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NEW INSIGHTS ON THE MECHANISMS CONTROLLING THE NICKEL DEPENDENCE OF SWELLING IN IRRADIATED Fe-Cr-Ni ALLOYS

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NEW INSIGHTS ON THE MECHANISMS CONTROLLING THE NICKEL DEPENDENCE OF SWELLING IN IRRADIATED Fe-Cr-Ni ALLOYS - J. J. Hoyt, Washington State University and F. A. Garner, Pacific Northwest Laboratory[a]

OBJECTIVE

The object of this effort is to determine the origins of radiation-induced changes in structural materials.

SUMMARY

In a previous report[1] the interstitial and vacancy biases for an edge dislocation in a binary alloy were examined, assuming the existence of an equilibrium Cottrell atmosphere around the line defect. The Larche' and Cahn treatment of stress relaxation due to a solute atmosphere was employed with the Wolfer and Ashkin formulation for the bias of an edge dislocation to compute the bias as a function of nickel concentration in the Fe-Ni system. Using the minimum critical void radius concept, the concentration-dependent bias was shown to offer a plausible explanation for the minimum in swelling observed at intermediate nickel levels and the gradual increase in swelling at higher nickel levels. In this report, a more realistic description of the composition dependence of vacancy diffusion has also been included, an addition which improves the model substantially.

PROGRESS AND STATUS

Introduction

The swelling behavior of irradiated metals is strongly dependent on composition. For example, in Fe-Cr-Ni alloys the swelling at relatively high temperatures decreases strongly with nickel until some intermediate level of 40-60% nickel is reached.[2] Thereafter, increases in nickel result in a more gradual increase in swelling. The strong decreases observed in swelling of austenitic alloys can be partially explained by the effect of various solute additions (Ni,Si,P) on vacancy diffusivity.[3-7] However, at present, no mechanism has been advanced for the slow upturn at higher nickel levels.

Although many studies have investigated the concentration dependence of various material parameters, few have considered the effect of compositional variations on microstructural bias factors. The interaction of a point defect, interstitial or vacancy, with the stress field of a given defect sink determines the bias toward one point defect over the other. Since the stress field is altered in the presence of a solute species, one would intuitively expect the bias to be dependent on its concentration.

Consider a binary alloy in which the solute atoms are oversized; i.e., the lattice parameter of the solute in the pure state is larger than that of the host species in its pure state. To reduce the total strain energy of a dislocation, the solute will tend to segregate on the tensile side and be repelled from the compressive side. In equilibrium a Cottrell atmosphere is established. Although this effect has long been known, it was only recently shown that the change in the stress field around a dislocation could be computed for concentrated solutions. We examine here the effect this change in stress field has on bias factors for edge dislocations in Fe-Ni alloys.

Marwick[8] computed the bias for a free surface due to solute redistribution by numerically solving the diffusion equations for solute, vacancy and interstitial species. The Marwick scheme is the preferred method of computing bias factors, but for a general distribution of defect sinks with non-homogeneous stress fields, the numerical solutions to the diffusion equations become quite intractable. We shall take a simpler approach and compute an <u>initial</u> bias by estimating the change in the stress field around an edge dislocation due to a Cottrell atmosphere. The emphasis on the word <u>initial</u> arises from the knowledge that sinks often become further enriched in various solutes via radiation-induced segregation.

Theoretical Background

Larche' and Cahn[9] have developed a general theory for the thermochemical equilibrium of solids under nonhydrostatic stress. A Cottrell atmosphere is one application of the theory and it was shown that the

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stress field with the solute atmosphere present is given by the stress field for a pure material but with the various elastic constants replaced by the open-field elastic constants. These constants, denoted by *, are given by

$$E^* = E/(1 + \chi\eta^2 E) \tag{1a}$$

$$\nu^* = (\nu - \chi\eta^2 E)/(1 + \chi\eta^2 E) \tag{1b}$$

$$(\kappa^{-1})^* = 3\ (1 - 2\nu^*)/E^* \tag{1c}$$

where linear elasticity has been assumed. The parameters E, κ and ν are, respectively, the elastic and bulk moduli and Poisson's ratio. The quantity η is the fractional change in the lattice parameter (a) with composition (c); i.e.,

$$\eta = \frac{1}{a}\left(\frac{da}{dc}\right) \tag{2}$$

Finally, χ is given as $(f'')^{-1}$, where f'' is the second derivative of the free energy with composition. All parameters are evaluated at the average concentration.

