namely the dislocation bias for interstitial absorption $B = (Z_i/Z_v - 1)$. Below we concentrate on the modification of B by the solute segregation at dislocations.

Substituting Eq. (5) into Eq. (9), one obtains

$$\beta\,\nabla^2 U_\alpha - \frac{\beta^2}{4}(\nabla U_\alpha)^2 = -\frac{R_0^2}{4r^4}\left[e_\alpha^2(1-\gamma C_{g\infty}e_g^2\Psi)^2 - 4\gamma C_{g\infty}e_\alpha e_g^3\Psi\right]. \qquad (13)$$

In the case of small solute misfit ($\gamma|e_g| \ll 1$) this relation can be approximated as

$$\beta\,\nabla^2 U_\alpha - \frac{\beta^2}{4}(\nabla U_\alpha)^2 \simeq -\frac{R_0^2 e_{*\alpha}^2}{4r^4}, \qquad (14)$$

where $e_{*\alpha}$ is the re-normalized point defect dilatation,

$$e_{*\alpha} = e_\alpha\left[1-\gamma C_{g\infty}e_g^2\left(1+2\frac{e_g}{e_\alpha}\right)\right]. \qquad (15)$$

The value of the bias factor in this case has the well-known form [7]

$$Z_\alpha = \frac{2\pi}{\ln(R_\mathrm{d}/|e_{*\alpha}|R_0)} \qquad (16)$$

and the modification of the dislocation bias B due to the solute is given by

$$B = B_0\left(1+\frac{2\gamma C_{g\infty}e_g^3(e_i-e_v)}{e_ie_v\,\ln|e_i/e_v|}\right), \qquad (17)$$

where B_0 is the bias in the absence of impurity. Note that the modification of B is sensitive to the sign of the solute misfit. Since usually $e_i > 0$ and $e_v < 0$, an undersized solute ($e_g < 0$) increases the dislocation bias, whereas an oversize solute decreases it.

Due to the requirement of small solute misfit, $|e_g| \ll 1/\gamma \simeq 0.1$ and at typical dilatation values $e_i \simeq 1.2$, $e_v \simeq -0.2$ [12] and $C_{g\infty} \simeq 5\%$ the value of the correction term in Eq. (17) does not exceed 0.5%. However, in application relevant materials the values of solute volume misfit can reach 0.3–0.4 (e.g. for iron or silicon impurity atoms in vanadium [4]), when the approximation $\gamma|e_g| \ll 1$ is no longer valid and Eq. (9) should be solved using the full expression (13). Since no analytical solution is possible in this case, we have solved Eq. (9) numerically by a finite difference method.

The resulting behavior of the bias as a function of the solute misfit e_g is shown in Fig. 1. The curves are obtained for host material parameters corresponding to vanadium, the dislocation density $\rho_\mathrm{d} = 10^8$ cm^{-2} and the temperature $T = 800$ K. It can be seen that at $|e_g| \geqslant 0.2$ the value of the bias factor begins to quite noticeably deviate from its solute-free value B_0. Sufficiently high concentration of solutes with dilatation $|e_g| \simeq 0.3$ can increase the bias by a factor of two (undersized solutes) or totally suppress the bias (oversized solute).

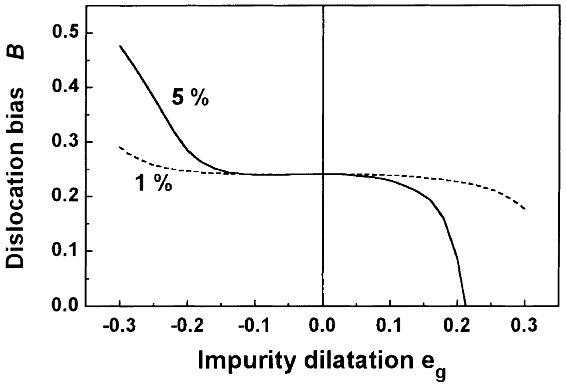

Fig. 1. Dislocation bias factor B as a function of the solute dilatation e_g for solute contents $C_{g\infty} = 1\%$ (a) and 5% (b).

The modification of the dislocation bias can affect the swelling in two ways. First of all, the swelling rate at the steady stage is directly proportional to B. However, the steady swelling rate in vanadium (if achieved) is expected to reach sufficiently high values of 1–2% dpa [13] and the modification of B by several tens percent is not of much importance in accelerating it. Second, the modification of the dislocation bias changes the critical radius of the void nucleation R_c, which is related to B as

$$R_\mathrm{c} \simeq \frac{2\gamma}{BD_\mathrm{v}\Delta_\mathrm{v}}, \qquad (18)$$

where D_v and δ_v are the vacancy diffusion coefficient and supersaturation, respectively. Since both the void nucleation rate and the swelling incubation time exponentially depend on the critical void size, modification of B can substantially affect the nucleation of voids, if the value of R_c falls in the range where the void nucleation barrier is highly sensitive to the critical radius modification. The latter condition is sensitive to a particular material and vanadium seems to be the case where it is satisfied. If so, the increase of the dislocation bias by undersized solute should accelerate the onset of swelling in vanadium alloys as compared to pure vanadium. On the contrary, oversize solutes can only delay the swelling. Since in pure vanadium the steady-state swelling does not arise at doses as high as 100 dpa, this means that the presence of oversized solutes practically do not affect the swelling behavior of vanadium. Both of these trends are in good qualitative agreement with the experimental observations [4].

4. Conclusions

In this paper we demonstrate that the accumulation of solutes at dislocations in vanadium can noticeably modify the dislocation bias for interstitial absorption and thus affect the onset of swelling. It is shown that undersized solutes increase the dislocation bias, thus accelerating the onset of swelling as compared to pure vanadium, whereas the oversized solutes can only slow down the swelling (which in pure vanadium is already quite low). These trends qualitatively correlate with experimental observations.

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References

[1] N. Sekimura, F.A. Garner, J.W. Newkirk, J. Nucl. Mater. 191–194 (1992) 1244.
[2] H. Matusui, D. Gelles, Y. Kohno, in: Effects of Radiation on Materials, 15th Int. Symp., ASTM STP1125, ASTM, Philadelphia, 1992, p. 928.
[3] F.A. Garner, D.S. Gelles, H. Takahashi, S. Ohnuki, H. Kinoshita, B.A. Loomis, J. Nucl. Mater. 191–194 (1992) 948.
[4] H. Nakajima, S. Yoshida, Y. Kohno, H. Matsui, J. Nucl. Mater. 191–194 (1992) 952.
[5] D.S. Gelles, S. Ohnuki, H. Takahashi, H. Matsui, Y. Kohno, J. Nucl. Mater. 191–194 (1992) 1336.
[6] Yu.V. Konobeev, V.A. Pechenkin, S.I. Rudnev, J. Nucl. Mater. 233–237 (1996) 1070.
[7] F.S. Ham, J. Appl. Phys. 46 (1959) 915.
[8] J.P. Hirth, J. Lothe, Theory of Dislocations, McGraw-Hill, NewYork, 1968.
[9] J.D. Eshelby, Solid State Physics, vol. 3, Academic Press, New York, 1956, p. 79.
[10] V.A. Borodin, A.I. Ryazanov, J. Nucl. Mater. 135 (1985) 46.
[11] A.D. Brailsford, R. Bullough, J. Nucl. Mater. 44 (1972) 121.
[12] H. Wollenberger, in: Physical Metallurgy, 3rd ed., Elsevier, Amsterdam, 1983, p. 1140.
[13] V.A. Borodin, A.I. Ryazanov, J. Nucl. Mater. 210 (1994) 258.