Nickel and Nitrogen Ion Irradiation Induced Void Swelling and Defect Microstructures in Ni-Al, Ni-Cr and Ni-Ti Solid Solutions

R. F. PINIZZOTTO, JR., L. J. CHEN, AND A. J. ARDELL

The effects of solute content, temperature, and irradiation dose on the void swelling characteristics of pure nickel and several nickel base solid solutions (Ni-Al and Ni-Ti containing up to 8 at. pct solute and Ni-Cr containing up to 16 pct Cr) have been investigated. Samples were irradiated in the temperature range 400 to 650°C to a maximum dose of 70 dpa using 3.5 MeV $^{58}Ni^+$, 400 keV $^{14}N^+$ and 400 keV $^{14}N_2^+$ ions. The irradiation induced microstructures were studied using transmission electron microscopy. In general, the addition of Al, Cr or Ti to Ni is found to decrease the void swelling and mean void diameter and to increase the dislocation density. The behavior of the void number density, N_v, as a function of solute content is found to be dependent upon the irradiation conditions as well as the particular solute addition. N_v passes through a maximum at approximately 2 pct solute content for Ni-Al and Ni-Cr alloys irradiated at 550°C, but through a minimum at 4 pct for Ni-Ti alloys irradiated at 550 and 600°C. N_v decreases monotonically as a function of Al content at 600 and 650°C. The results are discussed in terms of recent theories of void swelling suppression due to impurity or solute additions and in light of several correlations between void swelling and material parameters. The behavior of N_v is found to be best described by the actions of two competing processes. The first enhances void nucleation, is not strongly temperature dependent and is dominant at low solute contents. The second suppresses void swelling, is probably diffusion controlled and dominates in the more concentrated alloys.

THE discovery that Nimonic PE-16 is highly resistant to void swelling under neutron irradiation at elevated temperatures[1,2] has generated a great deal of interest in the study of nickel-base alloys as candidate cladding and structural materials in the LMFBR. Due to the complexity of the material, the swelling resistance of PE-16 to heavy ion as well as neutron irradiation is not well understood. It is therefore desirable to study simpler systems so that the various mechanisms suggested to be responsible for suppression of void swelling in Ni-base alloys can be evaluated. Ni-Al, Ni-Ti and Ni-Cr solid solutions were chosen for this study because of the relatively high solubility of the solutes (about 10 at. pct for Al and Ti and 20 at. pct for Cr) and the large changes in the stacking fault energy as a function of solute concentration in these systems. The three solutes are also important components of commercial Ni-base alloys. Samples of these alloys, as well as pure nickel, were irradiated in the temperature range 400 to 650°C using 3.5 MeV $^{58}Ni^+$, 400 keV $^{14}N^+$ and 400 keV $^{14}N_2^+$ ions. The results of these studies are presented and discussed in terms of recent correlations between void swelling and the effect of solute additions on various material parameters.

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EXPERIMENTAL PROCEDURES

1. Nickel Ion Irradiations

The preparation of the samples for the irradiations has been described in previous publications.[3,4] The irradiations were performed at the Argonne National Laboratories' Dual-Ion Facility using 3.5 MeV $^{58}Ni^+$ ions. The irradiation conditions are listed in Table I. The vacuum pressures during the irradiations were always less than 10^{-7} Torr. The temperatures of the samples were checked during the irradiations using an infrared pyrometer and were within 20°C of the reported values. Incident ion beam currents were found to be uniform to within 20 pct for all samples irradiated under the same conditions.

The damage profile was calculated using the NRL E-DEP-1 computer code[5] which is expected to be within 50 pct of the correct value.[6] The peak damage rates were between 2.5 and 3.6 × 10^{-3} dpa/s and occurred approximately 6000Å from the irradiated surface. Figure 1 shows the damage profiles vs depth from the irradiated surface for 3.5 MeV Ni$^+$ ions incident on Ni and Ni-8 at. pct Al. The biggest difference observed is near the peak damage region and is only several per cent. This is the largest difference in the calculated damage rate in any of the alloys studied, which indicates that the effect of alloying on the energy deposition in these solid solutions is quite small. The doses for samples examined by transmission electron microscopy (TEM) are quoted for the peak damage region.

Samples were prepared for TEM study using a modified form of the X-ray absorption method employed by Brager, *et al.*[7] Irradiated samples were jet polished from the unirradiated side to a thickness

Table I. 3.5 MeV ^{58}Ni$^+$ Irradiation Conditions

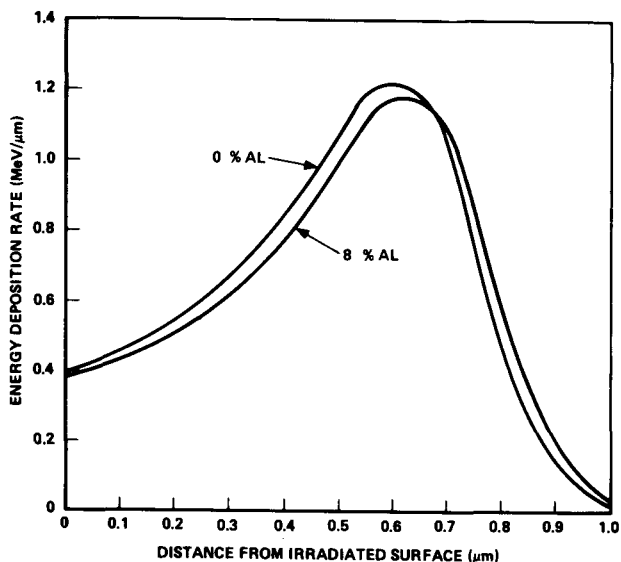| Temperature, °C	Dose, dpa	Ni	Ni-Al	Ni-Cr	Ni-Ti
550	9	X	X	X	X
550	18		X	X	
600	20	X	X		X
650	12	X	X		X

Fig. 1—Energy deposition rate of 3.5 MeV ^{58}Ni$^+$ ions incident on Ni and Ni-8 pct Al vs distance from the irradiated surface of the sample.

of $\sim$10 μm, with periodic interruptions for thickness measurements. The polishing rate for each sample was calculated and used to determine the polishing time needed to remove 5000Å of material from the irradiated surface. Measured polishing rates were typically 3000 to 4000Å/s. The accuracy of measuring the thickness of the material removed is estimated to be within ±1000Å, which could result in a 20 pct decrease in the damage rate as compared to the peak damage rate.

2. Nitrogen Ion Irradiations

The nitrogen ion irradiations were performed at the California State University at Los Angeles (CSULA) Van de Graaff Accelerator Laboratory using 400 keV ^{14}N$^+$ or ^{14}N$_2^+$ ions. The decision to use nitrogen ion beams was taken because the CSULA facility uses an ion source which can only utilize materials in the gas phase and nitrogen was the heaviest noninert gas available. The ion energy was selected because it is the lowest stable energy attainable at CSULA and a relatively high maximum damage rate near the irradiated surface could be obtained under controlled conditions.

The dose rate obtained using 400 keV N$_2^+$ ions is about four times larger than that of 400 keV N$^+$ for equal incident beam current densities. The dose rates integrated over a depth of 2000Å from the irradiated surface were about 7×10^{-4} and 3×10^{-3} dpa/s for the 400 keV N$^+$ and N$_2^+$ irradiations, respectively, for pure Ni, Ni-Al alloys and Ni-Ti alloys. In the Ni-Cr case,

these rates were somewhat larger, being 1.4 and 5.6 $\times 10^{-3}$ dpa/s. The damage profiles were again calculated using the E-DEP-1 computer code[5] and are shown in Fig. 2.

The irradiation chamber was maintained at a vacuum of about 10^{-6} Torr during the irradiation experiments using an oil diffusion pump and a liquid nitrogen cryotrap. The specimen holders were designed and constructed to be compatible with the apparatus used at the Argonne National Laboratories. Tests were performed from 200 to 650°C to determine the temperature gradients in the sample holder. It was found that the average sample temperature was about 5°C below the control temperature at 200°C and increased to 20°C below the set point at 600°C. The temperatures at the various sample positions were always within ±20°C of the average sample temperature during these experiments. Since the holder, procedure for loading the samples for the irradiations and typical energy deposition rates were all similar to those employed during the nickel ion irradiations, the variation in temperature of the samples during the nitrogen ion irradiations is estimated to be within 20°C of the reported value.

