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IRRADIATION-INDUCED SEGREGATION IN Ni-Si ALLOYS

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ABSTRACT

Radiation-induced segregation was studied in an Ni-1 at. % Si alloy after irradiation at a temperature of ~525°C with 3-MeV $^{58}Ni^+$ ions. Profiles of alloy composition as a function of depth from the irradiated surface were obtained by standard Auger techniques and ion-sputtering at room temperature. Rapid segregation of Si toward the irradiated surface was observed. The solubility limit of Si in Ni was reached at the surface after a dose of only 0.05 dpa. Segregation continued to increase up to the highest dose (6.5 dpa) which was investigated. Precipitation of Ni_3Si occured at the external surface and internally on dislocation loops. The experimental results are compared with calculations using the Johnson-Lam segregation model and a set of parameters that was used previously to fit the temperature dependence of radiation-induced segregation in Ni-1 at. % Si.

Key Words: radiation effects, mechanical properties, void swelling, nickel alloys, ion bombardment, radiation-induced segregation

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INTRODUCTION

Irradiation of metals at elevated temperatures creates fluxes of interstitial- and vacancy-type defects which terminate at spatially discrete defect sinks. In alloys, disproportionate transport of individual alloy constituents via defect fluxes can produce large, nonequilibrium concentration changes in the vicinity of the sinks. [1-3] Since internal imperfections, such as dislocations and grain boundaries, as well as external surfaces act as defect sinks, radiation-induced segregation can alter both bulk and surface properties of materials that are sensitive to alloy composition, e.g., mechanical strength, void swelling, phase stability, corrosion resistance, sputtering and radiation blistering. Radiation-induced segregation, therefore, impacts directly upon the performance of alloys in fission and fusion reactor environments.

Okamoto and Wiedersich [1] first suggested that size differences between solute and solvent atoms can influence the magnitude and direction of radiation-induced segregation. In particular, they proposed that because undersize atoms are more readily accomodated in interstitial sites than are larger atoms, the fraction of migrating interstitials that are undersize solute atoms, during irradiation at elevated temperature, may greatly exceed the fraction of undersize solute present in the alloy. Interstitial fluxes transfer atoms toward defect sinks. The preferential transport of undersize atoms via interstitial fluxes should therefore increase the concentration of undersize solute in the vicinity of a defect sink during irradiation at elevated temperatures. In the case of oversize solutes, the smaller solvent atoms should preferentially migrate via the

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interstitial fluxes and solvent enrichment (i.e., solute depletion) should occur near sinks. Enrichment of undersize and depletion of oversize solute elements near defect sinks have been observed in Ni-base binary alloys after irradiation at high temperatures. [3,4]

Radiation-induced segregation is strongly temperature dependent. When the irradiation-produced vacancies are relatively immobile, the recombination rate of vacancies and interstitials is high. This greatly reduces long-range defect fluxes at low temperatures, and concomitantly, the degree of segregation. At very high temperatures, rapid back diffusion, enhanced recombination due to the large equilibrium vacancy concentration, and the decreased effectiveness of defect-solute binding combine to inhibit radiation-induced segregation. The temperature dependence of radiation-induced segregation is thus expected to resemble the temperature dependence of void swelling, which also results from the flow of point defects to sinks. Composition versus depth profiles obtained by Auger analysis have shown that the temperature dependence of radiation-induced segregation in the Ni-1 at. % Si system [3] is indeed quite similar to that of swelling in pure Ni [5], although the maximum in the segregation occurs slightly below the maximum swelling temperature. The lower temperature of the segregation peak is believed to result from back-diffusion of solute, which inhibits segregation at high temperatures but plays no role in the swelling of pure Ni.

A kinetic model has been developed by Johnson and Lam (J-L) [2] which describes the radiation-induced segregation process by a set of coupled rate and diffusion equations. The model has recently been extended to include the effects of surface precipitation [6] and a depth-dependent defect production rate [7]. In the case of binary Ni-Si alloys, the J-L model assumes preferential participation of the undersize Si atoms in interstitial fluxes.

The purpose of this paper is to report measurements of the dose dependence of radiation-induced segregation in an Ni-1 at. % Si alloy. For comparison, segregation profiles have been calculated as a function of dose using the modified J-L model and a set of parameters that was previously used [7] to model the temperature dependence of radiation-induced segregation in the same alloy.

