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Effect of interfacial impurities on intermixing of bilayers

V. SRINIVASAN
Universal Energy Systems, Inc., 4401 Dayton-Xenia Road, Dayton, Ohio 45432, USA

Mixing experiments were performed on Ni/Pt and René N4/Pt systems to understand the effect of interfacial impurities on the ion-beam mixing process. A layer of platinum 15 or 50 nm thick was deposited on metallographically polished sputter-cleaned nickel and René N4 substrates as well as on metallographically polished uncleaned René N4 by electron-beam deposition techniques. These targets were exposed to the bombardment of a Pt^+ 1 MeV beam. A range of fluences, 2×10^{15} to 2×10^{16} Pt^+/cm^2 was used to cause intermixing. The amount of mixing was evaluated by Rutherford backscattering spectroscopy and Auger sputter depth profiling. The mixing rates were the same for Ni/Pt and René N4/Pt with the clean interface. However, it was significantly less in René N4/Pt with an interfacial native oxide/impurity layer. The initial high volume fraction of γ' precipitates in René N4 along the ion path became disordered under bombardment, and the alloying elements present significantly in the resultant solid solution did not influence the mixing process. Mixing in Ni/Pt and René N4/Pt with the clean interface appears to be dominated by thermochemical influences.

1. Introduction

Mixing can be induced in multilayered solids by ion bombardment. Passage of energetic ions through the layers of different elements causes this intermixing. Several mechanisms of mixing may be operative. These mechanisms are recoil implantation, ballistic collisional and thermochemical processes [1, 2]. The former two processes are not as efficient as the latter. The efficiency of mixing depends on the nature of the interface. In this paper the effects of interfacial cleanliness on ion-beam mixing are discussed.

2. Experimental materials and methods

René N4 and commercial purity nickel were the substrates in this study. René N4 was a single-crystal nickel-base superalloy, of nominal chemical composition (wt %) 9.25 Cr, 1.5 Mo, 3.7 Al, 4.5 Ti, 6.0 W, 7.0 Co, 4.0 Ta, 0.5 Nb, Ni bal. In the fully heat-treated condition this alloy contained a large volume fraction of cuboidal gamma prime (ordered Ni_3Al) precipitates [3]. The commercial purity nickel substrate was used as a standard reference to compare the mixing efficiency in René N4 alloy.

Coupons were machined from the heat-treated René N4 cast slab and the as-received nickel foil with approximate dimensions of 1 cm × 1 cm × 0.1 cm. The primary faces of René N4 were within about 15° of the $\{100\}$ plane. One side of each coupon was metallographically polished, cleaned thoroughly in trichloroethylene, acetone and deionized water and then dried. The polished surfaces of one set of René N4 coupons and nickel coupons were sputter-cleaned with 800 eV Ar^+ ions at a current density of about 250 μA for approximately 15 min to remove surface impurities and the native oxide layer. Without breaking the vacuum of about 10^{-6} torr, a single layer of platinum, about 50 nm thick, was deposited on the sputter-cleaned surface of the coupon by electron-beam evaporation. Another set of René N4 targets for ion-beam mixing studies were prepared by depositing a single layer of platinum, about 15 nm thick, on the polished surface of coupons without initial sputter-cleaning by the same evaporation technique. The platinum layer thickness was followed during evaporation by a calibrated quartz oscillator. In choosing the final thickness of the platinum layer the projected range, R_p, of the incident ion and the sputtering losses were taken into account. The Monte Carlo TRIM program was used to estimate the projected range, R_p, the energy straggling, ΔR_p and the energy deposited at the substrate–platinum layer interface [4]. High-energy 1 MeV Pt^+ ions from a Tandetron accelerator were used to induce mixing in the target. Four fluences, 2×10^{15}, 5×10^{15}, 1×10^{16} and 5×10^{16} Pt^+ ion/cm^2 were used to study the dependency of mixing rate on dose. High-resolution Rutherford backscattering spectroscopic (RBS) analysis and Auger electron spectroscopic (AES) sputter-depth profiling method were used to evaluate the ion-beam mixing. The RBS analysis was accomplished with 3.05 MeV He^{2+} beam at angles of incidence and scattering at 75° (or 70°) and 168°, respectively. A beam of Ar^+ with energy of 1 keV was used in a vacuum of 5×10^{-5} torr to sputter-profile platinum in the as-deposited and ion-beam mixed conditions.