The irradiation chamber was electrically isolated, enabling us to measure the total beam current by connecting it to ground potential via a nanoammeter. The beam size was defined by a circular aperture 25.4 mm in diam. The uniformity of the current density was checked by measuring the total beam current using concentric apertures 12.70, 19.05 and 25.4 mm in diam to define the beam size. The current density was found to be uniform to within 30 pct.
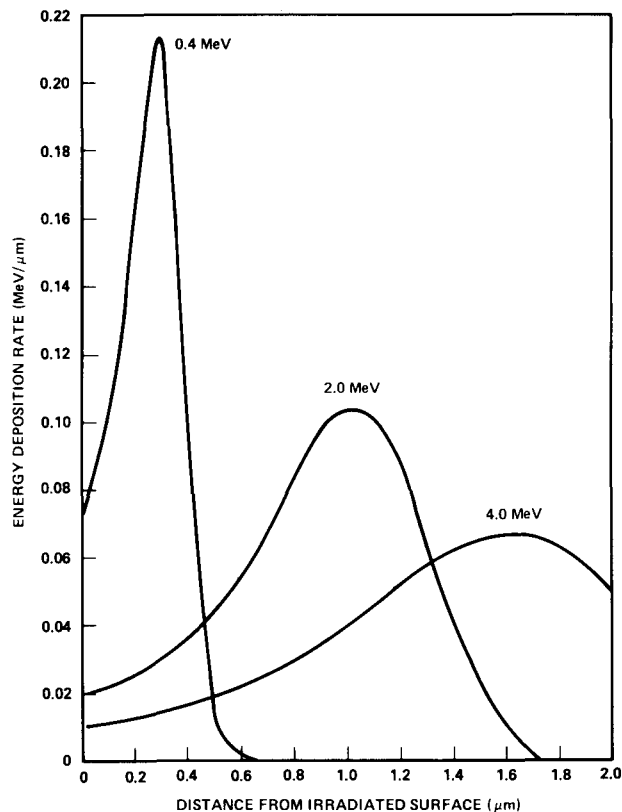

Fig. 2—Energy deposition rates of ^{14}N$^+$ ions of several energies incident on Ni vs distance from the irradiated surface of the sample.

Alignment of the beam was accomplished using a quartz plate attached to a linear motion feed-through. The quartz plate also acts as a beam stop, which can be positioned so that successive rows of the sample array are exposed to the beam. Dose effects can therefore be studied without changing any of the irradiation, vacuum or temperature conditions.

Ni, Ni-Al and Ni-Cr samples were irradiated in bulk form and subsequently jet polished to perforation from the unirradiated side for use in the TEM investigations. In addition, perforated thin foils of Ni-Al were irradiated at 500°C to 10 dpa using 400 keV N^+ and perforated thin foils of Ni-Cr were irradiated to 10 dpa using 400 keV N_2^+ at 550°C. All the nitrogen ion irradiation conditions are summarized in Table II.

Nitride formation was observed to occur in the Ni-Ti and Ni-Cr systems, but not in the Ni-Al alloys. In the Ni-Ti alloys nitride formation was so extensive that the experiments were abandoned. The results obtained in the Ni-Cr system using nitrogen ions are qualitatively similar to those obtained using nickel ions, and indicate that the presence of CrN does not significantly alter the trends observed in the Ni-Cr system. No nitride particles were observed during the TEM investigation of the Ni-Cr alloys, but extra spots due to nitride formation did occur in the selected area diffraction patterns.

3. TEM Examinations

The microstructures induced by ion irradiation were examined using a JEM-120 transmission electron microscope operating at either 100 or 120 kV. Foil thickness was determined by counting thickness fringes, by using standard stereo microscopy methods or by the method of Wolff.[8] The methods were found to agree to within ±10 pct. If none of these methods could be applied, a value of 1500Å was used for Ni, Ni-Al and Ni-Ti samples or 1000Å for the Ni-Cr samples.

The methods used to determine the nature of dislocation loops were described previously.[3] Dislocation densities, ρ_d, were calculated by the line intercept method.[9]

Data on the void sizes and distributions were obtained from micrographs using an electronic digitizer which converts the experimentally obtained data directly into a computer card data set. The void coordinates,

foil thickness, t, area, A, and magnification, M, were used as inputs to a Fortran code which calculates the mean void size, $\langle d \rangle$, standard deviation of the mean void size, the void number density, N_v, and the void volume fraction, S. The size distribution is then plotted. The program corrects N_v to account for the voids that intersect the foil surfaces using the expression

$$N_v = \frac{N_{v(\text{measured})}}{1 - \langle d \rangle / t} \; . \tag{1}$$

The void volume fraction is given by

$$S = \frac{\sqrt{2}}{3} \frac{\sum\limits_i d_i^3}{At} \frac{1}{1 - \langle d \rangle / t} \tag{2}$$

where d_i is the size for the i-th size interval.

The void volume fraction was calculated assuming that the voids are of octahedral morphology. The correction factor of $\sqrt{2}/3$ was not used wherever the voids were observed to be of cubic morphology. The errors estimated for the experimentally measured parameters are: t (±15 pct); $\langle d \rangle$ (±20 pct); N_v (±35 pct); S (±55 pct); ρ_d (±25 pct). In the case of the nitrogen ion irradiations, the effect of the free surface(s) may have introduced additional errors into the experimental data, although these would be systematic for any series of samples.

RESULTS

The observations of faulted and multiple-faulted dislocations loops were reported previously for nitrogen ion irradiations.[3] Since we have obtained similar results for nickel-ion irradiations (see Fig. 3), we conclude that the formation of multiple-layer loops appears to be a fairly general phenomenon in these alloys. All the faulted loops were identified to be of the interstitial type.

The overwhelming majority of voids in the Ni^+ irradiated pure nickel and nickel-base alloys are truncated octahedra. A small fraction of dendritic voids have been observed in pure nickel,[10] Ni-2 pct Al, and in the Ni-2 pct Cr and Ni-4 pct Cr samples under N_2^+ and Ni^+ irradiation (see Fig. 4). The voids shapes in the nitrogen-ion irradiated samples are both truncated octahedra and cuboids.

Void ordering was observed in Ni-Al alloys irradiated by $^{14}N_2^+$ to high doses (20 to 70 dpa) at 500°C. This phenomenon is described in detail elsewhere.[11]

1. Nickel Ion Irradiations

The measurements of the mean void size, dislocation density, void number density and swelling resulting from the Ni^+ irradiations are shown in Figs. 5, 6 and 7. Representative micrographs of both the void and dislocation microstructures for a series of Ni-Cr alloys are shown in Fig. 8. These microstructures are very similar to those observed in almost all the the alloys irradiated under the various irradiation conditions employed. The exceptions are the cases of the 4 pct Al alloys irradiated to 20 dpa at 600°C and 12 dpa at 650°C where very heterogeneous void distributions were observed (Fig. 9).

In general, $\langle d \rangle$ and S decrease and ρ_d increases with

Table II. 400 keV Nitrogen Ion Irradiation Conditions

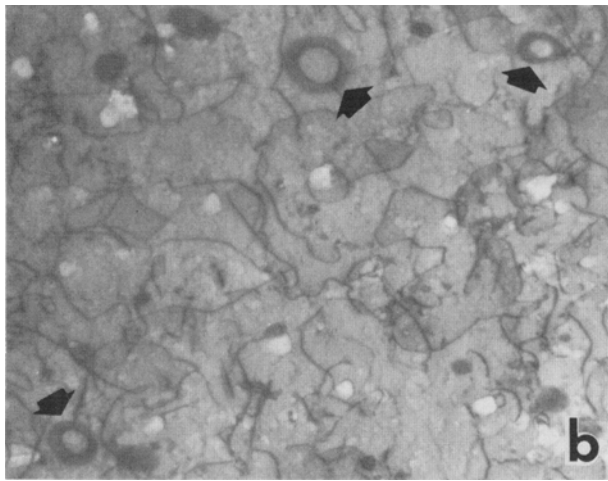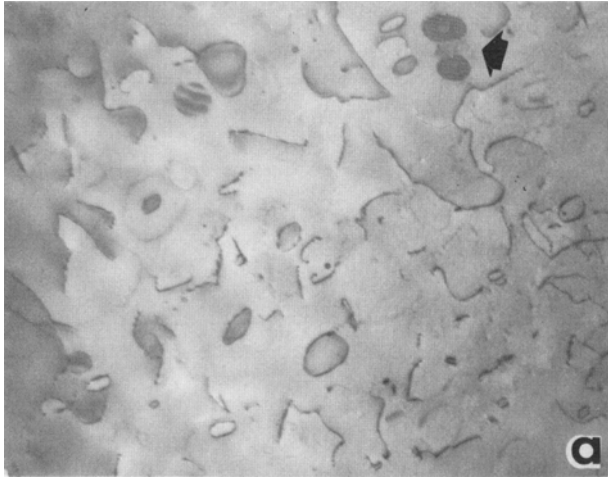| Temperature, °C	Dose, dpa	Ni Bulk	Ni Thin Foil	Ni-Al Bulk	Ni-Al Thin Foil	Ni-Cr Bulk	Ni-Cr Thin Foil
$^{14}N^+$ Irradiation							
500	10	X	X	X	X		
$^{14}N_2^+$ Irradiations							
400	20	X		X			
500	10		X	X			
500	20	X		X		X	X
500	40	X		X			
500	70	X		X			
550	10	X		X			

Fig. 3—Multiple layer loops (indicated by arrows) in: (a) Ni-6 pct Al irradiated to 20 dpa at 600°C and (b) Ni-6 pct Ti irradiated to 9 dpa at 550°C with 3.5 MeV Ni$^+$ ions.
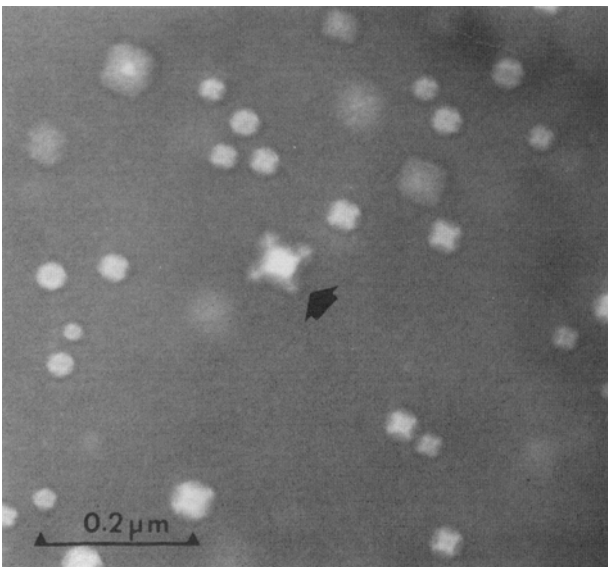