To model in an approximate way the Fe-Ni system, the various material parameters need to be evaluated. In general, E, κ and ν are dependent on the average concentration, but for simplicity we assume they are constant. The values employed for the subsequent computations are the same as employed in an earlier study and represent conditions typical of fast reactor irradiation.[10] The fractional change in lattice parameter is found by assuming a linear dependence vs. the concentration of Ni; i.e., Vegard's law. Lattice parameters of pure Ni and pure Fe are readily obtained.

To estimate χ, a model for the free energy of mixing in Fe-Ni must be assumed. (Since we are ultimately concerned with the second derivative, the free energy and free energy of mixing can be used interchangeably.) The simplest nontrivial free energy model is the regular solution approximation with a free energy of mixing of the form

$$f = \omega c(1 - c) + RT(c \ln c + (1 - c)\ln(1 - c)) \tag{3}$$

where c is the Ni concentration, R is the gas constant and ω is an interaction parameter. The first term on the right of Equation 3 is the temperature-independent enthalpy of mixing, ΔH. By adjusting ω to fit the experimentally measured ΔH, a better approximation to ΔH is established.

Figure 1 shows the enthalpy of mixing data for Fe-Ni measured by Kubaschewski et al.[11] and the assumed model used in the calculations (ω = 8510 J/mol). The assumed ΔH vs. c model is a reasonable approximation up to the Invar concentration but is rather poor at higher Ni levels. Nevertheless, for the first evaluation we expect the results to be qualitatively correct.

Using a perturbation technique for non-linear diffusion equations, Wolfer and Ashkin[12] derived the bias of an edge dislocation. In the absence of applied stress the bias is

$$Z_{i,v} = 1 + \left(\frac{Bo_{i,v}}{kt}\right)^2 / [16a^2 \ln(\frac{R}{a})] \tag{4}$$

where R and a are outer and inner cutoff radii respectively, measured in units of the Burgers vector and k is the Boltzmann's constant. The subscript i or v refers to interstitial or vacancy. The quantity $Bo_{i,v}$ is given by

$$Bo_{i,v} = v_{i,v} K\ (1 - 2\nu)/2\pi\ (1 - \nu) \tag{5}$$

where $v_{i,v}$ is the difference between the defect volume and atomic volume.

Equation 5 was derived assuming a stress field around a dislocation in an compositionally homogeneous alloy. We now examine the change in Z when the stress field relaxation is due to a solute atmosphere. Thus, Equations 1-3 are employed in conjunction with Equations 4 and 5 to arrive at the initial bias as a function of average Ni concentration.

Figure 2 shows the ratio of Z_i over Z_v vs. concentration of Ni (C_{Ni}) at various temperatures. The curves are symmetric about C_{Ni} = 0.5, a direct consequence of employing the regular solution approximation. The magnitude of the change in Z_i/Z_v is only a few percent, but this small change can have a large effect on the swelling behavior.[13,14] Note that the change of Z_i/Z_v is more pronounced at lower temperatures. Recall, however, that the bias is only one factor which controls void nucleation and growth.

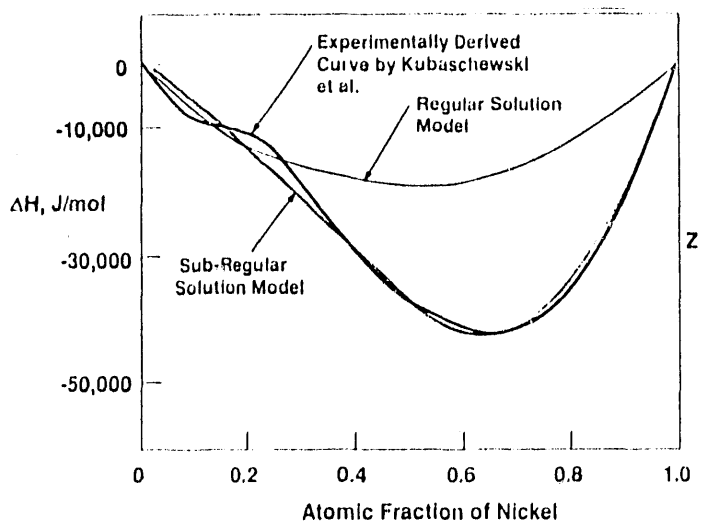

FIGURE 1. Mixing Enthalpies of Solid Fe-Ni Alloys, as Published by Kubaschewski and Coworkers[11] and the Regular and Sub-Regular Models Assumed in This Study for Illustration Purposes.