3. Results and discussion

Figs 1 to 3 show the RBS spectra obtained from three

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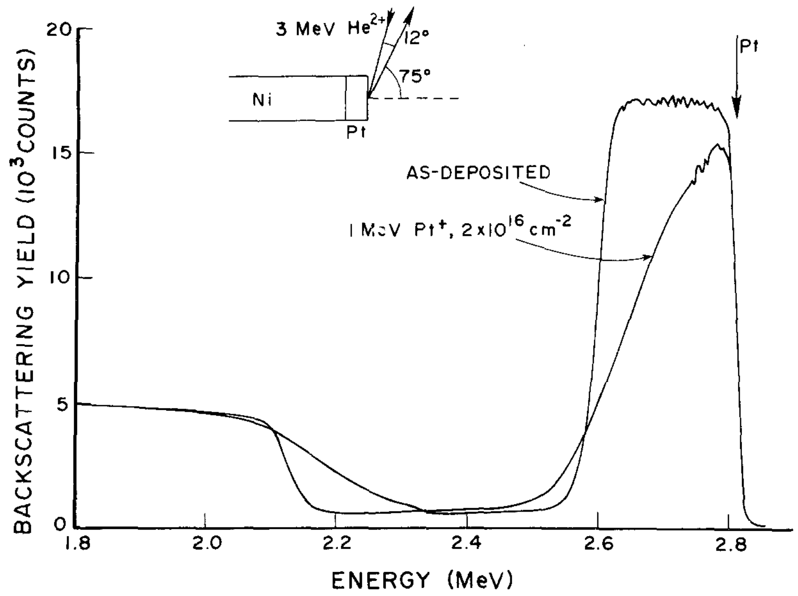

Figure 1 Rutherford backscattering spectra from the as-deposited and ion-beam mixed Ni/Pt targets with the clean interface.

types of target: Ni/Pt, René N4/Pt with the clean interface and René N4/Pt with an impurity/native oxide layer before and after ion-beam mixing. The amount of mixing was characterized by the width between the 16% and 84% points of the platinum signal assuming that this signal has the form of an error function. This width was used to estimate the change in the variance (energy), $\Omega^2_{\text{mix}}(E)$

$$\Omega^2_{\text{mix}}(E) = \Omega^2_{\text{irr}}(E) - \Omega^2_{\text{unirr}}(E) \qquad (1)$$

The change in the energy variance, $\Omega^2_{\text{mix}}(E)$, was converted to the change in the depth variance, $\sigma^2_{\text{mix}}(d)$ by assuming the stopping power of NiPt and an average of the atomic densities of nickel and platinum for both Ni/Pt and René N4/Pt systems.

The results of Auger sputter depth profiling before and after ion beam mixing in the case of René N4/Pt with the interfacial impurity/native oxide layer are shown in Figs 4 to 6. Carbon and oxygen were the constituents of the interfacial impurity/oxide layer as revealed by their peaks in the Auger sputter-depth profile, Fig. 5. These peaks were smoothed out under ion bombardment, Fig. 6. The amount of mixing was estimated from the Auger sputter-depth profiles obtained before and after ion bombardment, Fig. 4.

The effect of the fluence, ϕ, on the amount of mixing is described in Fig. 7 by the relationship between the variance, $2\sigma^2(=4Dt)$ and ϕ where $4Dt$ is twice the square of the diffusional distance. This figure brings out three important aspects of mixing. The amount of mixing in Ni/Pt and René N4/Pt with the clean interface increased linearly with the dose within the present experimental scope. The mixing rates were almost identical in Ni/Pt and René N4/Pt with the sputter-cleaned interface. However, in the case of René N4/Pt with an interfacial impurity layer the mixing rate was considerably slower by an order of magnitude. The straight line passing through the experimental points was obtained by least square fit.