Fig. 4—A dendritic void (indicated by the arrow) in Ni-4 pct Cr irradiated with 3.5 MeV Ni$^+$ ions to 20 dpa at 550°C.
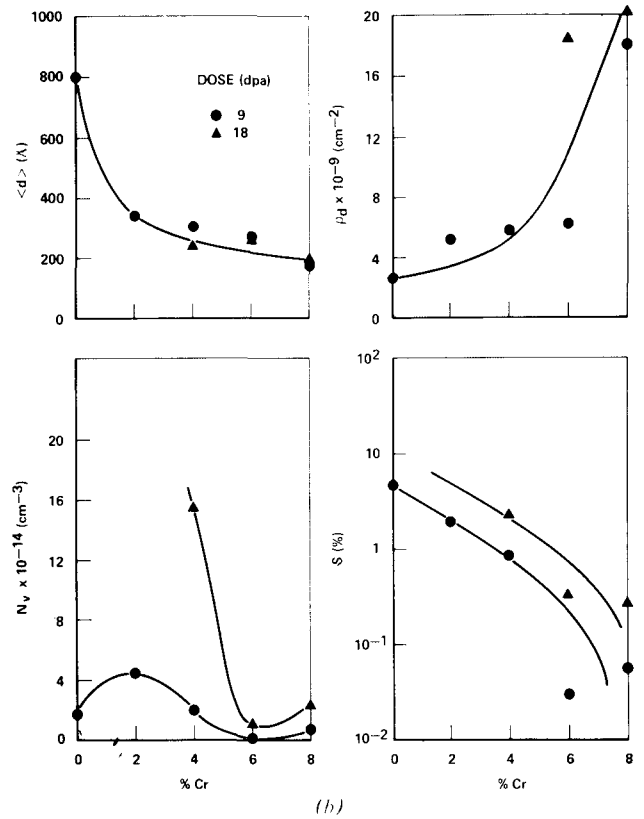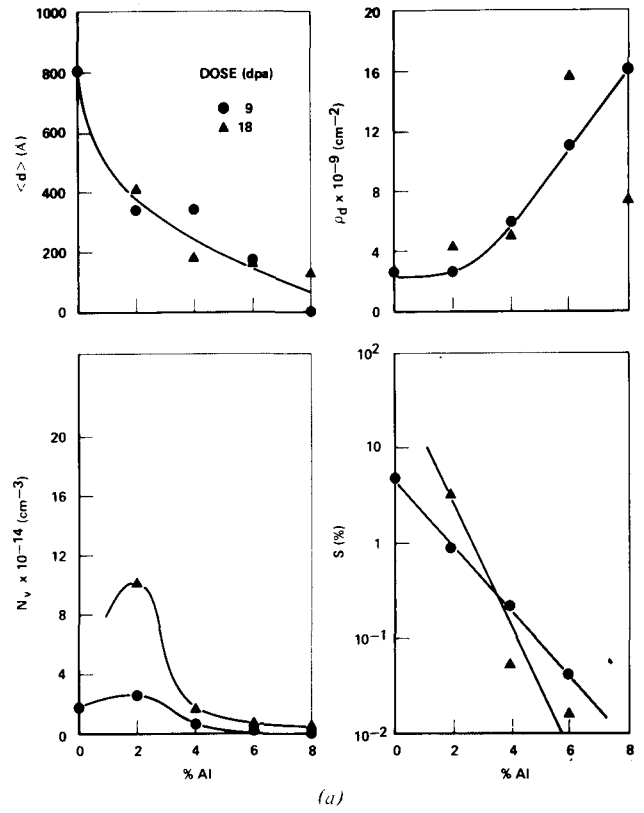

Fig. 5—$\langle d \rangle$, ρ_d, N_v and S vs solute content for samples irradiated at 550°C with 3.5 MeV Ni$^+$ ions: (a) Ni-Al alloys, 9 and 18 dpa, (b) Ni-Cr alloys, 9 and 18 dpa, and (c) Ni-Ti alloys, 9 dpa.
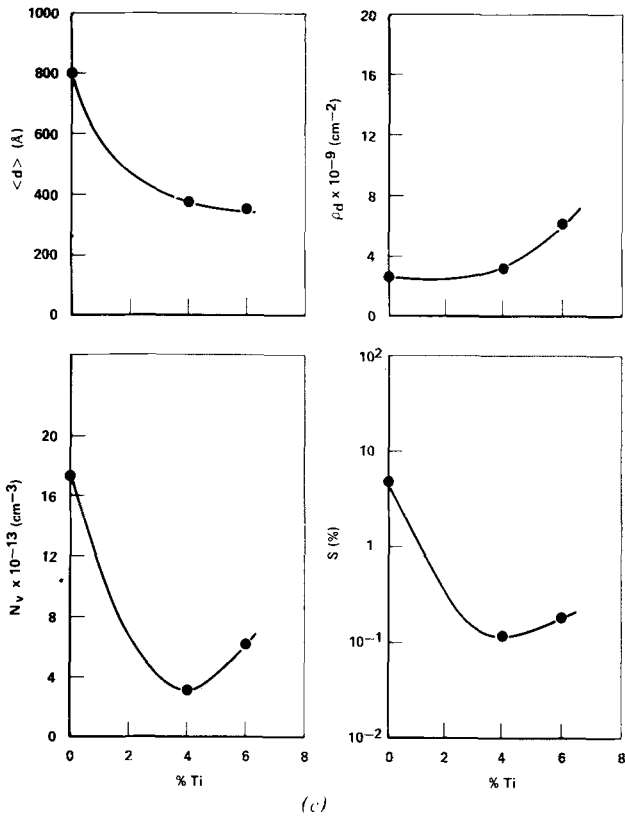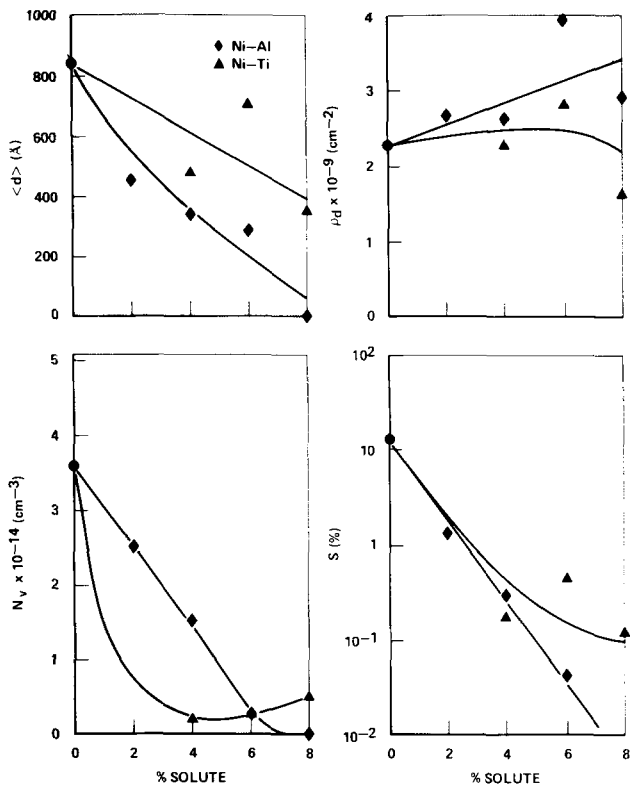
Fig. 5—Continued

Fig. 6—$\langle d \rangle$, ρ_d, N_v and S vs solute content for Ni-Al and Ni-Ti alloys irradiated to 20 dpa at 600°C with 3.5 MeV Ni+ ions.