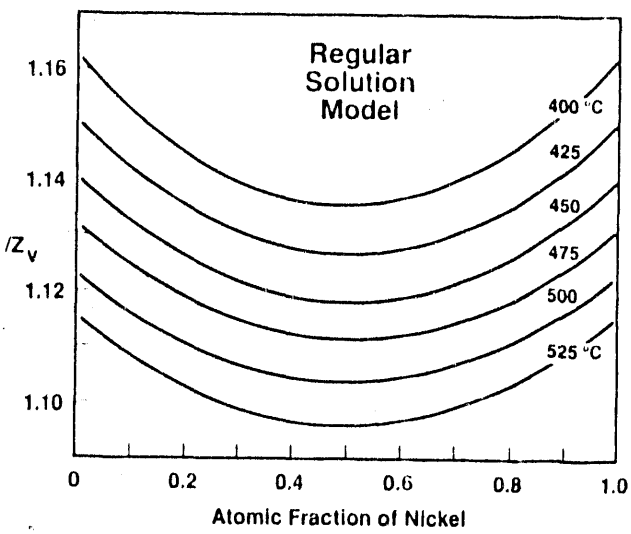

FIGURE 2. Calculated Ratio of Z_i/Z_v vs. Nickel Concentration for Various Irradiation Temperatures.

The interactive effect of a concentration-dependent bias factor and other relevant parameters on swelling behavior can be examined using the concept of a minimum critical radius, R_{mc}. For a void to grow it must nucleate as a vacancy cluster and reach a critical size. Below this critical size, a cavity will spontaneously decrease in size unless stabilized by gas atoms.

The bubble to void conversion idea was first discussed by Sears[13], and later developed by Odette and Stoller[14] and Coghlan and Mansur.[15] It was also employed by Coghlan and Garner[10] to examine the effect of Ni concentration on R_{mc} in simple austenitic alloys. The latter study focused on the effect of compositional changes in vacancy diffusivity on the minimum critical radius. The equations involved in the computation of R_{mc} are lengthy and the reader is referred to reference 13 for details. The various material and kinetic parameters needed are identical to those of reference 10. In the following it is assumed that the system bias is equal to the bias of an edge dislocation; i.e., that the ratio of void bias for an interstitial to that of a vacancy is unity. This may not be completely accurate but it is a common assumption and simplifies the calculation.

Figure 3 shows the critical radius of Fe-Ni alloys vs. C_{Ni} at 475°C. Again due to the symmetric form chosen for the free energy, a peak is observed at $C_{Ni} = 0.5$ with an approximately 10% increase in R_{mc} over that of the pure metals. Figure 3 suggests that the swelling behavior of Fe-Ni would also be symmetric. However, this conclusion neglects changes in vacancy diffusivity, the importance of which has been stressed in earlier papers.[2-7] In particular, it was shown that changes in the pre-exponential factor D_v^o with Ni content are very important. As shown in Figure 4 D_v^o is a moderately strong function of nickel content in Fe-Ni alloys, peaking at intermediate nickel levels.

Esmailzadeh and Kumar[6] define the effective vacancy diffusion coefficient as

$$D_v^{eff} = D_{Fe,v} C_{Fe} + D_{Ni,v} C_{Ni} \tag{6}$$

where C is the concentration and $D_{Fe,v}$ is the tracer diffusion coefficient normalized by the equilibrium concentration of vacancies; i.e., $C_v^{eq} = \exp(-\Delta H_f/kT)$.

Thus,

$$D_v^{eff} = [D_o^*(Fe) C_{Fe} + D_o^*(Ni) C_{Ni}] \exp(-\Delta H_m/kT) \tag{7}$$

where the term in brackets is D_v^o.

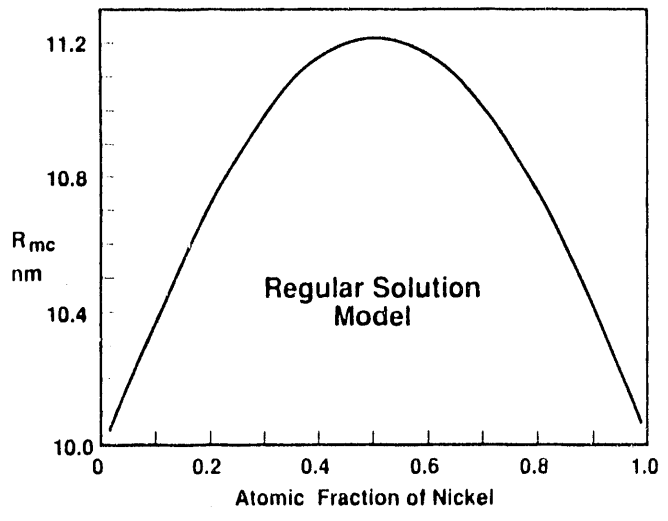

FIGURE 3. Calculated Values of Minimum Critical Radius of FeNi Alloys at 475°C, Assuming the Regular Solution Model.