EXPERIMENTAL PROCEDURES

The Ni-1 at. % Si alloy was prepared by arc-melting and subsequent levitation melting in an induction furnace. Specimens in the form of 3-mm disks were punched from ∿0.25-mm foils that had been rolled from this stock. The disks were annealed at 900°C for 2 hours in a vacuum of $\sim 10^{-8}$ torr and then electropolished.

Irradiations were performed with 3-MeV $^{58}Ni^{+}$ ions in a vacuum of $\sim 10^{-8}$ torr at the ANL Dual-ion Irradiation Facility. Details of the irradiation procedures may be found elsewhere [8]. Thermocouples were used to monitor and control the temperature of the sample holder. Individual sample temperatures were measured during the irradiation with a previously calibrated infrared pyrometer. Total doses are given at the peak damage depth. They were calculated using a threshold displacement energy of 40 eV and the Brice Codes RASE3 and DAMG2 [9]. The peak damage rate was $\sim 2.5 \times 10^{-3}$ displacements per atom per second (dpa/s) and occured at a depth of ∿550 nm. Near the surface, the displacement rate was $\sim 10^{-3}$ dpa/s.

Auger analysis [10] was done with a primary electron beam of 5 kV. Depth profiling was accomplished by sputtering an area ∿2 mm in diameter with 2 kV Ar ions in an Ar atmosphere of 5×10^{-5} torr. Sputtering was interrupted to record the Auger spectra. Measurements of the total sputtering depth in several different samples gave sputtering rates of 11 ± 2 nm per minute. A value of 11 nm per minute was used to convert the measured sputtering times into depths. Analysis of unirradiated control specimens showed no significant variation of composition with depth. Standard alloys containing 0, 1, 2, 4, 12.8 and 25 at. % Si were used to determine the relationship between concentration and Auger peak-to-peak ratio.

RESULTS AND DISCUSSION

Measured Dose Dependence

The Si/Ni Auger peak-to-peak ratios measured at various depths below the irradiated surface in Ni-1 at. % Si specimens exposed at ∿525°C to doses of 0.05, 0.16, 0.5, 2.8 and 6.5 dpa at the damage peak are presented in Fig. 1. Si/Ni peak-to-peak ratios obtained from unirradiated Ni alloys containing known amounts of Si are indicated on the right-hand side of the figure. The peak-to-peak ratio is a smoothly varying and monotonically increasing function of Si concentration. The nominal irradiation temperature of 525°C lies ∿50° below the peak segregation temperature. [3,7]

The irradiated surface serves as an unsaturable sink for both vacancy- and interstitial-type defects. Significant segregation of the undersize Si atoms toward the surface is evident in all five samples. Segregation continues with dose throughout the investigated damage range from 0.05 to 6.5 dpa. At the lowest dose, the concentration of Si on the surface is ∿10 at. %. As the irradiation dose is increased, both the surface concentration of Si and the thickness of the enriched layer increase. Enrichment of Si near the surface is accompanied by depletion at intermediate depths. For example, the depleted zone in the 6.5 dpa sample extends from a depth of ∿25 nm to ∿200 nm (off scale in Fig. 1) before the measured Si concentration returns to the 1 at. % level.

It should be emphasized that the Auger peak-to-peak ratio is a measure of the alloy composition averaged over the area of the analysis beam (∿100 μm^2) on the sample. The return of this ratio in the irradiated specimens to the value found in the unirradiated Ni-1 at. % Si standard demonstrates only that no net flow of solute to the surface has occured from deeper in the sample; it does not indicate the absence of radiation-induced segregation at these depths. The effectiveness of the surface as a sink diminishes for defects produced at greater depths because of internal sinks, which gradually become the predominant termini for defect fluxes. Since the area analyzed by the Auger technique is of sufficient size to encompass many internal sinks, the depleted and enriched regions are averaged at depths sufficiently removed from the external surface, and the same peak-to-peak ratio is found regardless of whether or not segregation to internal sinks has occured.