Fig. 7—$\langle d \rangle$, ρ_d, N_v and S vs Al content for samples irradiated to 12 dpa at 650°C with 3.5 MeV Ni+ ions.

increasing solute content at a given dose and temperature. The behavior of N_v cannot be described in such broad terms, however, because this parameter behaves differently for each alloy system, and evidently
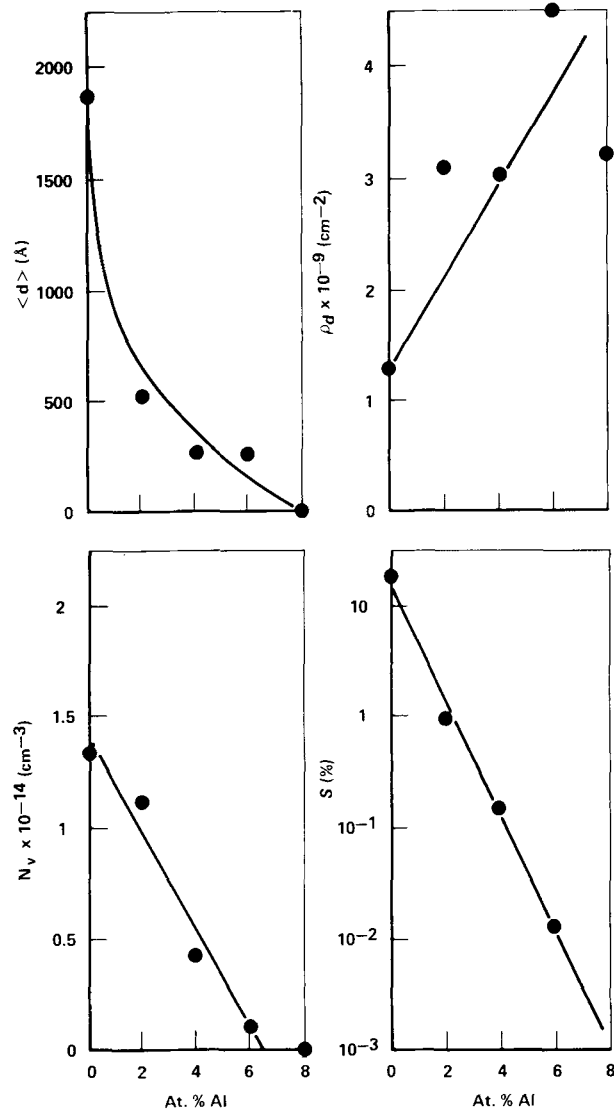
changes as a function of the irradiation conditions. In the case of the Ni-Al alloys, irradiated to maximum doses of 9 and 18 dpa at 550°C, N_v initially increases as the Al concentration increases (Fig. 5(a)). A maximum occurs at approximately 2 pct Al after which further increases in the Al content cause N_v to decrease. However, at higher irradiation temperatures (600 and 650°C), N_v was observed to decrease monotonically with increasing Al content, as can be seen in Figs. 6 and 7.

The values of N_v in the Ni-Cr alloys irradiated at 550°C change in a similar fashion to those observed in the Ni-Al system (Fig. 5(b)), except that a minimum is observed at 6 pct Cr.

The Ni-Ti alloys irradiated by Ni+ to doses of 9 dpa at 550°C and 20 dpa at 600°C (Figs. 5(c) and 6, respectively) behave somewhat differently from the other two alloy series. The number density decreases, passing through a minimum at 4 pct Ti. It should be noted, however, that the initial variation of N_v with increasing Ti concentration is not known since no alloys with less than 4 pct Ti were irradiated. As can be seen in the figures, Ni-6 pct Ti swells more than Ni-4 pct Ti
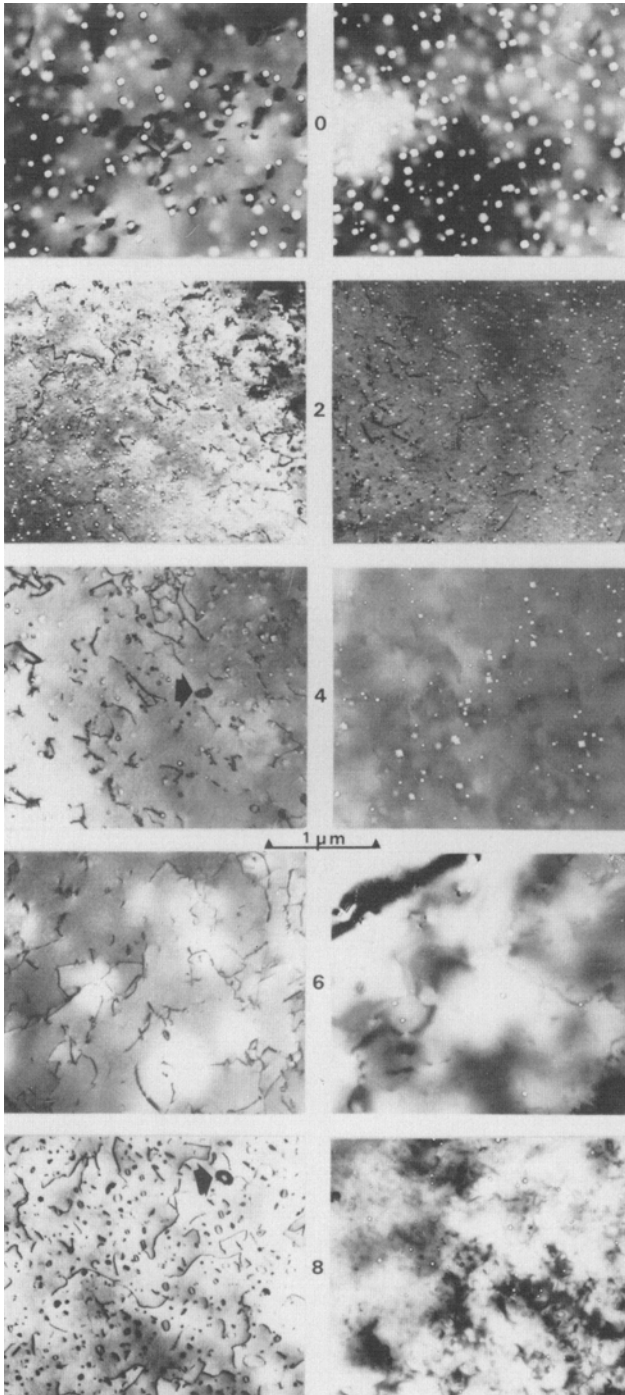
Fig. 8—Typical void (right) and dislocation (left) microstructures observed in Ni and Ni-Cr alloys irradiated at 550°C to 9 dpa with 3.5 MeV Ni$^+$ ions. A few multiple layer loops are indicated with arrows. The alloy content is indicated by the number between the figures.

for both irradiation conditions. The Ni-Ti alloys did not swell at all at 650°C.

The absence of void swelling in Ni-Ti alloys irradiated at 650°C seems to be consistent with the finding of Potter, *et al*[12] that 1 pct Ti added to nickel is effective in suppressing swelling during Ni$^+$ irradiation at temperatures slightly above the peak swelling temperature for nickel (close to 625°C (Ref. 13)). The swelling behavior of Ni-6 pct Ti compared to Ni-4 pct Ti at 550°C and 600°C is somewhat puzzling, since one would
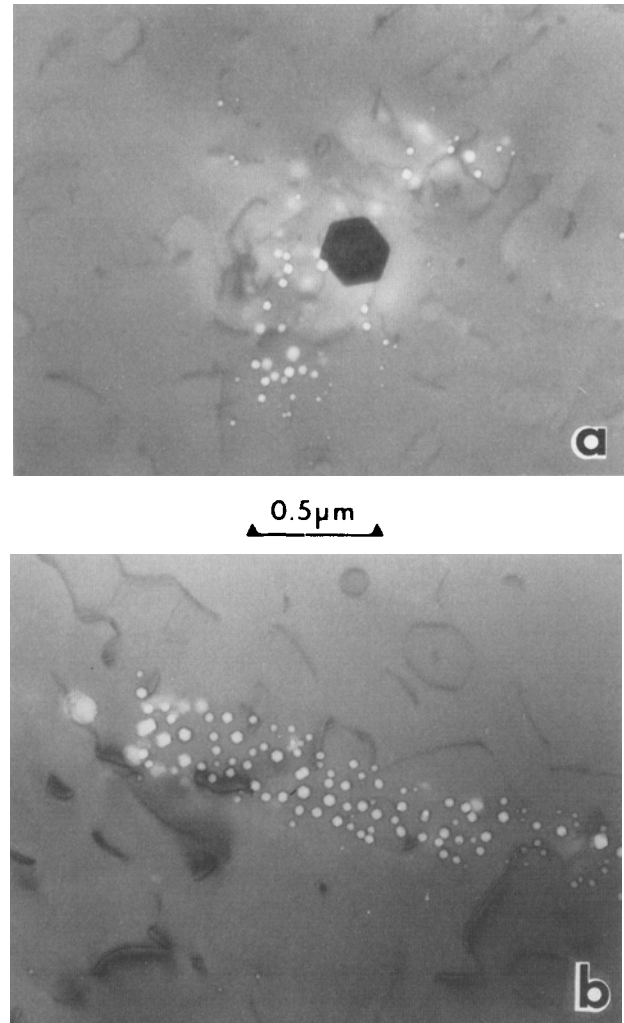

0.5μm

Fig. 9—Heterogeneous void distributions in Ni-4 pct Al samples irradiated with 3.5 MeV Ni$^+$ ions: (*a*) 20 dpa at 600°C and (*b*) 12 dpa at 650°C.