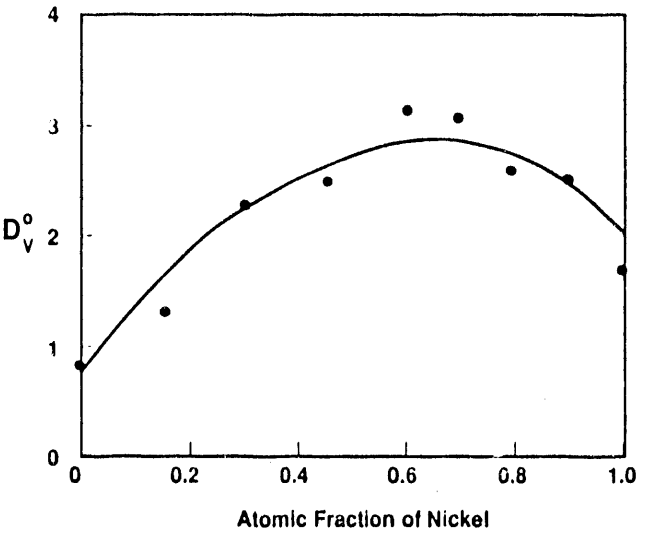

FIGURE 4. Dependence of D_v^o in Fe-Ni Alloys, on Nickel Content, Derived from D_v^* Values of Ruzikova', Million and Kucera.[16]

The quantities D_o^* for Fe and Ni in Fe-Ni binaries are given by Ruzikova', Million and Kucera[16] and were used to calculate D_v^o in Figure 4. The parabolic fit also shown in 4 was used with the sub-regular solution model for the enthalpy of mixing to calculate the bias factors for an edge dislocation (Figure 5) and the resulting minimum critical radius (Figures 6 and 7). In the sub-regular model the interaction parameter ω is assumed to be concentration dependent. In Figure 1 a sub-regular model fit was obtained by assuming that ω varied linearly with nickel concentrations.

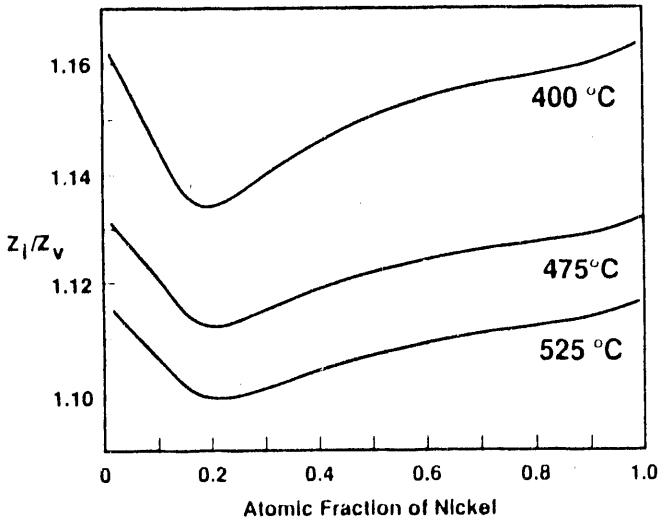

FIGURE 5. Calculated Values of Z_i/Z_v vs Nickel Concentration for Various Irradiation Temperatures, Using the Sub-Regular Solution for Mixing Enthalpy.

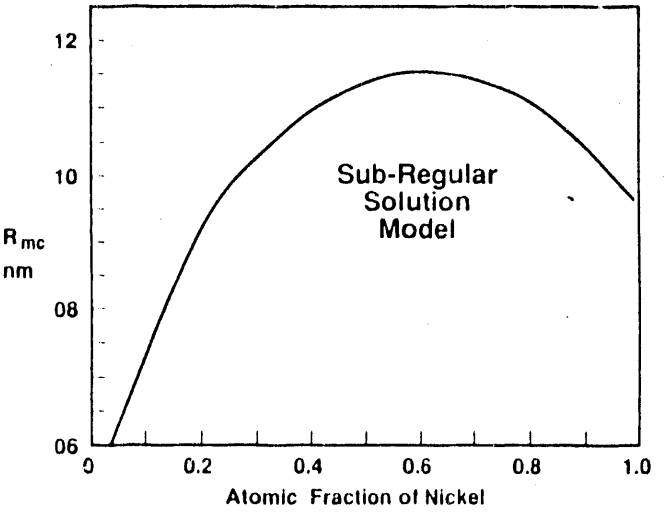

FIGURE 6. Calculated Values of Minimum Critical Radius of FeNi Alloys at 475°C.