Layers of Ni_3Si have previously been identified on the surface of irradiated Ni-Si alloys by means of Auger analysis, [3] electron diffraction and x-ray flourescence. [11] The phase diagram reveals that at the present irradiation temperatures, precipitation of the ordered Ni_3Si γ' phase should initiate wherever the local Si concentration surpasses the solubility limit of 10 at. %. [12] In the present experiments, this limit is exceeded at the irradiated surface for all doses greater than 0.05 dpa. Auger ratios between $\sim 20 \times 10^{-3}$ and 45×10^{-3} correspond to two-phase regions of the matrix containing Ni_3Si precipitates in an Si enriched background. The existence of a complete surface layer of Ni_3Si is apparent in the profiles of the two highest dose specimens in Fig. 1. In particular, the Auger peak-to-peak ratios that were measured at the first three sampled depths in the 6.5 dpa specimen all indicate a Si concentration of ~ 25 at. %. However, the precipitate-matrix interface is not as sharply defined as in a previous study. [3]

Calculated Dose Dependence

Concentration profiles shown in Fig. 1 were produced by irradiation of identically prepared samples at the same dose rate and at approximately the same temperature. The J-L model requires several parameters as input in order to predict the dose dependence of solute concentration profiles. The parameters include migration energies and pre-exponential factors for self-interstitials, vacancies and solute-defect complexes, solute-defect binding energies and the vacancy formation energy. The parameters used in the present calculations are listed in Table I, and are characteristic of Ni-base alloys and undersize solute atoms such as Si in Ni. The same parameters have been used previously to reproduce qualitatively the temperature dependence of radiation-induced segregation in the Ni-1 at. % Si alloy [7]. Precipitation is assumed to occur when the surface concentration exceeds 10 at. %; the excess solute is allowed to flow through the precipitate-matrix interface to form the Ni_3Si precipitate layer. For a discussion of the details of the calculations, the reader is referred elsewhere [2,6,7]. A depth-dependent damage rate characteristic of 3-MeV $^{58}Ni^+$ ions incident on Ni was used.

It should be emphasized that the present experimental situation is considerably more complex than that assumed for the model calculations, where internal sinks and clustering effects are neglected. The experimental profiles were obtained from specimens with a depth-, time- and temperature-dependent internal sink structure. The model also assumes that the alloy may be treated as an ideal dilute solid solution. Clearly, the latter condition is not fulfilled when the solute concentration near sinks approaches the solubility limit. Chemical rather than dilute alloy diffusion theory would then more adequately model the segregation behavior.

Once the Si solubility limit is attained at the specimen surface, the one-dimensional J-L segregation model assumes formation of a continuous layer of Ni_3Si. The Si concentration profiles which were calculated for several doses at an irradiation temperature of 550°C drop sharply from the solubility limit of 10 at. % at the precipitate-matrix interface to below the Auger detection limit (≲0.2 at. % Si) within a few nanometers. Thus, the calculated profiles are considerably steeper than those that were found experimentally. Of course, the model cannot reproduce the two-phase regions seen in Fig. 2.

The calculations predict that the surface concentration of Si will reach the solubility limit of 10 at. % after a dose of ∿0.2 dpa, which can be compared to the experimental result of 0.05 dpa. In addition, the enriched region in the 0.05 dpa specimen is considerably thicker than that shown by the calculations after a similar dose. Hence, the initial stages of Si migration toward the irradiated surface occur more rapidly than the model predicts on the basis of the parameters in Table I.

However, the total amounts of precipitate contained in the calculated layer and observed experimentally in the near-surface region are remarkably similar. The calculations show initial coverage of the surface by a one-atom-thick layer of precipitate at ∿0.5 dpa. Between 1 and 5 dpa, the calculated precipitate layer grows from a thickness of ∿1 to 5 nm. Considering the complexity of the experimental situation which is modeled and the fact that the parameters in Table I were chosen to fit the temperature-dependence of irradiation-induced segregation, the agreement is considered good.

Effect of Damage Profile

During irradiation, fluxes of defects are established not only between the matrix and defect sinks, but also in regions where gradients exist in the defect production rate. Defect fluxes originate in regions where the production rate is high and flow toward regions of lower defect production. Particularly large variations in the defect production rate occur adjacent to the peak damage region in ion-irradiated materials. The J-L model has recently been modified [7] to include a spatially nonuniform defect production rate. In cases of strong defect-solute interactions such as occurs, for example, in Ni-Si alloys, the J-L model predicts a redistribution of solute between the peak damage region and the matrix immediately beyond the maximum penetration depth of the ions.

