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VOID SWELLING AND SEGREGATION IN DILUTE NICKEL ALLOYS*

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Five binary alloys containing 1 at. % of Al, Ti, Mo, Si and Be in nickel were irradiated at temperatures from 525 to 675°C with 3.5-MeV $^{58}Ni^{+}$ ions. The resultant microstructures were examined by TEM, and void diameters, number densities and swelling are presented for each alloy over the temperature interval investigated. A systematic relation between solute misfit (size factor) and void swelling is established for these alloys. Solute concentration profiles near the irradiated surface were determined and these also exhibited a systematic behavior--undersize solutes segregated to the surface, whereas oversize solutes were depleted. The results are consistent with calculations based on strong interstitial-solute trapping by undersize solutes and vacancy-solute trapping by oversize solutes that are weak interstitial traps.

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Introduction

Void swelling in pure nickel irradiated with Ni^+ ions has been measured by several investigators, including Ryan (1) and Sprague et al. (2). Okamoto et al. (3) have investigated the effects of small additions of Be on void swelling of Ni. In addition, Okamoto et al. (4), Wiedersich et al. (5) and Johnson et al. (6) have presented theoretical models and calculations that treat defect-trapping effects on void swelling, irradiation-induced segregation, and segregation effects on void swelling. These calculations predict that the magnitude of void swelling and irradiation-induced segregation are directly related to the solute-defect binding energies and may also depend on whether solute-interstitial or solute-vacancy binding predominates. The present investigation seeks to establish experimentally the effects of a series of solute elements in nickel on both void swelling and segregation. Five binary alloys of 1 at. % Al, Ti, Mo, Si and Be in nickel were investigated after high-temperature irradiation by TEM for void swelling and by Augér spectroscopy for the depth distribution of solute near the irradiated surface. Al, Ti and Mo are oversized in nickel with misfits of +0.052, +0.10 and +0.12, respectively. Here, misfit is the fractional change in lattice parameter of solid solutions with solute concentration per atom fraction of solute addition. These oversize solutes are not expected to form the mixed-dumbbell interstitials but rather a more weakly bound interstitial-solute complex (7). These solutes may also be vacancy traps. Si and Be are undersized with misfits of -0.025 and -0.12, respectively, and these elements produce strong interstitial traps (7).

Experimental Procedure

The alloys were irradiated at the ANL Dual-ion Facility with 3.5-MeV $^{58}Ni^+$ ions. The irradiation procedures have been described in detail elsewhere (8). Vacuum pressures during irradiation were always in the 10^{-8} torr range. The thermocouples inserted in the tungsten blocks holding sets of four samples were used to monitor and control the nominal irradiation temperatures of 525, 575, 625 and 675°C. The individual sample temperatures, read with the beam off using an infrared pyrometer, are included in the present paper.

The damage doses were calculated by the Brice codes RASE3 and DAMG2 (9) using a displacement energy of 40 eV. The dose reported for the TEM samples was calculated at the section depth. The samples were generally extracted at a depth of ∿5500 Å, somewhat short of the peak damage depth of 6500 Å. Doses for samples examined by Auger spectroscopy are quoted for a depth of 5500 Å beneath the surface. The peak damage rate is ∿2.5×10^{-3} dpa/s for an ion flux typical of our work, ∿2.1×10^{12} ions/cm^{2}s.

The void-swelling parameters were determined using a 100-kV TEM and a commercial particle-size analyzer. Foil thicknesses were determined using conventional stereo techniques. Auger analysis was performed using a primary electron beam of 5 kV and 10 μA to excite the transitions. Depth profiling was performed by sputtering with 1-kV argon ions, which produced a measured sputtering rate of ∿0.8 Å/s. Sputtering was interrupted during the time when spectra were recorded to increase the sensitivity.

