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P. R. Okamoto,* L. E. Rehn,* R. S. Averback,*
K.-H. Robrock** and H. Wiedersich*

*Materials Science Division
Argonne National Laboratory
Argonne, IL 60439

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**Institut für Festkorperforschung der Kernforschungsanlage
Jülich, BRD

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Mechanism and Kinetics of Radiation-Induced Segregation In Ni-Si Alloys

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* Materials Science Division, Argonne National Laboratory, Argonne, IL 60439
** Institut für Festkorperforschung dev Kernforschungsanlage, Jülich, BRD

Rutherford-backscattering and Auger chemical-depth-profiling measurements show that films of the γ'-Ni_3Si phase produced on the ion-bombarded surfaces of Ni-Si alloys obey simple parabolic growth kinetics. At low temperatures the film growth-rate constant exhibits Arrhenius behavior and varies with the fourth root of the dose rate. The apparent activation energy in this low temperature region is ~ 0.3 eV. At high temperatures the growth constant is independent of the dose rate. The results are consistent with a diffusion-controlled growth model, which assumes Si atoms migrate in the form of a fast-diffusing Si-interstitial complex.

I. INTRODUCTION

Defect flux-driven segregation processes which lead to local partitioning of alloy constituents have assumed an increased importance for a number of materials problems where alloys are subjected to energetic particle irradiations. One of the most striking and best documented examples of the phenomenon is the formation and growth of coherent Ni_3Si films on the surfaces of ion bombardment Ni-Si alloys [1]. Recent Rutherford backscattering and Auger chemical depth profiling measurements have shown that such films obey parabolic growth kinetics [2]. Moreover, the temperature-dependent growth constant was found to exhibit Arrhenius behavior at low temperatures with an apparent activation energy of ~ 0.3 eV. In this low temperature Arrhenius region, the growth constant varies with the fourth root of the dose-rate, and is independent of dose-rate at high temperatures [3]. Some results demonstrating the parabolic growth of Ni_3Si films on the surfaces of 3-MeV Ni^+ ion bombardment Ni-Si samples are shown in Fig. 2.

Here we show that the observed growth kinetics can be explained by a diffusion-controlled growth model in which the rate-limiting step is the transport of fast migrating Si-interstitial complexes to the surface. Although definite experimental proof is still lacking, there is evidence to support the view that the segregation mechanism for Si is via interstitials. For example, recent observations of Si segregation to the surfaces of irradiated Ni-Si alloys below room temperature strongly suggest that Si migrates via an interstitial mechanism, presumably in the form of a fast diffusing Si-interstitial complex [4]. Direct evidence for the formation of Si-interstitial complexes has been obtained from internal friction and resistivity recovery measurements on dilute Ni-Si foils after electron irradiation at 4.7 K [5]. The results (see Fig. 1) show that at least one type of complex created during stage I annealing remains stable and immobile up to 200 K where it either dissociates or becomes mobile. Taking 0.14 eV as

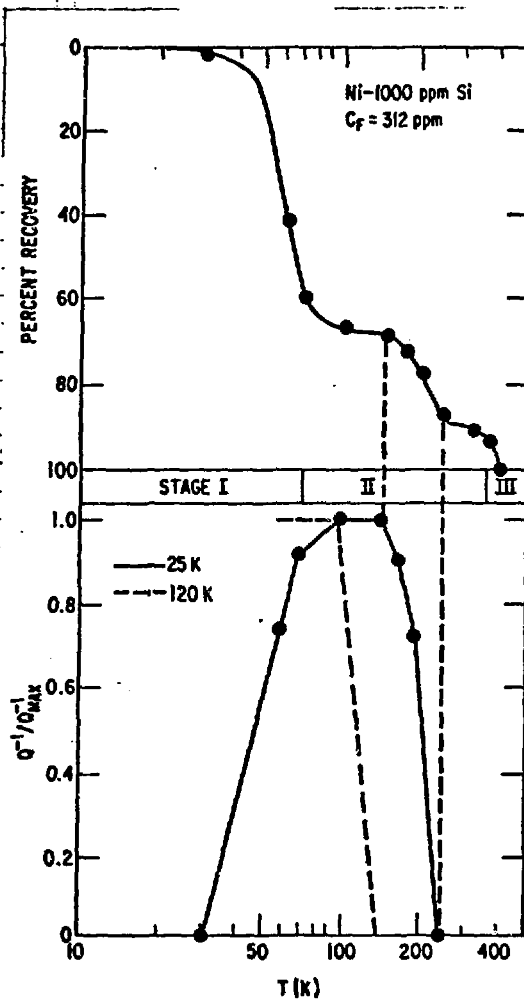

Fig. 1. Resistivity recovery (top) and normalized internal friction peak heights (bottom) as a function of annealing temperature T. Q^{-1}_{MAX} is the maximum peak height obtained during the annealing. 25 K and 120 K are the temperatures where peaks are first observed.

the migration energy for the self-interstitial in Ni, the first interpretation implies a binding energy of $H^B_{is} \sim 0.46$ eV for the complex, while the second implies a migration energy of $H^m_{is} \sim 0.6$ eV, and a binding energy greater than 0.6 eV. The latter interpretation is consistent with the observation of Si segregation below room temperature and with the theoretical estimate of $H^B_{is} \sim 0.9$ eV obtained by Gupta [6] for the Si-interstitial complex in Ni.