A displacement energy of 40 eV was used with the Brice Codes RASE3 and DAMG2 [9] to calculate the spatially dependent damage rate for 3-MeV $^{58}Ni^{+}$ ions on Ni shown in Fig. 2. The damage peak is located at 0.54 μm from the irradiated surface and the total damage range is ∿1.1 μm. The damage profile indicates that the larger number of defects produced in the peak damage region should create a net flux of interstitials from the peak damage region to depths greater than the total damage range. In a manner similar to that observed near the irradiated surface, preferential participation of Si in this interstitial flux would be expected to cause depletion of Si near the peak damage region and enrichment at greater depths.

The Ni-1 at. % Si sample which had been irradiated to 6.5 dpa at 522°C was sputter-profiled with the Auger technique from the irradiated surface to a depth of ∿2 μm, which is well beyond the ion penetration depth. Although strong surface segregation and an underlying depletion layer were observed (Fig. 1), no measurable changes in the Si concentration were found in or beyond the peak damage region. The J-L model predicts enrichment to ∿1.2 at. % Si beyond the peak damage depth under these irradiation conditions. This is considerably less than the compositional changes observed near the surface and lies near the sensitivity limit of the Auger technique. The present measurements therefore suggest that the degree of enrichment which is predicted beyond the peak damage region by the J-L model using the parameters in Table I and the damage profile in Fig. 2 is an upper limit.

An indication that the J-L model may overestimate the degree of one-dimensional solute redistribution can be seen in the transmission electron micrograph shown in Fig. 3. The micrograph is a dark-field image taken with a Ni_3Si superlattice reflection of an Ni-4 at. % Si specimen after irradiation to 3 dpa at 525°C. Very severe segregation of Si to dislocation loops is evident. Similar effects have been reported by Barbu and Ardell. [13] The segregation is sufficient to form coatings of Ni_3Si on the loops. Internal sinks appear to dominate the point defect diffusion near the peak damage range, and may prevent the establishment of long-range defect fluxes. The J-L model neglects internal sinks, and therefore may overestimate the redistribution of solute beyond the peak damage region.

CONCLUSION

The experimentally determined dose-dependence of radiation-induced segregation in an Ni-1 at. % Si alloy is in good qualitative agreement with predictions of the J-L segregation model. The experimental results and theoretical analysis both show that the irradiation doses required to cause significant compositional changes at the external surface, are remarkably low. Large compositional changes at grain boundaries can be expected to occur after equivalent doses, and to have a significant effect on the mechanical behavior of an irradiated alloy. The present results therefore suggest that radiation-induced segregation may affect the mechanical behavior of alloys long before the onset of void swelling.

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REFERENCES

[1] Okamoto, P. R. and Wiedersich, H., *Journal of Nuclear Materials*, Vol. 53, 1974, p. 336.

[2] Johnson, R. A. and Lam, Nghi Q., *Physical Review B*, Vol. 13, 1976, p. 4364.

[3] Rehn, L. E., Okamoto, P. R., Potter, D. I. and Wiedersich, H., *Journal of Nuclear Materials*, in press.

[4] Pronko, P. P., Okamoto, P. R. and Wiedersich, H., *Proc. Third Intl. Conf. on Ion Beam Analysis, Nuclear Instruments and Methods*, Vol. 149, 1978, p. 77.

[5] Ryan, T. D., *Ph.D. Thesis*, University of Michigan, Ann Arbor, MI, 1975.

[6] Lam, Nghi Q., Okamoto, P. R., Wiedersich, H. and Taylor, A., submitted to *Metallurgical Transactions*.

[7] Lam, Nghi Q., Okamoto, P. R. and Johnson, R. A., submitted to *Journal of Nuclear Materials*.

[8] Taylor, A., Wallace, J. R., Potter, D. I., Ryding, D. G. and Hall, B. Okray, *Proc. Intl. Conf. on Radiation Effects and Tritium Technology for Fusion Reactors*, CONF-750989, Vol. I, 1976, p. I-158.

[9] Brice, D. K., SLA-73-0416, Sandia Laboratories, Albuquerque, NM, 1973.

[10] Chang, C. C. in *Characterization of Solid Surfaces*, P. F. Kane and G. B. Larrabee, Ed., Plenum Press, New York, 1974.

[11] Potter, D. I., Rehn, L. E., Okamoto, P. R. and Wiedersich, H., *Scripta Metallurgica*, Vol. 11, 1977, p. 1095.

[12] Rostogi, P. K. and Ardell, A. J., *Acta Metallurgica*, Vol. 10, 1971, p. 321.

[13] Barbu, A. and Ardell, A. J., *Scripta Metallurgica*, Vol. 9, 1975, p. 1233.