expect a monotonic relationship between void swelling and solute content. However, the experimental conditions during irradiation of the Ni-Ti alloys to 9 dpa by Ni$^+$ at 550°C were somewhat uncertain owing to experimental difficulties encountered during that run.
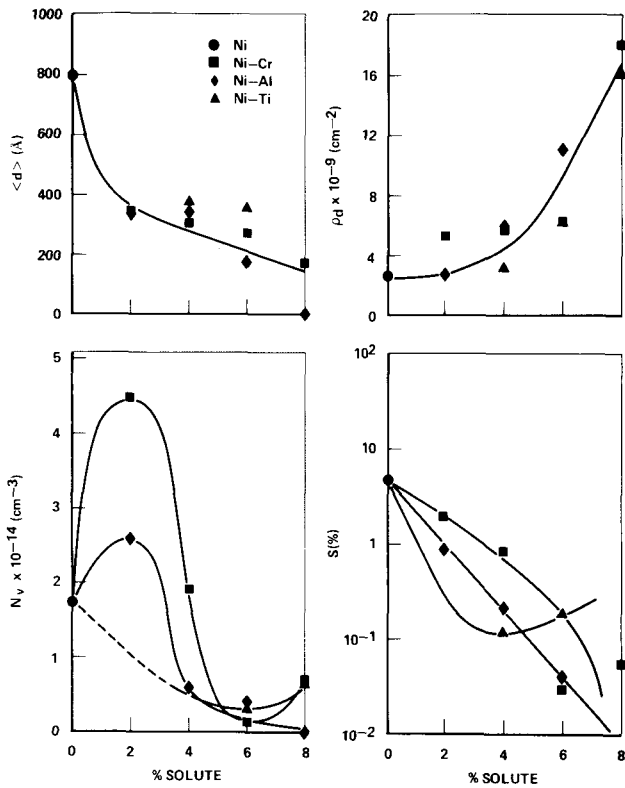
While the dislocation density generally increases with increasing solute content, it does not necessarily do so monotonically, as implied by the curves drawn in Figs. 5 to 7. In some cases (specifically Ni-Al at 550°C, 18 dpa; Ni-Al at 600°C, 20 dpa; Ni-Al at 650°C, 12 dpa; Ni-Ti 600°C, 20 dpa) ρ_d appears to go through a maximum, although the experimental uncertainties are such that the maxima observed may be apparent rather than real.

A comparison of the data on the Ni-Al, Ni-Cr and Ni-Ti alloys irradiated by Ni$^+$ to 9 dpa at 550°C is shown in Fig. 10(*a*). Ti additions are observed to be the most efficient and Cr the least efficient in suppressing void swelling at alloy concentrations <4 pct. The results are ambiguous for the larger solute concentrations, possibly due to the large experimental uncertainties in the swelling measurements for values less than 0.1 pct.
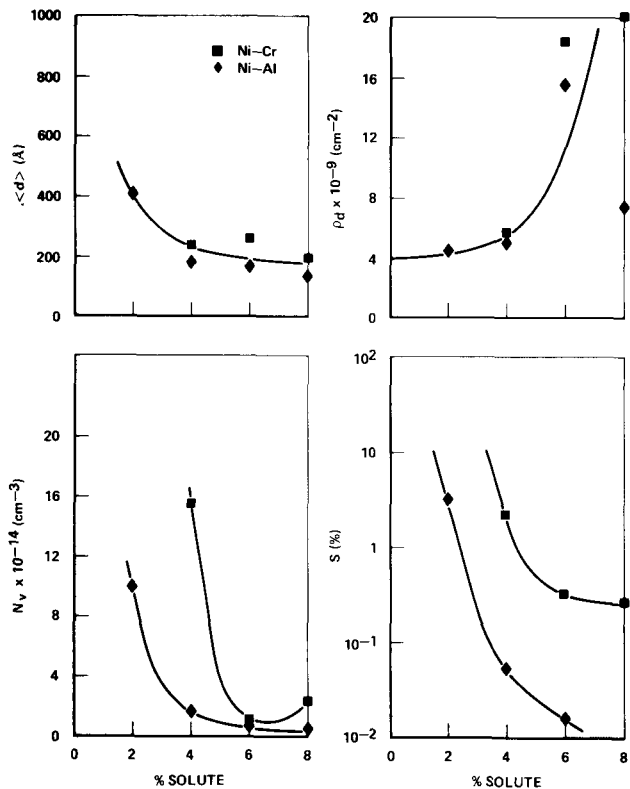
Figure 10(*b*) shows a comparison of the data on the Ni-Al and Ni-Cr alloys irradiated to 18 dpa at 550°C.

Al additions are observed to reduce both N_v and S more than Cr does for all the alloys.

In the case of the alloys irradiated to 20 dpa at 600°C, Ni-4 pct Ti swells less than Ni-4 pct Al, but the 6 and 8 pct Ti alloys swell more than the 6 and 8 pct Al alloys (Fig. 6(a)).

The temperature dependence of void swelling in Ni and Ni-6 pct Al irradiated by Ni⁺ is shown in Fig. 11. The suppression of void swelling by solute additions is slightly more effective at 550°C. The peak swelling temperatures, T_p, probably vary somewhat with alloy content. As can be seen in Fig. 11, all the experiments reported in this paper were performed below T_p, thus differences in T_p due to alloying cannot be ascertained.

2. Nitrogen Ion Irradiations

The only alloys irradiated to the same dose at the same irradiation temperature using both N^+ and N_2^+ were the Ni-Al alloys. The results of that experiment are shown in Fig. 12. The dislocation density is seen to be independent of the type of nitrogen ion used, although larger values of N_v and S, but smaller values of $\langle d \rangle$, result when N_2^+ is used to irradiate the samples. This behavior is consistent with the higher dose rates in the N_2^+ irradiations.

The differences in the irradiation damage response that arise when irradiating thin foils as compared to bulk samples can be seen from Fig. 13. In the Ni-Al system, irradiated using 400 keV N^+ at 500°C (Fig. 13(a)), the voids observed in the thin foils are smaller, but N_v is much larger. The thin foils were observed to swell less than the bulk samples. Dramatic differences in the behavior of thin foils and bulk samples were not observed in the case of the Ni-Cr alloys. The void size in the bulk samples was slightly smaller than in the thin foils (Fig. 13(b)), opposite to the behavior observed in the Ni-Al case, but no differences were observed in N_v or S, both decreasing monotoni-

Fig. 10—Comparison of the data on the alloy series for samples irradiated with 3.5 MeV Ni⁺ at 550°C: (a) Ni, Ni-Cr, Ni-Al and Ni-Ti alloys irradiated to 9 dpa and (b) Ni-Cr and Ni-Al alloys irradiated to 18 dpa.

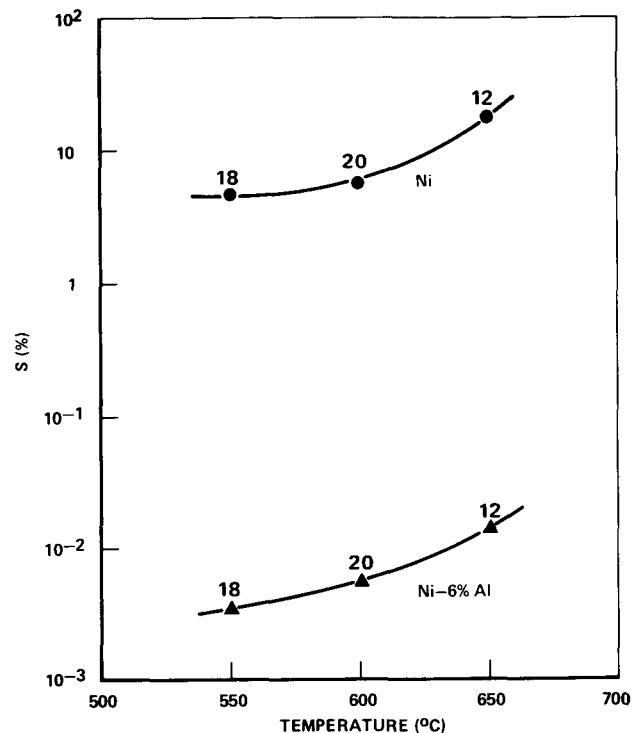Fig. 11—Temperature dependence of the void swelling in Ni and Ni-8 pct Al irradiated by 3.5 MeV Ni⁺ ions. The numbers above the data points indicate the dose.
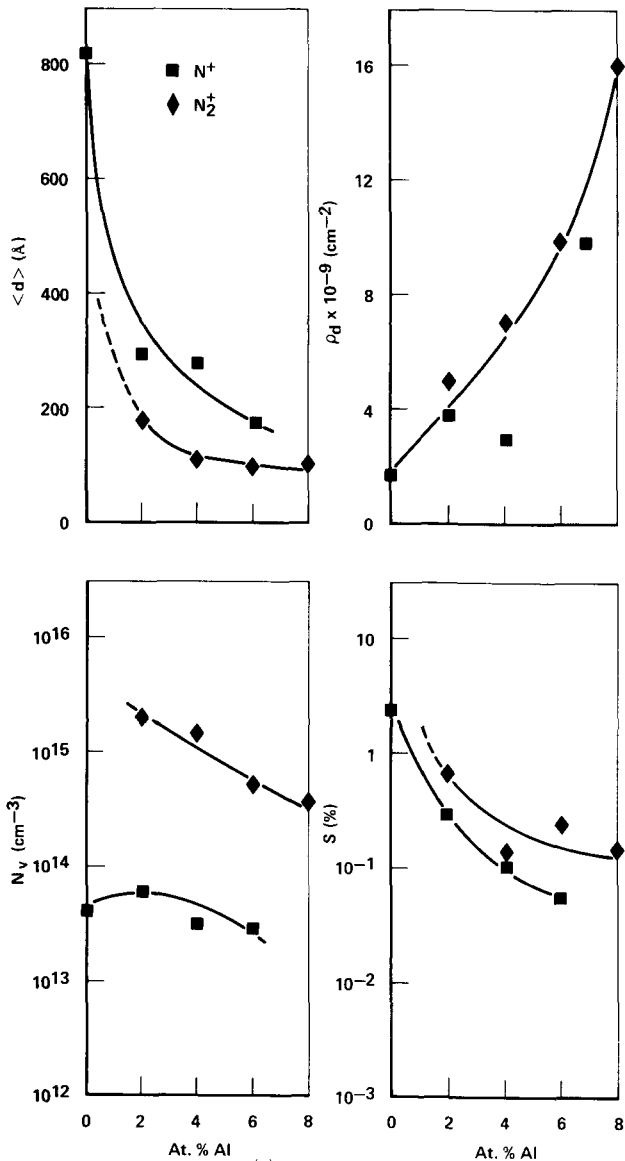
Fig. 12—Comparisons of $\langle d \rangle$, ρ_d, N_v and S for Ni-Al samples irradiated to 10 dpa at 500°C with 0.4 MeV N^+ and 0.4 MeV N_2^+ ions.