II. FILM GROWTH MODEL

A simple growth model based on the assumption that film growth is limited by the rate at which Si-interstitial complexes can diffuse across a solute depleted zone has been found to give a good quantitative account of the observed growth kinetics. A detailed description of the model is given elsewhere [7] and only a brief qualitative discussion is given here. The model assumes tight-binding between solute atoms and interstitials so that in the bulk region where the initial solute concentration is maintained, all interstitials are bound. Film growth is also assumed to occur under quasi-

steady state conditions for interstitial-solute (i-s) complexes and vacancies, and that quasi-steady state concentrations C_{is}^m and C_v^m in the bulk are those given by standard rate theory.

The model leads to the following expression for the film thickness, W_p

$$W_p = A\sqrt{t-t_o} \tag{1}$$

where

$$A = \left[\frac{2C_s^o}{C_s^p(C_s^p-C_s^o)}\right]^{1/2} \sqrt{D_{is}C_{is}^m} \tag{2}$$

and t_o is the incubation time for precipitation of the film, C_s^o is the initial solute concentration in the alloy, C_s^p is the solute concentration in the precipitate film, D_{is} is the diffusion coefficient for the i-s complex, and C_{is}^m, its quasi-state concentration far from the surface is given by

$$C_{is}^m = \frac{2K_o(1+\beta)}{p_{is}\nu_{is}\eta} \left\{\left[1 + \frac{\eta}{(1+\beta)^2}\right]^{1/2} - 1\right\} \tag{3}$$

where

$$\eta = \frac{4K_o a_6(\nu_v+\nu_{is})}{p_{is}p_v\nu_{is}\nu_v}$$

and

$$\beta = \frac{a_6\bar{C}_v(\nu_v+\nu_{is})}{p_{is}\nu_{is}} \tag{4}$$

Here K_o is the production rate of freely migrating vacancies and interstitials, a_6 is the number of lattice sites in the recombination volume for vacancies and i-s complexes, (ν_{is},ν_v) and (p_{is},p_v) are jump frequencies and sink annihilation probabilities for vacancies and i-s complexes, and $\bar{C}_v$ is the thermal equilibrium concentration of vacancies.

When $D_{is} \gg D_v$, it can be shown that for low temperatures

$$\sqrt{D_{is}C_{is}^m} \propto (K_oD_v)^{1/4} \tag{5}$$

and for high temperatures

$$\sqrt{D_{is}C_{is}^m} \propto \left(\frac{K_o}{\bar{C}_v}\right)^{1/2} \tag{6}$$

These equations show that the growth rate should exhibit Arrhenius behavior at low and high temperatures. The apparent activation energy for the low temperature region was experimentally found to be ~ 0.3 eV. From eq. (5) this should correspond to an effective vacancy migration energy of H_v^m ~ 1.2 eV.

III. COMPARISON WITH EXPERIMENTS

To compare model predictions with experimental observations, the measured growth-rate constant i.e. A in eq. (1), is divided by $M^{1/2} = [2C_s^o/C_s^p(C_s^p-C_s^o)]^{1/2}$. As shown by eq. (2) $A/M^{1/2}$ should be equal to $\sqrt{D_{is}C_{is}^m}$. Plots of ln $A/M^{1/2}$ vs $(kT)^{-1}$ obtained from growth-rate measurements of Ni_3Si films on Ni-1, 6 and 12.7 at. % Si alloys bombarded with either 3-MeV Ni^+ or 2-MeV He^+ are shown in Fig. 3. All data points refer to the 12.7 Si alloy except for the symbols (◆) and (▲), which refer to 1 and 6 at. % Si alloys. The calculated atomic displacement rates, K_s, at the surface

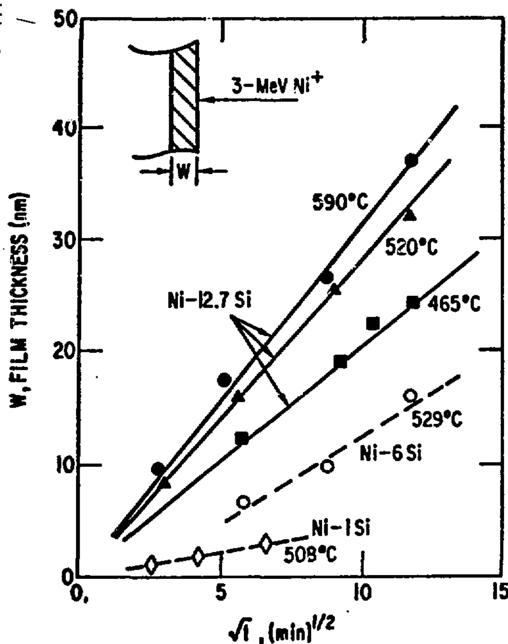

Fig. 2. Growth curves for Ni_3Si films produced on the surfaces of 3-MeV Ni^+ ions bombarded Ni-Si alloys.

determined from the ion currents and energies are 3.1×10^{-4} dpa/s and 2.6×10^{-5} dpa/s for the 2-MeV He^+ irradiations and 6.9×10^{-4} dpa/s for the 3-MeV Ni ions.