FIGURE CAPTIONS

Figure 1. Si/Ni Auger peak-to-peak ratios as a function of depth from the irradiated surface for five Ni-1 at. % Si specimens irradiated to different doses. Irradiation parameters are given on the figure. Peak-to-peak ratios measured in unirradiated samples containing known amounts of Si are indicated on the right-hand ordinate.

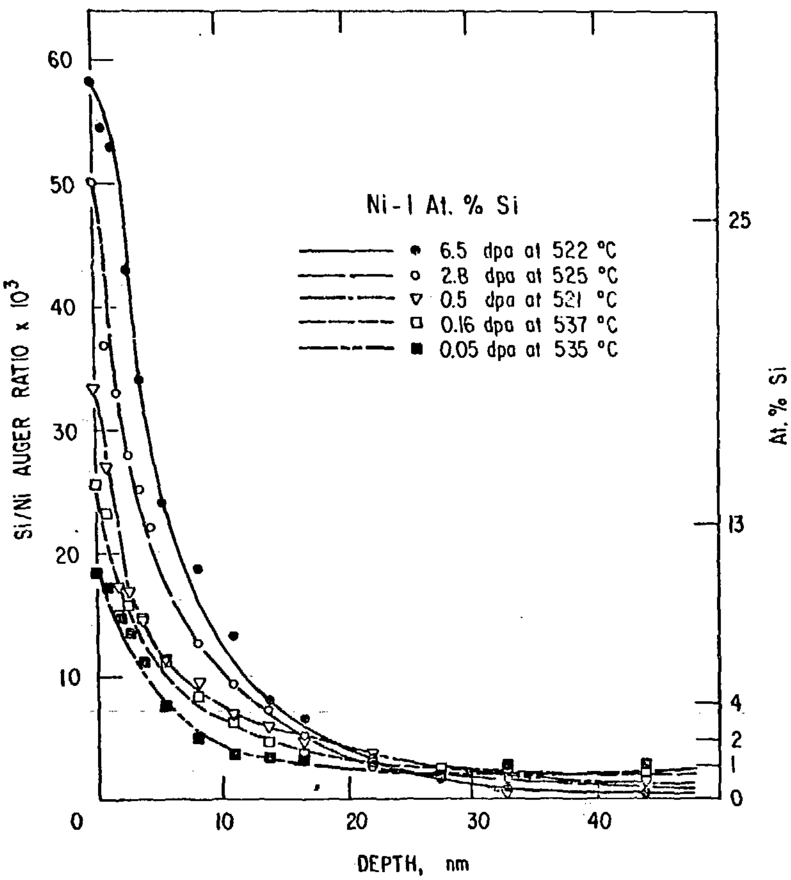
Figure 2. Normalized defect production rate as a function of depth from the irradiated surface.

Figure 3. (a) Bright-field image of interstitial Frank loops in a Ni-4 at. % Si specimen irradiated to 3 dpa at 525°C. (b) Dark-field image formed with a γ' superlattice reflection. Note the precipitation of γ' on the dislocation loops.

TABLE I. Parameters Used in Calculations

Parameters	Values
Vibration frequency factor for interstitial	5×10^{12} s^{-1}
Vibration frequency factor for type-a interstitial-solute complex	5×10^{12} s^{-1}
Vibration frequency factor for vacancy	5×10^{13} s^{-1}
Vibration frequency factor for vacancy-solute complex	5×10^{13} s^{-1}
Migration energy of interstitial	0.15 eV
Formation energy of vacancy	1.60 eV
Migration energy of vacancy	1.28 eV
Migration energy of vacancy-solute complex	1.28 eV
Migration energy of type-a interstitial-solute complex	1.28 eV
Binding energy of type-a interstitial-solute complex	1.88 eV
Binding energy of vacancy-solute complex	0.0
Formation entropy of vacancy	3 k*