Results

All TEM results reported here were obtained from samples irradiated to a nominal dose of 2 dpa. The measured average void size, void number density and swelling are summarized in Table I. Figure 1 shows the temperature

dependence of void swelling for the alloys. The curve for pure nickel was estimated from data of Ryan (1) and Sprague et al. (2) by linearly scaling the swelling determined by these authors to a dose of 2 dpa.

In general, the solutes suppress swelling over most of the temperature range, except for Al, which exhibits greater swelling than pure Ni at the highest irradiation temperature of 675°C. Johnston (10) also found that ∿1 at. % Al enhanced swelling in the austenitic alloy Fe-15Cr-20Ni at 675°C, the peak swelling temperature of that alloy. The undersize solutes, Be and Si, eliminate swelling at 2 dpa except for the highest irradiation temperature where some swelling is observed in Ni-1 at. % Be. The Be alloy contained profuse precipitates at the two lowest irradiation temperatures. The precipitation in the alloy, which is a solid solution throughout the temperature range in the absence of irradiation, is attributed to irradiation-induced segregation (4,5). Precipitates were not observed in the Be sample irradiated at 617°C; this sample also showed zero swelling. The Be sample irradiated at 690°C did not contain precipitates in the matrix, but the

Table I. Measured Void Parameters

Irradiation Temperature (°C)	Dose (dpa)	Void Diameter (Å)	Number Density (x 10^{-15} cm^{-3})	Swelling (%)
Ni-1 at. % Al				
505	1.7	158	0.88	0.21
575	1.5	247	0.56	0.50
620	1.9	437	0.06	0.28
667	1.6	372	0.27	0.81
Ni-1 at. % Ti				
525	1.7	137	1.54	0.23
575	1.4	231	0.37	0.27
639	1.9	0	0	0
656	1.9	295	0.09	0.15
Ni-1 at. % Mo				
525	1.7	146	1.5	0.28
575	1.6	174	0.42	0.14
613	2.0	264	0.05	0.05
647	1.9	0	0	0
Ni-1 at. % Si				
517	2.0	115	0.005	0.00013
575	2.0	109	0.022	0.005
620	1.9	103	0.007	0.0004
681	1.6	0	0	0
Ni-1 at. % Be				
512	2.2	0	0	0
575	2.1	128	0.027	0.004
617	1.4	0	0	0
690	1.5	270	0.1	0.13

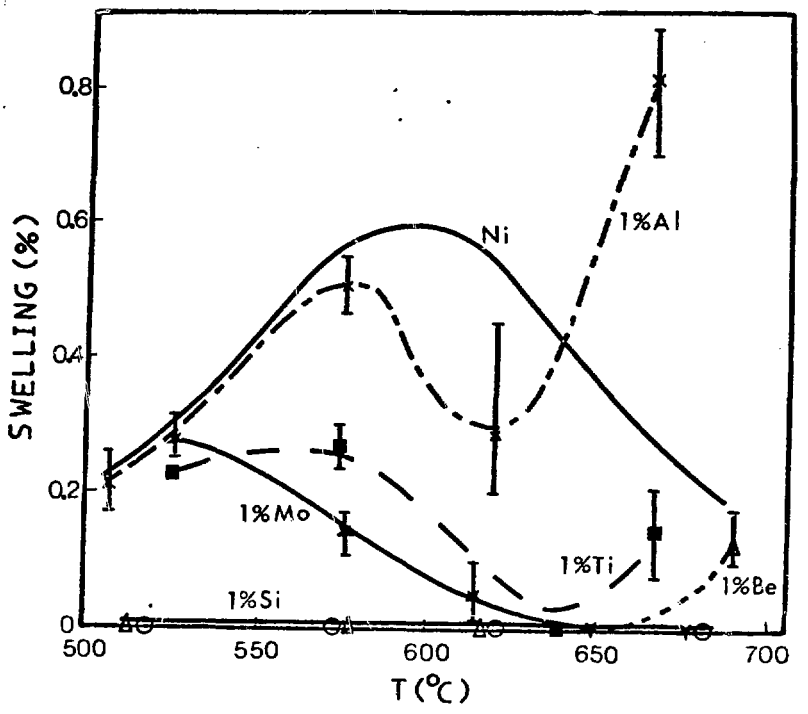

Fig. 1 - Void swelling as a function of temperature for the five binary alloys investigated. See text for discussion of Ni curve.