The experimental results obtained on Pt/Ni and Pt/René N4 systems are compared with the predictions of models based on cascade mixing and thermochemical effects. An expression for change in full-width-at-half-maximum (ΔFWHM) of gaussian distribution of deposited atoms relating the ion dose ϕt and the loss in nuclear collision $(\mathrm{d}E/\mathrm{d}x)_{\text{n}}$ is given by

$$\Delta\text{FWHM} = \left(\frac{2}{3}\right)^{1/2} R\left[\frac{(\mathrm{d}E/\mathrm{d}x)_{\text{n}}\phi t}{4E_{\text{d,min}}N}\right]^{1/2} \qquad (2)$$

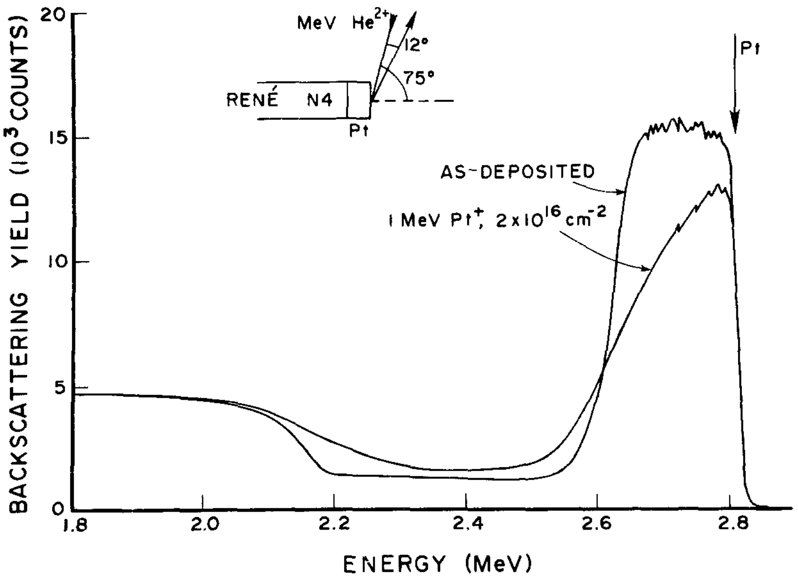

Figure 2 Rutherford backscattering spectra from the as-deposited and ion-beam mixed René N4/Pt targets with the clean interface.

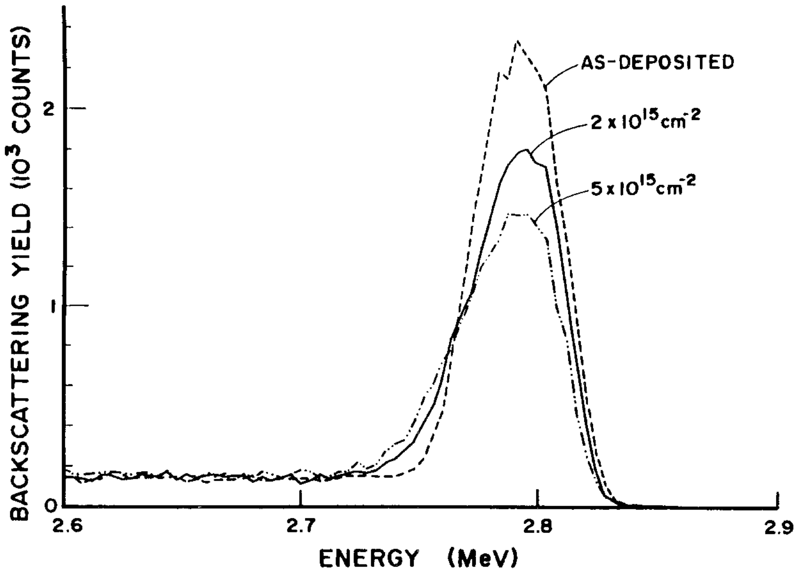

Figure 3 Rutherford backscattering spectra from the as-deposited and 3.05 MeV He^{2+} ion-beam mixed René N4/Pt targets with the interfacial impurity layer.