cally with increasing solute concentration. It should be noted that the Ni-Cr alloys were irradiated using N_2^+ ions, which could account for the different relative behavior between the thin foils and bulk samples compared to the Ni-Al alloys. In the Ni-Al alloys irradiated to 20, 40 and 70 dpa by N_2^+ at 500°C, S, N_v and $\langle d \rangle$ did not vary much as functions of solute concentration, concomitant with the formation of void lattices in these solid solutions.[11]

The results obtained for the Ni-Al alloys irradiated to 10 dpa at 550°C are shown in Fig. 14. No swelling was observed in the 6 or 8 pct Al alloys. The Ni-Al alloys were also irradiated to 20 dpa at 400°C using N_2^+, but no voids were observed in any of the samples.

DISCUSSION

One of the goals of this study was to determine whether nitrogen ions could be used in a meaningful way in simulation studies of void swelling. A few remarks concerning the differences between nickel and

nitrogen ion irradiations are thus in order before discussing the trends observed as a function of alloy content. Although the alloys were not irradiated under duplicate conditions, in general, it is possible to arrive at some conclusions from the results of the experiments done at the lower irradiation temperature (cf. the results in Fig. 5 with those in Figs. 12, 13, and 14). By and large the same trends are visible, for example, the maxima in N_v at about 2 pct solute and the decreases in $\langle d \rangle$ and S with increasing solute content. The most notable discrepancies are the absence of a swelling minimum at 6 pct Cr in the N_2^+ irradiated alloys and the nearly constant void size and monotonically decreasing void concentration in the N_2^+ irradiated bulk Ni-Cr samples. These exceptions notwithstanding, we believe that the nitrogen ion irradiations can be used to simulate self-ion irradiation damage provided that nitride formation is not extensive. This conclusion is partially suppprted by our observations of similar types of defects, such as multiple layer loops[3] and dendritic voids[4,10] in these alloys under both types of irradiations.

The different swelling behavior of the thin foils and bulk samples during nitrogen ion irradiation is puzzling. The smaller void diameters observed in the thin foils of the Ni-Al alloys (Fig. 13(a)) is consistent with slower void growth rates in these samples due to vacancy losses at the free surfaces. However, this explanation is inconsistent with the results on the Ni-Cr alloys with regard to swelling (Fig. 13(b)) in which case the effect of the free surfaces is small. In addition, the larger values of N_v observed in the Ni-Al thin foils imply a higher vacancy supersaturation, which is not consistent with vacancy escape at the free surfaces. We are unable to provide a convincing explanation for these observations as of this writing.

Solute additions in nickel have been found by other investigators to produce major changes in the irradiation-induced void swelling behavior. Our results also demonstrate that solutes can significantly affect all the void swelling parameters. The applicability of several correlations proposed by other researchers has been investigated in an attempt to rationalize the observed behavior.

The correlations used by Jones and Atteridge[20] and Watkin[21] are based on the use of the electronic structures of an alloy's constituents to predict the thermodynamically stable phases of the system. The matrix electron vacancy number,[22] E_v, used by Watkin varies from 2 to 3 in the commercial alloys he considered. He observed that low swelling occurred when E_v was less than 2.58, which is close to the value of 2.52 derived by Woodyatt, et al[23] for the appearance of the σ-phase in high nickel alloys. The values of E_v for the matrix of the Ni-Al, Ni-Cr and Ni-Ti alloys investigated here vary from 0.6 to 1.4 and are thus well beyond the range of Watkin's correlation. The Engel-Brewer correlation (EBC),[24] as modified by Jones and Atteridge, however, is applicable to any alloy system. We used the calculations employed by those authors to construct Fig. 15, which shows how the void swelling varies as a function of the number of bonding d electrons for our alloys and also the alloys of several other investigators. The swelling values in Fig. 15 are normalized to the value, $S(0)$, obtained for pure Ni under identical irradiation

Fig. 13—Comparisons of $\langle d \rangle$, N_v and S for alloys irradiated in thin foil and bulk sample form. (a) Ni-Al alloys irradiated at 500°C to 10 dpa with 0.4 MeV N^+ ions. (b) Ni-Cr alloys irradiated to 18 dpa at 500°C with 0.4 MeV N_2^+ ions.
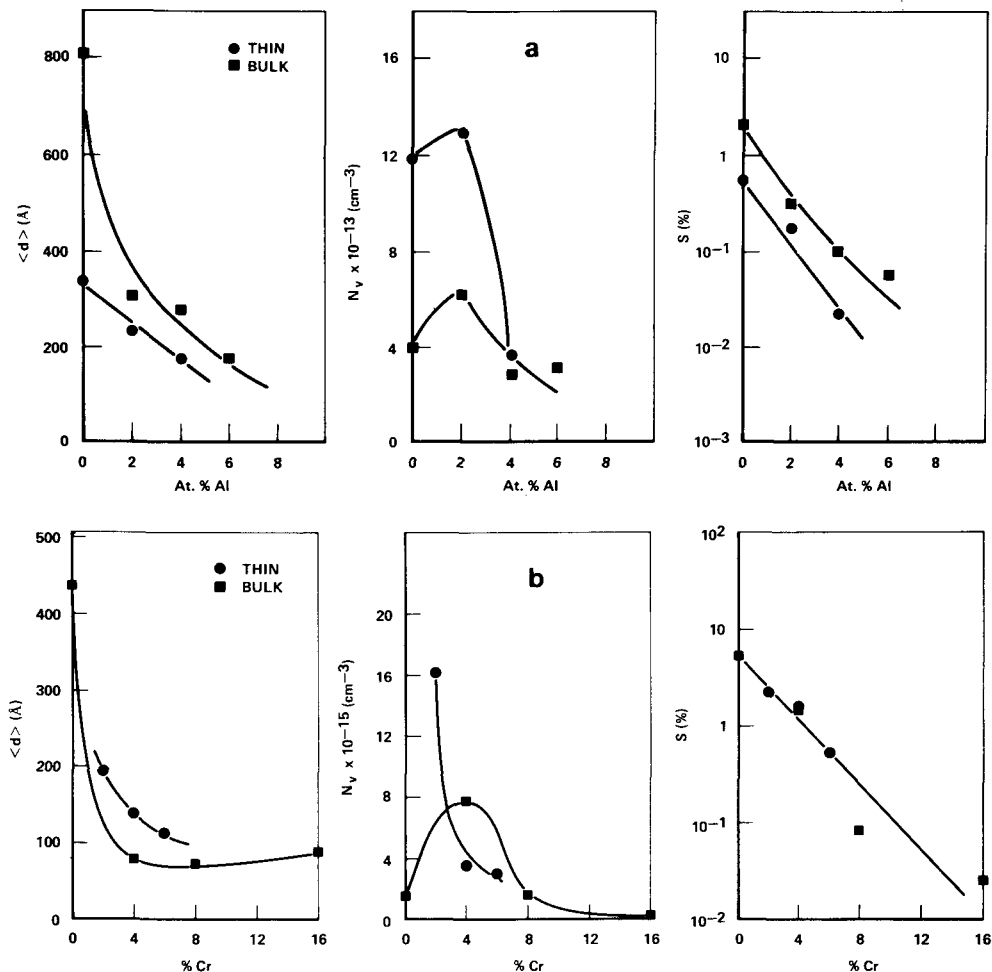
conditions, as was done by Jones and Atteridge. It is interesting to note that all of the data fit fairly well on a smooth curve except for the data of Hudson, *et al*[14] on Ni-Al alloys. Jones and Atteridge imply that this discrepancy is due to an uncertainty in knowing how the empty d-shell of a nontransition metal interacts with the bonding d electrons. It seems more likely that the values of $S/S(0)$ are artifically high due to the swelling saturation effects in pure Ni observed by Hudson, *et al* at the high doses (100 dpa) used in their experiment. These points aside, it is tempting to use the results of Fig. 15 as a good demonstration of a correlation between void swelling and electronic structure. There is a major shortcoming in the methodology, however. Jones and Atteridge arbitrarily assign integral values to the number of bonding d electrons, E_d, for all pure metals. Any alloy then, must have a nonintegral value of E_d assigned to it. The swelling maxima which occur at E_d values of 2, 3 and 5 in this scheme correspond to pure Cu, Ni and Fe, respectively. The lower values of $S/S(0)$ between these maxima is just another way of saying that the addition of solute to these metals generally suppresses void swelling. For this correlation to be useful in understanding the basic causes of void swelling suppression by solute additions, it is necessary that an alloy with E_d = 2, 3 or 5 be irradiated and found to swell more than other alloys of the same components with nonintegral E_d values.
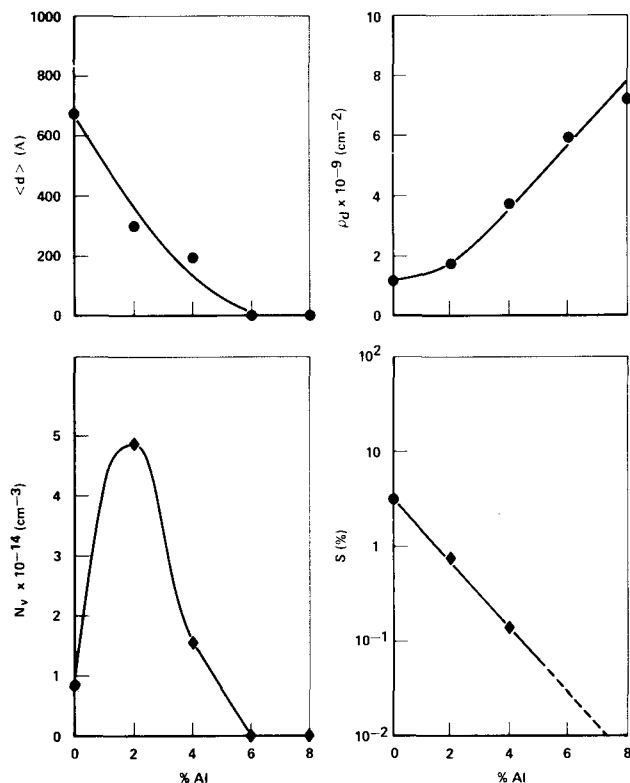