*k is the Boltzmann constant



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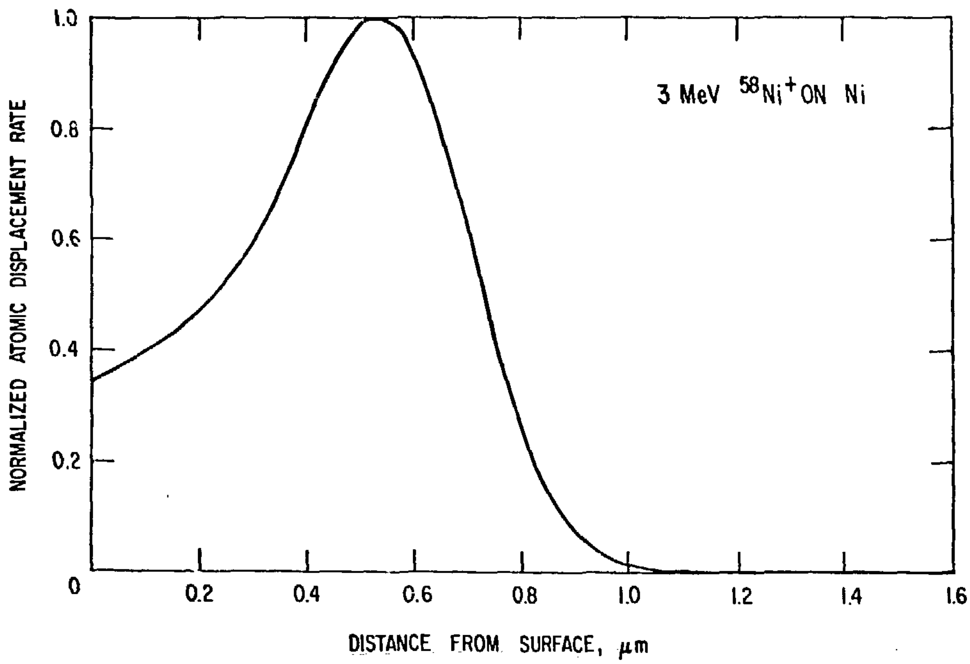

Figure 2. Normalized defect production rate as a function of depth from the irradiated surface.

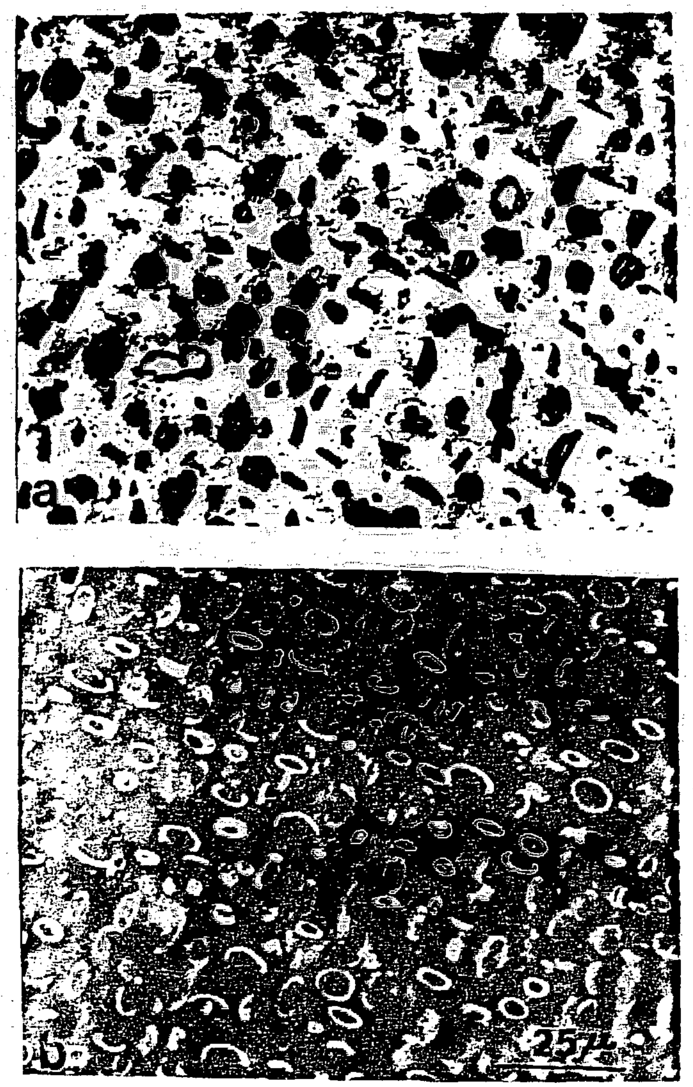

Figure 3. (a) Bright-field image of interstitial Frank loops in a Ni-4 at. % Si specimen irradiated to 3 dpa at 525°C. (b) Dark-field image formed with a γ' superlattice reflection. Note the precipitation of γ' on the dislocation loops.