∿270 Å voids were clearly coated with a thin shell of precipitate. With the possible exception of the 1 at. % Mo and 1 at. % Ti alloys at ∿625°C, none of the other alloys contained precipitates. After irradiation at ∿625°C, the Mo and Ti samples contained an extremely fine (≲20 Å) and dense dispersion of precipitates or defect aggregates that appeared as "black-spot" damage.

The oversize solutes Al, Ti and Mo are effective in reducing void swelling, as Figure 1 demonstrates. Unlike the undersize solutes, they tend to be less effective at the lower irradiation temperatures where the swelling curves for the alloys with Al, Mo and Ti rejoin the curve for pure nickel. The oversize solutes are most effective in suppressing swelling at temperatures slightly above the peak swelling temperature for Ni where Ti and Mo reduce swelling at ∿2 dpa to near zero. The effectiveness of the oversize solutes in reducing the swelling of nickel decreases in the order Al, Ti and Mo at the intermediate temperatures, as can be seen in Figure 1.

Typical results of the Auger analyses are presented in Figure 2. Auger spectra were obtained in the usual fashion as first derivatives of the number of secondary electrons emitted from the sample surface with respect to energy. As a first approximation, the concentration of a given element can be assumed proportional to the peak-to-peak height of this derivative at an appropriate transition energy of the element. The ratio of solute peak-to-peak heights to that of nickel is plotted in Figure 2. The value of this ratio at depths ≳2500 Å, where the signal no longer changes appreciably with depth, reflects the concentration of the bulk alloy, i.e., 1 at. % solute.