Fig. 14—$\langle d \rangle$, ρ_d, N_v and S *vs* Al content for samples irradiated to 10 dpa at 550°C with 0.4 MeV N_2^+ ions.

METALLURGICAL TRANSACTIONS A
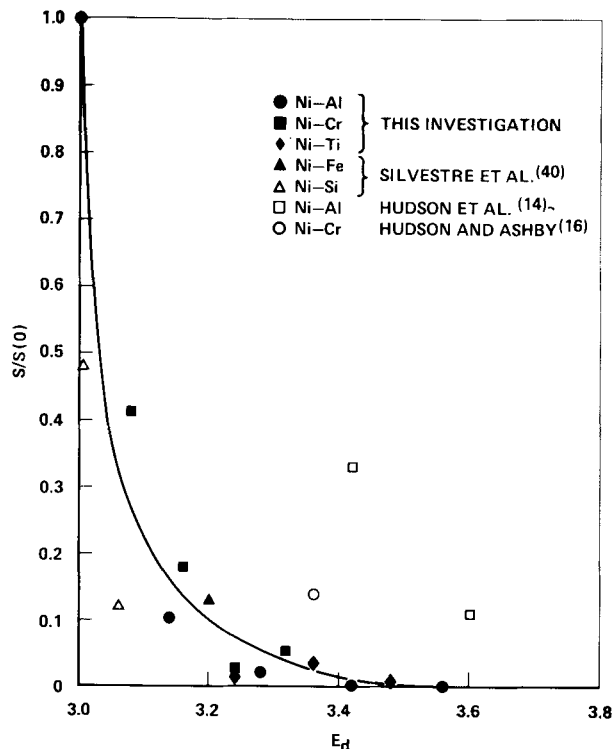
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Fig. 15—Normalized swelling vs the number of bonding d-electrons for Ni-base solid solutions.

Gittus and Watkin[25] have proposed that in austenitic alloys, greater thermodynamic stability of the fcc phase compared to the bcc phase would predict a smaller amount of void swelling under irradiation. Their calculations were applied to our Ni-Cr alloys, but a poor correlation was found. The thermodynamically stable phase of Cr is bcc, thus Cr additions to fcc Ni should lower the thermodynamic stability of the fcc solid solutions. If the correlations were applicable, swelling of the Ni-Cr alloys should increase with increasing Cr content, opposite to what is observed experimentally.

Venker and Ehrlich[26] have developed a model which relates the swelling behavior of alloys to the intrinsic diffusion coefficients of their components. This model cannot be fully tested here, since there are no data on the diffusion of Al, Cr, and Ti in Ni alloys as a function of solute content. In these systems, the activation energies and diffusion constants of the components have similar values, so that no strong effects on the void swelling are expected. Al diffuses faster than Cr in Ni[27] and the Ni-Al alloys are observed to swell less than the Ni-Cr alloys, consistent with Venker and Ehrlich's model. The swelling results of the Ni-Ti alloys, however, lead to ambiguous results. Ti diffuses faster in Ni than Al does[27] and thus would be expected to be more efficient in suppressing swelling than Al. At both 550 and 600°C, the 4 pct Ti alloy swells less than the 4 pct Al alloy, although at higher solute contents the reverse is true (Figs. 6 and 10a). This behavior indicates that the correlation holds at the lower solute contents where the diffusion data are valid. This is supported by the data of Potter et al[12] who have observed that Ni-1 pct Ti swells much less than Ni-1 pct Al in the temperature range investigated in our study. It may be concluded that this correlation

leads to the proper order of void suppression in dilute alloys, but that the intrinsic diffusion constants must be determined as a function of alloy content before the correlation can be applied to an entire alloy system.

The general trends of our data also correlate well with the fact that the stacking fault energy decreases with increasing solute content in the Ni-Al, Ni-Cr and Ni-Ti alloy systems.[28] It is especially noteworthy that the stacking fault energy decreases more rapidly as a function of solute content in Ni-Ti alloys than in Ni-Al alloys, and that the Ni-Al alloys seem to be less swelling resistant at low solute concentrations. The addition of Cr is least effective in lowering the stacking fault energy and the Ni-Cr alloys always swell more than the corresponding Ni-Al alloys. Other mechanisms must be invoked to account for the swelling of the 6 pct Ti alloys since they swell more than the 6 pct Al alloys. Moreover, Ni-6 pct Ti swells more than Ni-4 pct Ti, although the stacking fault energy decreases monotonically with increasing Ti content.

It is obvious that changes in one material parameter alone cannot explain the swelling behavior of these alloy systems in detail because the void concentrations do not vary monotonically with alloy content at the lower irradiation temperatures. If we neglect the minimum at 6 pct Cr, N_v passes through a maximum at approximately 2 pct solute content and then decreases rapidly with solute content at 550°C (Figs. 5, 12, 13 and 14). This behavior implies that in addition to the large number of mechanisms that have been proposed to explain the suppression of void swelling by solute additions, there is at least one mechanism that enhances void nucleation in these alloys at low solute concentrations.

It is clear that these effects in N_v are not associated with peculiarities in ρ_d since ρ_d increases monotonically and rapidly with alloy content in the dilute alloys at all irradiation temperatures. Even in those few cases where ρ_d goes through an apparent maximum in the more concentrated alloys, there is no corresponding effect on N_v (or S or $\langle d \rangle$, for that matter).

Any process that stabilizes void embryos should cause N_v to increase. The computer experiments of Beeler and Beeler[29] have shown that oversized solute atoms can stabilize clusters containing up to thirteen vacancies. Al, Cr and Ti all have atomic sizes larger than that of Ni. Thus all the solutes could enhance void nucleation on the basis of the Beeler model. It is likely that vacancy-solute atom binding occurs, which can significantly affect the nucleation rate, as shown by Russell and Hall.[30] However, such vacancy trapping also decreases the vacancy supersaturation, as was pointed out by Smidt and Sprague.[31] The relative importance of these two effects cannot be assessed.

Nucleation theory shows that the critical void nucleus size is a strong function of the surface energy of the material. The nucleation rate may be increased by several orders of magnitude by only a small change in σ. In the alloys studied in this paper, surface energy data are available only for pure Ni and for a Ni-20 pct Cr alloy.[32] The Cr addition lowers σ from 2280 mJ/m^2 to 2160 mJ/m^2 at 1060°C. Moreover, σ is observed to decrease with alloy content
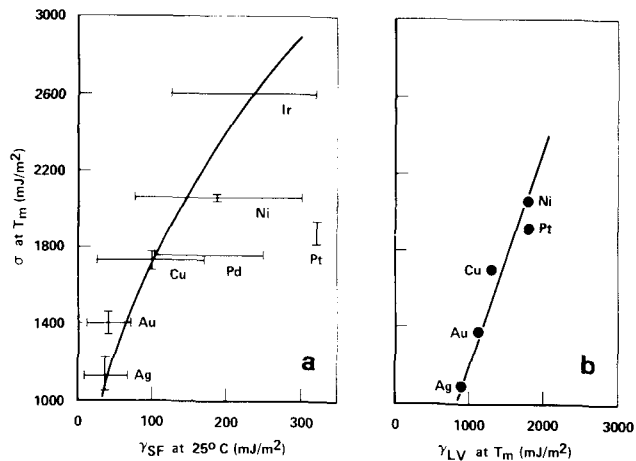
Fig. 16—(a) Correlation between surface free energy, σ, and stacking fault energy, γ_{SF}, for the fcc transition metals. The σ values for Ir and Pd were derived from the correlation shown in Fig. 16(b) which illustrates that σ and the liquid-vapor interfacial energy, γ_{LV}, of these metals are linearly related.

for many other alloy systems.[32] Figure 16 shows a correlation between stacking fault energy, γ_{SF}, and σ for the fcc transition metals for which data are available. The error bars indicate the range of values reported in the literature. As can be seen from Fig. 16, there is a general tendency for the surface free energy to decrease as the stacking fault energy decreases. (Pt is the one element that does not follow the trend, which may be due to the large uncertainty in γ_{SF} expected when the stacking fault energy is large). From the above discussion, it is thus reasonable to assume that Al, Cr and Ti additions lower the surface energy of binary nickel alloys since they all lower γ_{SF} as the solute content is increased. Void nucleation would then be enhanced by the addition of all three solutes.