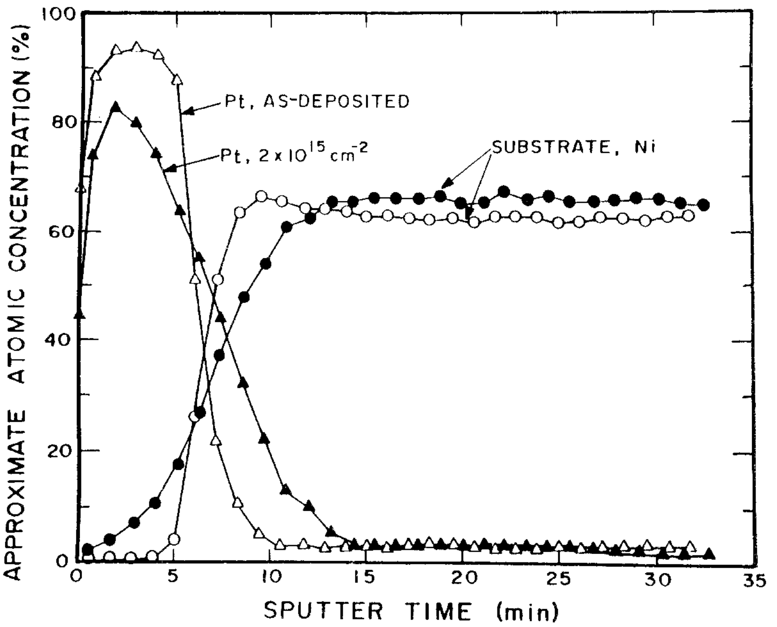

Figure 4 The Auger sputter-depth profiles of (○) platinum and (●) nickel in the as-deposited and ion-beam mixed René N4/Pt targets with an interfacial impurity layer.

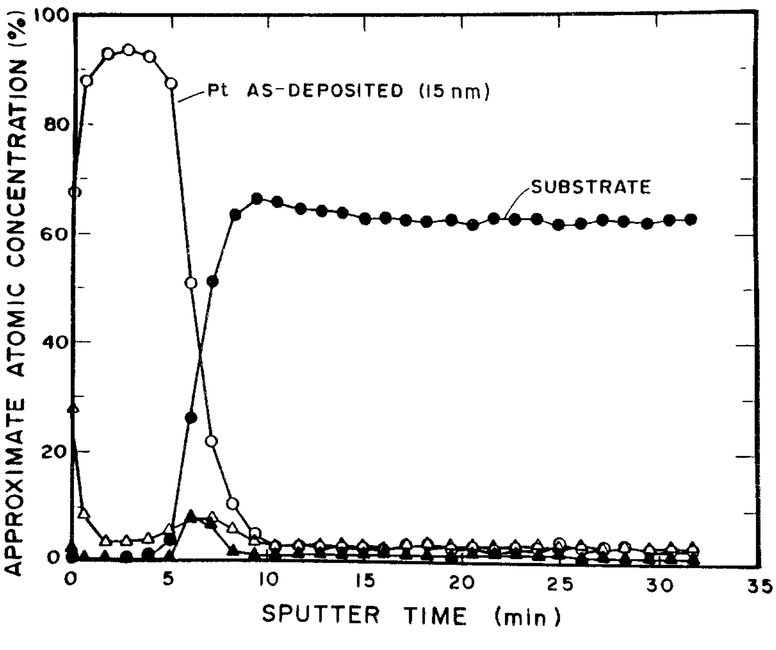

Figure 5 The Auger sputter depth profiles of (○) platinum, (●) nickel, (△) carbon and (▲) oxygen in the as-deposited René N4/Pt target with the interfacial impurity/native oxide layer. Note the small peaks of carbon and oxygen at the interface.