The change in R_{mc} with nickel content is also a function of temperature and increases strongly at higher temperatures. Note that the asymetric maxima in Figures 6 and 7 offer a plausible explanation for the observed gradual upturn in swelling at high Ni levels. A similar conclusion cannot be drawn by considering solely the impact of changes in D_v^o.

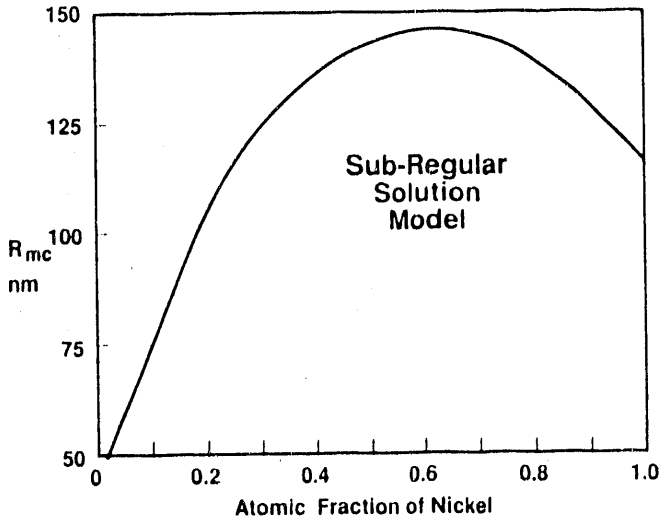

FIGURE 7. Calculated Values of Minimum Critical Radius of FeNi Alloys at 525°C. Note Large Increase of Radius Relative to That at 475°C.

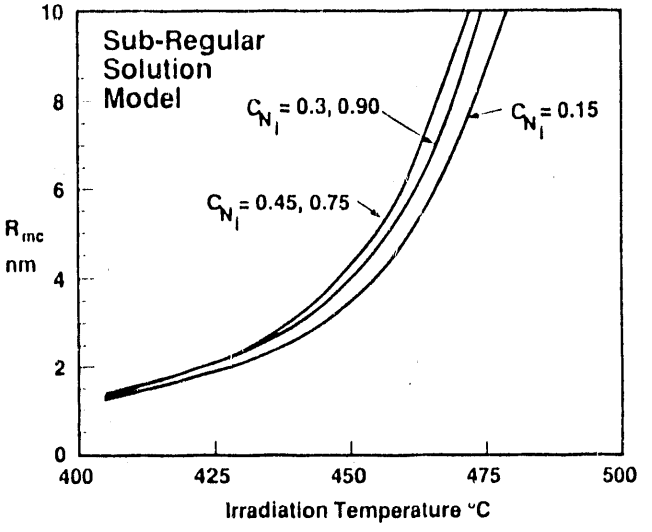

FIGURE 8. Minimum Critical Radius as a Function of Irradiation Temperature and Composition, Calculated Using Composition-Dependent Values of D_v^o and ω.

Figure 8 shows a plot of R_{mc} vs. temperature for various nickel levels. These curves show that R_{mc} is not very sensitive to nickel or temperature at relatively low temperatures, but is a steep function of temperature at higher temperatures while being moderately sensitive to nickel, all in agreement with experimental observations[5].

Discussion

It must be stressed that the composition-dependent bias presented in this work refers to an initial bias. The Larche' and Cahn formalism for the solute atmosphere around an edge dislocation refers to a system in thermal equilibrium. During irradiation, a material cannot be considered in equilibrium, and dynamic factors such as the inverse Kirkendall effect or solute drag become important. In the Fe-Ni-Cr system, nickel always segregates at microstructural sinks. It would be unjustified to extend the above ideas to the steady-state swelling behavior at late times without incorporating the time dependence of C_{Ni} at the sinks. Wolfer and coworkers have shown that segregation of nickel at sinks changes their bias.[17,18]

CONCLUSIONS

Changes with composition of the pre-exponential coefficient for vacancy diffusion have previously been invoked to explain the rapid decrease in swelling with Ni additions in irradiated steels. However, this factor alone cannot explain the gradual increase in swelling with Ni content for $C_{Ni} \geq 0.5$. It has been shown that the combined effect of a concentration-dependent bias factor and changes in D_v^o offers one possible explanation for the swelling behavior in Fe-Ni. The change in bias was assumed to arise from the existence of a Cottrell atmosphere of nickel atoms around the dislocations.

FUTURE WORK

This effort will continue, exploring the interaction between the Cottrell atmosphere effect and other composition-dependent operating mechanisms.

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