The subsequent decrease of N_v at the higher alloy contents (>2 pct) can be understood by using models of solute atom-defect trapping for either vacancies[31] or interstitials.[33] These models predict a decrease in void swelling due to the enhancement of the point defect recombination rate. It is also probable that dislocation poisoning by solute atoms, proposed by Norris,[34] occurs in these alloys and contributes to the void swelling suppression. Both of these mechanisms lower the void concentration by decreasing the vacancy supersaturation.

It is conceivable that dissolved gas atom (e.g., O or N)-solute atom complexes are responsible for the observed behavior of N_v. It has been well documented that isolated noninert gas atoms, such as oxygen, have a pronounced effect on void nucleation in pure metals.[35,36] It is also well-known that Al, Ti, and Cr are strong oxide and nitride formers, so that chemical association between these solutes and O and N would be expected. If void nucleation is favored by the interaction of vacancies with some form of gas-solute atom complexes, it follows that void nucleation will become easier with the addition of small amounts of solute until all the gas atoms are saturated with solute atoms. Beyond this concentration the excess solute will play its evidently normal role of making void nucleation more difficult. The idea of the formation of such complexes seems reasonable in light of the computer experiments of Beeler and Beeler,[29]

which demonstrate that impurities can stabilize void embryos. It is also consistent with the theory of void nucleation of Katz and Weidersich, extended to include gas clusters.[37] In their calculations, Katz and Weidersich found only modest increases in the nucleation rate due to single gas atoms, but substantial increases in the rate due to cluster formation.

There are many difficulties, however, with the above suggestion. We do not know the dissolved gas content of the irradiated samples, but it is reasonable to conclude that it was far smaller than the solute content, even in the most dilute (2 pct) alloys. While it is possible that the maximum in N_v actually occurs at less than 2 pct solute, we have evidence to suggest that the maximum lies between 1 and 2 pct in Ni-Cr alloys.[38] Why then does the maximum occur at solute concentrations significantly greater than the likely gas content? It is conceivable that large numbers of solute atoms participate in the proposed complex, but while this is not impossible, it seems unlikely. A related problem is the absence of a maximum in N_v at irradiation temperatures of 600°C and above. It could be that the maximum occurs in alloys containing between 0 and 2 pct solute, or that the complexes are less stable at higher temperatures (which would be expected). Another difficulty with this suggestion is that the maxima in N_v are observed at around 2 pct solute in the Ni^+ irradiated samples as well as the N_2^+ irradiated samples. Since the N_2^+ irradiated samples necessarily contain considerably more nitrogen, the maximum in N_v should be pushed to higher solute contents in these samples. That such is not the case indicates either that the proposed complexes are unrealistic, or that nitrogen is ineffective in this regard.

The smaller values of $\langle d \rangle$ and S observed in the 2 pct alloys compared to pure Ni imply that the increase in the nucleation rate is not due to a higher vacancy supersaturation, since this would tend to accelerate void growth, as well as nucleation. It is therefore clear that the enhanced void nucleation in the 2 pct alloys is associated with the stabilization of void nuclei. This observation is compatible with all of the models described above.

The behavior of N_v as a function of solute concentration can thus be explained in terms of two competing effects. The first promotes void nucleation through the stabilization of void embryos and the second lowers N_v by decreasing the vacancy supersaturation. The factors affecting void nucleation are predicted to be only weakly temperature dependent but the void swelling suppression mechanisms rely on atomic transport processes and are diffusion controlled. The latter effects should thus become increasingly important as the irradiation temperature is raised. Our data reflect this; maxima in N_v do not occur in the alloys irradiated at 600 and 650°C. Additional evidence of a diffusion controlled void suppression mechanism is the observation that the relative swelling, $S/S(0)$, of the 2 pct Al alloy decreases as the irradiation temperature increases (from 0.19 at 550°C to 0.055 at 650°C).

As is apparent from the above discussion, there are several mechanisms which can be used to explain the reduction in void swelling due to solute additions. At the present time it is not possible to unambiguously

determine which are responsible for the observed behavior because of a lack of data on material constants such as the surface free energy, stacking fault energy and diffusion coefficients as a function of solute concentration. When swelling is the only parameter measured (e.g., by immersion density or profilometry), it is tempting to explain the data by invoking one or more of the factors cited earlier without regard to how those factors influence N_v and $\langle d \rangle$ separately. For example, within experimental error, the swelling decreases monotonically with increasing solute content under all our irradiation conditions, and for all the alloys. This behavior could be due to stacking fault energy, through its influence on the bias factor. Either of these effects, or both acting in concert, would, with the aid of our measured values of ρ_d, enable us to apply an existing swelling theory, such as the Brailsford-Bullough[39] theory of void growth, to our data with a considerable measure of success. The maxima observed in N_v clearly obviate this procedure.

SUMMARY AND CONCLUSIONS

1) The irradiation induced microstructures of Ni-Al, Ni-Cr and Ni-Ti solid solutions are significantly different from those induced in pure nickel irradiated under the same conditions.

2) In general, the void swelling values and mean void diameters decrease and the dislocation densities increase as a function of solute concentration for Al, Cr or Ti additions to pure Ni irradiated to maximum doses of 20 dpa in the temperature range of 400 to 700°C.

3) The behavior of the void concentration as a function of solute content depends upon the irradiation conditions used as well as the particular solute addition. N_v passes through a maximum at 2 pct solute content for Ni-Al and Ni-Cr alloys irradiated at 550°C, but decreases monotonically as the solute content increases for Ni-Al alloys irradiated at 600 and 650°C. For Ni-Ti alloys irradiated at 550 and 600°C, N_v passes through a minimum at ~4 pct Ti, but Ni-Ti alloys do not swell at all when irradiated at 650°C to a maximum dose of 12 dpa.

4) $^{14}N^+$ or $^{14}N_2^+$ ion irradiations can be used to simulate $^{58}Ni^+$ ion self-ion irradiations in the 400 to 700°C temperature range to total doses of 20 dpa provided that nitride formation is not extensive. This conclusion is based on the observation that all of the void swelling parameters follow the same trends as a function of solute content, regardless of the incident ion used. Additionally, the same microstructural features, such as multiple layer loops and dendritic voids, are observed to occur.

5) The data compiled from experiments in which thin foils and bulk samples were irradiated under duplicate conditions have led to ambiguous results. The trends in the data obtained for the Ni-Al system are opposite to those obtained for the Ni-Cr alloys.

6) The Jones and Atteridge correlation between void swelling and electronic structure does not aid in understanding the mechanism of void swelling suppression due to solute additions, because it only predicts that the alloys used in this study swell less than pure Ni and does not treat the various void swelling parameters (such as $\langle d \rangle$ and N_v) independently.

7) The hypothesis of Gittus and Watkin, that the more thermodynamically stable the fcc phase of an alloy is as compared to the bcc phase the less it will swell, does not hold here as all the Ni-Cr alloys swell less than pure Ni.

8) Venker and Ehrlich's model of void swelling suppression due to differences in the intrinsic diffusion coefficients can explain the order of void swelling suppression efficiency at the low solute contents. Ti is most effective and Cr least effective in lowering void swelling and Ti diffuses the fastest, Cr the slowest in Ni.

9) The initial behavior of N_v as a function of solute concentration and temperature suggests that there are two competing mechanisms affecting N_v. The first enhances void nucleation, is not strongly temperature dependent, and dominates at low solute contents. Void embryo stabilization due to oversized solute atoms, a lowering of the surface free energy with solute content or gas atom-solute atom complex formation are all possible explanations for this behavior. The second mechanism lowers the vacancy supersaturation, is probably diffusion controlled and dominates the behavior of N_v in the more concentrated alloys. This suppression of N_v may be due to a change in the dislocation bias factor as a result of dislocation poisoning by solute atoms, or to defect trapping at solute atoms, either of which will lead to an enhanced vacancy-interstitial recombination rate.

10) While our swelling data can be made to fit various void swelling theories by proper choice of the adjustable arbitrary parameters, the results indicate that the variations in $\langle d \rangle$ and N_v must be treated separately in order to fully understand the mechanisms of void swelling suppression due to solute additions.

ACKNOWLEDGMENTS

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