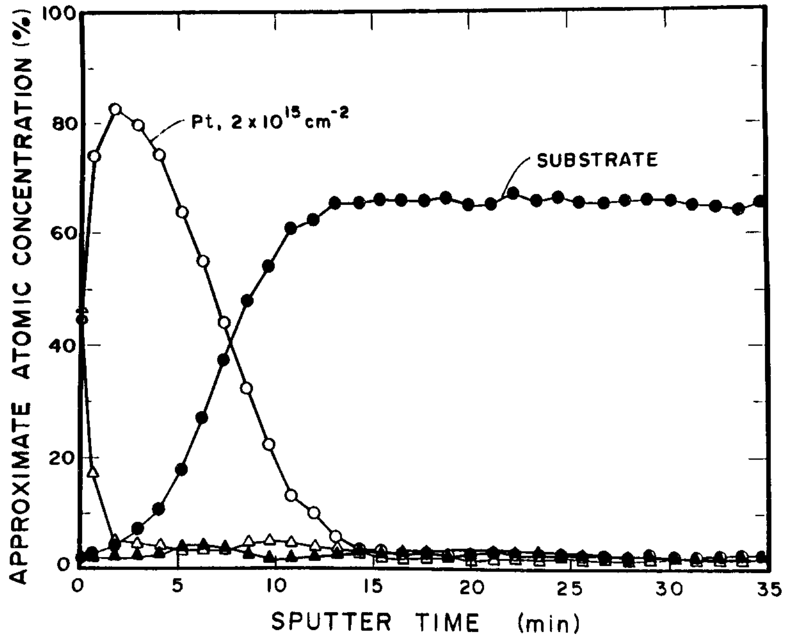

Figure 6 The Auger sputter depth profiles of (○) platinum, (●) nickel, (△) carbon and (▲) oxygen in the ion-beam mixed René N4/Pt target with the initial impurity/native oxide layer. Ion bombardment caused mixing of impurities/oxide layer and the peaks of carbon and oxygen were absent.

where R is the root-mean-square separation for a vacancy–interstial pair, $E_{d,min}$, the minimum displacement energy and N, the atomic density of the solid. This relation was obtained using Andersen's model and the Kinchin–Pease relation [5–7]. Assuming, after Andersen [5], $R = 1$ nm and $E_{d,min} \simeq 23$ eV, ΔFWHMs were calculated for 1 MeV Pt^+ for Pt/Ni and René N4/Pt systems. For comparison purposes, the values of ΔFWHM were converted into twice the square of the diffusion distance, 4Dt, and are given in Table I.

Johnson *et al.* [8] derived a phenomenological equation for the effective diffusion rate per dose based on the thermochemical properties of the mixing species and energy deposition in nuclear collisions

$$\frac{4Dt}{\phi t} = \frac{10^2 K_1 \varepsilon^2}{\varrho^{5/3} \Delta H_{coh}^2}\left[1 + K_2 \frac{\Delta H_{mix}}{\Delta H_{coh}}\right] \qquad (3)$$

where $4Dt$ is the diffusion parameter, ϱ the average atomic density, K_1, a constant that depends on the thermal conductivity and specific heat, K_2, a universal dimensionless constant, and ε the energy deposited in nuclear collisions expressed in eV nm^{-1}. ΔH_{coh} is the binding enthalpy per atom of an alloy (in eV/atom) given by

$$\Delta H_{coh} = C_A \Delta H_A^0 + C_B \Delta H_B^0 + 2 C_A C_B \delta \qquad (4)$$

where ΔH_A^0 and ΔH_B^0 are the heats of sublimation of pure metals, ΔH_{mix} is the heat of mixing and given by