The procedure used to fit the data was as follows. Theoretical values for $\sqrt{D_{is} C_{is}^m}$ were first calculated for the He^+ data assuming $K_o = K_s$, $H_v^M = 1.25$ eV $H_{is}^B = 0.9$ eV and $H_{is}^M = 0.6$ eV. The remaining parameters (mainly H_v^F, S_v^F and a_6) were systematically varied to obtain curves of best fit for $p_v = 1 \times 10^{-4}$ and $p_v = 3 \times 10^{-4}$ which represent the range of sink densities typically produced by the irradiations. This fitting procedure yielded the set of optinum parameters given in Table I. The same set of physical parameters was then used to fit the Ni^+ data by adjusting K_o. As shown in Fig. 3, the best fit value of $K_o = 6 \times 10^{-5}$ dpa/s is 8% of the calculated atomic displacement rate ($K_s = 6.9 \times 10^{-4}$ dpa/s). This method for determining K_o provides a critical test of the model since eq. (6) shows that $\sqrt{D_{is} C_{is}^m}/K_o$ and the corresponding experimental quantity $A/(MK_o)^{1/2}$ should be independent of K_o at high temperatures and vary as $(K_o)^{-1/4}$ at low temperatures. The good agreement between the model and experimental results shown in Fig. 4 indicate that film growth-rate measurements may provide an elevated temperature method for determining the number of freely migrating defects which escape recombination and clustering within cascades produced by ions of differing mass and energy.

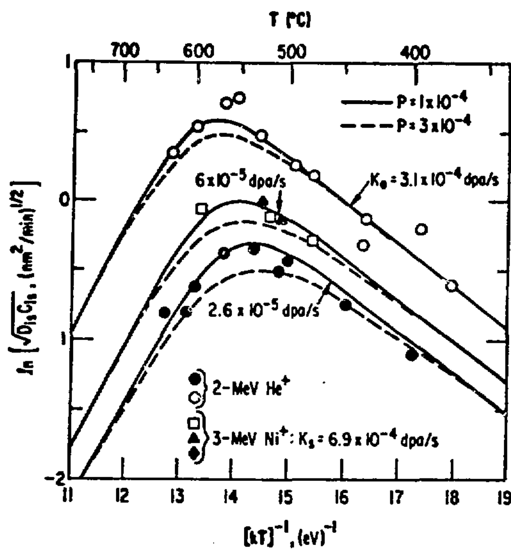

Fig. 3. Temperature dependence of Ni_3Si film growth rates during 3-MeV Ni^+ and 2-MeV He^+ irradiation of Ni-Si alloys. Growth rate expressed in $(nm^2/min)^{1/2}$.

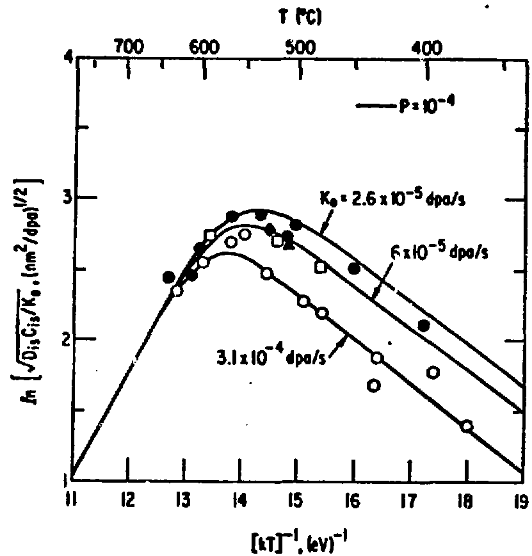

Fig. 4. Temperature dependence of Ni_3Si films growth data shown in Fig. 3 but with the growth rate expressed in $(nm^2/dpa)^{1/2}$

Table 1. Basic Model Parameters.

Parameter	Notation	Value
Vibration frequency factor for intersitial	ν_i^o	$5 \times 10^{12} s^{-1}$
Vibration frequency factor for vacancies	ν_v^o	$5 \times 10^{-13} s^{-1}$
Vibration frequency factor for i-s complexes	ν_{is}^o	$5 \times 10^{-12} s^{-1}$
Migration energy of interstitial	H_i^M	0.15 eV
Formation energy of vacancy	H_v^F	1.5 eV
Migration energy of vacancy	H_v^M	1.25 eV
Formation entropy of vacancy	S_v^F	4.0 k
Lattice constant	a_o	3.52Å
Recombination volume (# of sites)	a_6	150
Sink annihilation probability for vacancies	p_v	$(1-3) \times 10^{-4}$
Sink annihilation probability for i-s complex	p_{is}	$(1 - 3) \times 10^{-4}$

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