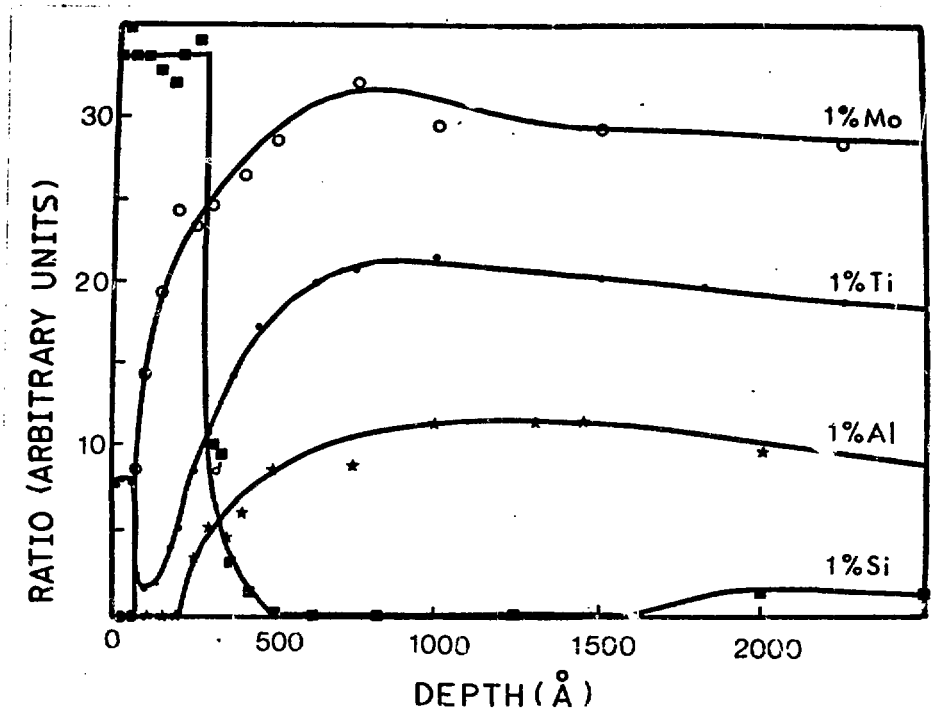

Fig. 2 - Peak-to-peak ratio of solute-to-Ni lines as a function of depth obtained by Auger spectroscopy. The samples were irradiated as follows: Ni-Si, 8.5 dpa at 560°C; Ni-Al, 10.7 dpa at 620°C; Ni-Ti, 8.5 dpa at 575°C; Ni-Mo, 11.2 dpa at 617°C.

Results presented in Figure 2 show that the undersize solute Si is enriched at the irradiated surface, whereas the oversize solutes are depleted. Considerably more transport of Si is required to produce its measured profile than for the other three elements investigated. The Ni-to-Si ratios near the surface agree well with tabulated values for Ni containing ∿25 at. % Si. This shows that the Si couples very strongly with the defect flux to the surface. This coupling is sufficiently strong to produce a precipitate film of Ni_3Si ∿300 Å thick at the irradiated surface. We have used TEM to observe these precipitate films, with thicknesses as great as 5000 Å, in irradiated two-phase alloys of Ni-12.7 at. % Si (11). Unirradiated control samples did not contain the film. As can be seen in Figure 2, the enrichment of Si at the irradiated surface causes an Si-depleted region extending to a depth of ∿2000 Å. The Be concentration in Ni could not be obtained by Auger spectroscopy because of serious overlap of the lines. Pronko et al. have shown by depth profiling with the p-d reaction of Be that the Be concentration profiles are similar to those of Si; a strong enrichment at the surface and a depletion at intermediate depth (12). For the alloys with oversize solutes depletion at the surface is accompanied by slight enrichment extending to a depth of ∿2000 Å. These near-surface depleted regions have also been observed with TEM (13) in a two-phase Ni-12.8 at. % Al alloy. Similar to regions surrounding internal sinks for defects (loops and voids), the surface regions do not contain γ' precipitates that are homogeneously distributed

throughout the remainder of the alloy. The dimensions of the solute depleted and enriched regions as functions of irradiation dose and temperature are currently being investigated.

Discussion

The present results show that the undersize solutes Si and Be suppress swelling at low doses much more strongly than the oversize solutes Al, Ti and Mo. Auger results show that the undersize solute Si segregates to the irradiated surface, whereas the oversize solutes are depleted at this surface. In addition, results of Pronko et al. (12) show that Be in Ni-1 at. % Be segregates to the irradiated surface. We now wish to show that the results are consistent with strong interstitial-solute trapping for undersize solutes as mixed dumbbells and with a less strong interstitial trapping as immobile complexes and/or vacancy-solute trapping for oversize solutes.

Segregation effects will be neglected in the present discussion of the effects of defect trapping by solutes on void swelling. The more general case that includes segregation has been presented by Okamoto et al. (4). In the present case, swelling as a function of temperature was calculated using the Wiedersich (14) rate theory modified for defect trapping according to the hindered diffusion model of Schilling et al. (15) and also for enhanced thermal vacancy concentrations as discussed by Okamoto et al. (4). The results of these calculations, using parameters typical of moderately damaged Ni, are presented in Figure 3. The interstitial-solute binding energies for

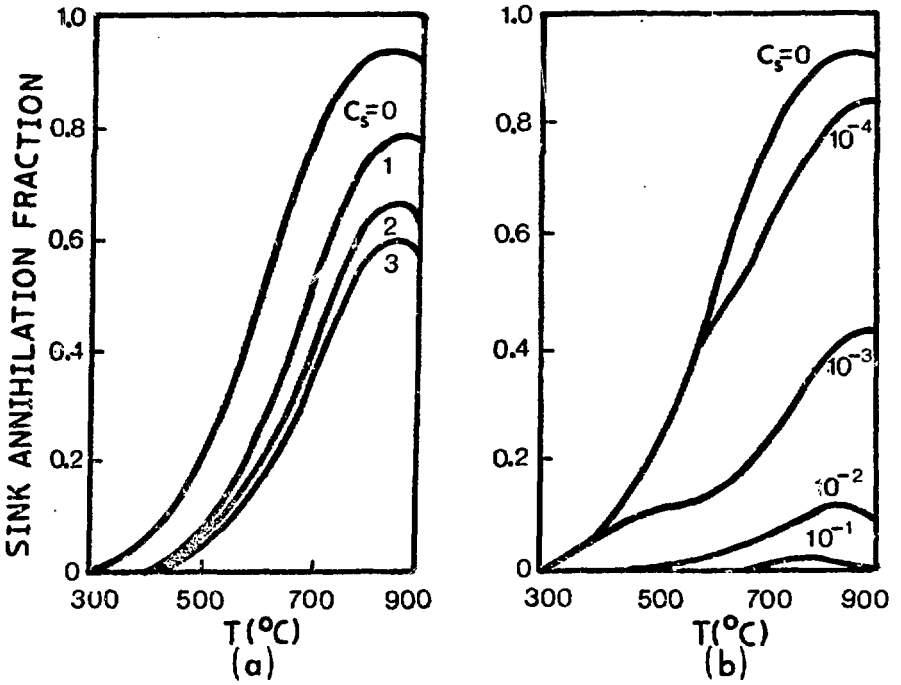

Fig. 3 - Calculated swelling curves for (a) vacancy-solute trapping and (b) interstitial solute trapping. Parameters (6) used in these calculations are 10^{-3} dpa/s, $P_I = P_V = 10^{-4}$, $H_V^M = 1.28$ eV, $H_V^F = 1.60$ eV, $H_I^M = 0.15$ eV, $\nu_I^o = 5\times10^{12}$/s, $\nu_V^o = 5\times10^{13}$/s, and for (a) $H_{Iia}^B = 0$, $H_{Iib}^B = 0$, $H_{vi}^B = 0.2$ eV and for (b) $H_{Iia}^B = 1.88$ eV, $H_{Iib}^B = 1.13$ eV and $H_{vi}^B = 0$.

configurations a and b, as described by Johnson and Lam (6), were chosen in accordance with the conventions suggested by these authors. A vacancy-solute binding energy of 0.2 eV was chosen as typical of the upper limit of experimentally observed binding energies.

Figure 3 demonstrates that swelling is suppressed much more effectively by strong interstitial trapping than by vacancy trapping. At solute concentrations as low as 10^{-2} at. %, swelling has almost been eliminated by interstitial trapping. However, such low solute concentrations have almost no effect in the vacancy trapping case where concentrations $\gtrsim$1 at. % are required to produce a significant reduction in swelling.

Calculations by Dederichs et al. (7) based on solute-size misfit suggest that the interstitial-solute binding energy increases as the misfit increases. In addition, these calculations show that interstitial-solute complexes, i.e., mixed dumbbells, exist only for undersize solutes. This is in agreement with the experimental work of Swanson et al. (16). Thus, one expects that Be and Si in Ni would behave as strong interstitial traps, and the experimentally observed void-swelling suppression agrees with the calculations for this case, Figure 3b. Likewise, one would expect the oversize solutes Al, Ti and Mo to exhibit behavior more closely paralleling Figure 3a. To the extent that swelling in the latter alloys is less strongly suppressed, they do follow the calculated behavior for vacancy trapping when compared with interstitial trapping. However, the experimentally observed void-swelling suppression in the oversize solute case is greater than calculated.

The relative effectiveness of the oversize solutes in suppressing swelling is most discernible at ~575°C. Figure 4 is a plot of the measured void swelling as a function of solute misfit. This plot demonstrates the

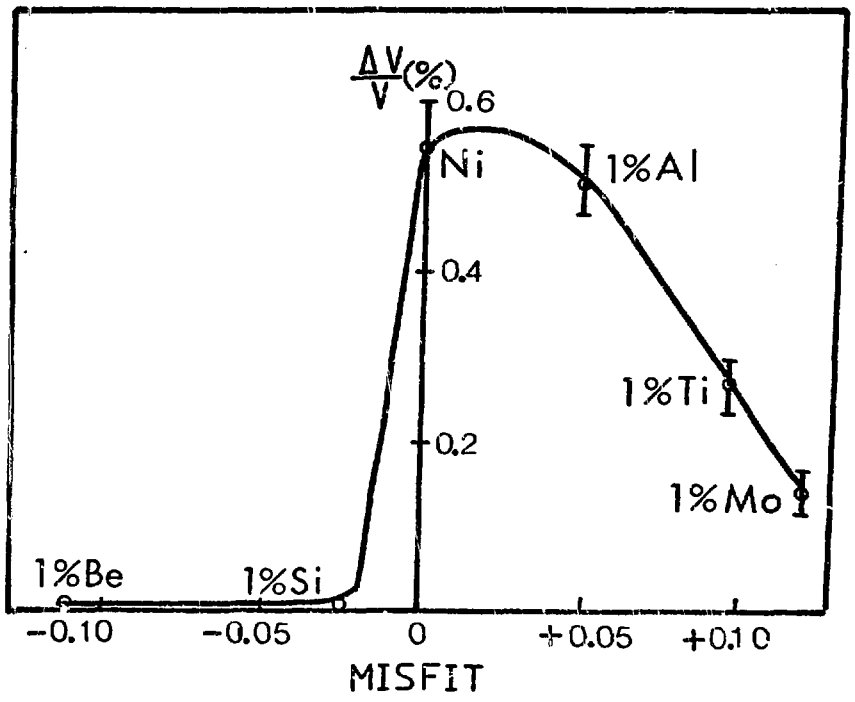

Fig. 4 - Void swelling at 575°C plotted versus solute misfit.

experimentally observed increased swelling suppression with solute misfit, particularly for oversize solutes. To the extent that increased misfit correlates with increased solute-vacancy binding, these results are consistent with the decreased swelling with increased binding energy predicted by Okamoto et al. (4).

The Auger results are also consistent with the binding scheme described above. The observed depletions of oversize solutes Al, Ti and Mo (see Figure 3) are easily understood qualitatively. According to the calculations of Dederichs et al. (7), the mobile interstitial-solute complex, i.e., the mixed dumbbell, is energetically unfavorable. Hence, the interstitials avoid oversize solute atoms and migrate preferentially via solvent atoms. This induces a solvent atom flux to the surface. A moderate vacancy-solute binding should not reverse the solute depletion (5). The case of solute enrichment due to interstitial-solute binding of undersize solutes follows naturally from the formation of mobile mixed-dumbbell interstitials. These carry Be and Si toward the surface. The precipitation at the irradiated surface, as observed in Ni-Si alloys, is a consequence of solute enrichment beyond the solubility limit.

Conclusions

The following conclusions can be drawn based on our results:

(1) the undersize solutes, Si and Be, are more effective in suppressing void swelling in Ni than the oversize solutes, Al, Ti and Mo;

(2) the reduction of swelling in Ni by Al, Ti and Mo solute additions increases with their misfit;

(3) the oversize solutes tend to lose their effectiveness in suppressing swelling at the lower temperatures investigated, whereas the undersize solutes do not;

(4) the undersize solutes segregate strongly to the irradiated surface, whereas the oversize solutes are depleted; and

(5) experimental void swelling and irradiation-induced segregation results are consistent with calculations that assume strong interstitial trapping of undersize solutes and vacancy trapping by oversize solutes.

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