$$\Delta H_{mix} = 2 \delta C_A C_B \qquad (5)$$

C_A and C_B are the atomic fractions of components A and B. Johnson *et al.* [8] obtained 0.0039 nm and 27 for K_1 and K_2, respectively, by fitting the experimental data to Equation 3, and using δ from Miedema's work [9]. Here $\Delta H_A^0 = \Delta H_{Pt}^0$ and $\Delta H_B^0 = \Delta H_{René\,N4}^0$ or ΔH_{Ni}^0. $\Delta H_{René\,N4}^0$ is obtained from $\Sigma C_i \Delta H_i^0$ where ΔH_i^0 is the heat of sublimation of the ith alloying component in René N4, and C_i is its atomic fraction. Similarly, ΔH_{mix} for René N4/Pt is obtained as the weighted average of $\Sigma C_i \Delta H_{mix,i}$ where C_i is the atomic concentration of the ith alloying element, and $\Delta H_{mix,i}$ is the heat of mixing for the ith alloying element with platinum at equiatomic concentrations. Values thus calculated for $2\sigma^2 = 4Dt$ are given in Table I. It is evident that these values are closer to the experimental values, thus bringing out the importance of thermochemical effects in mixing.

The ordered γ' precipitates were normally unstable under ion bombardment [10]. The precipitates that lie in the path of energetic Pt^+ ions became disordered. This disordering resulted in the supersaturation of several alloying elements in the nickel matrix of René N4. The equality of mixing rates in Ni/Pt and René N4/Pt systems suggests that the presence of several alloying elements in significant quantities in solution

TABLE I Comparison of experimental values of $4Dt$ with the prediction of the models

Dose (ion/cm^2)	$2\sigma^2 = 4Dt$ (10^{-2} nm^2)					
	Experimental			Theoretical		
	Pt/Ni	Pt/René N4†		Cascade*: Pt/Ni or Pt/René N4	Johnson *et al* [8]	
		1	2		Pt/Ni	Pt/René N4
2×10^{15}	–	0.34	–			
5×10^{15}	5.1	0.44	4.62	0.1	2.5	3.3
1×10^{16}	8.2	–	7.22	0.2	5.0	6.6
2×10^{16}	14.6	–	15.6	0.4	10.0	13.2

*As the values of parameters in Equation 2 are not available for René N4, and not sensitive to chemistry and microstructure, the same suggested values were used for nickel and René N4.

†1, With the interfacial impurity/native oxide layer; 2, with the clean interface.

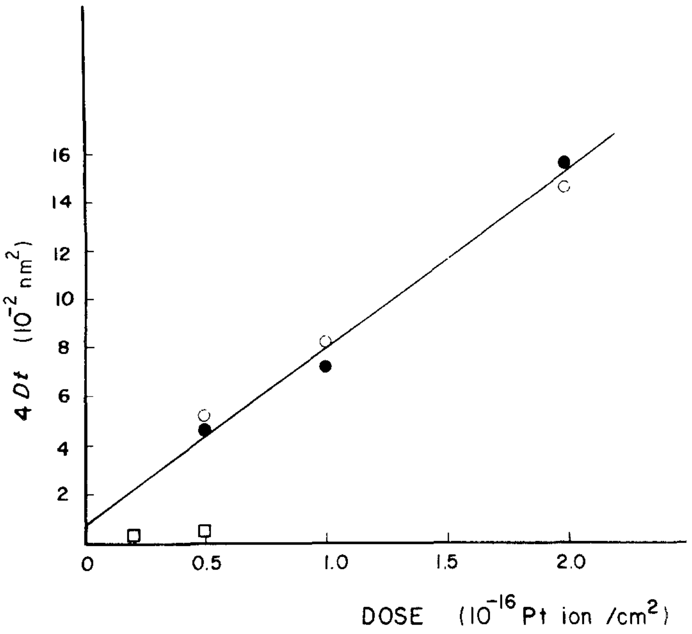

Figure 7 The relationships between the amount of mixing and the dose for Ni/Pt and René N4/Pt. (●) 1 MeV Pt^+ ion-beam mixed Pt/René N4, RT, with clean interface. (○) 1 MeV Pt^+ ion-beam mixed Pt/Ni, RT, with clean interface. (□) 1 MeV Pt^+ ion-beam mixed Pt/René N4, RT, with impurities in the interface. RT = room temperature.

in René N4 has no significant influence on the mixing process.

4. Conclusion

The mixing rates of Pt/Ni and René N4/Pt with the clean interface are almost identical under similar experimental conditions. The high volume fraction of ordered second phase became disordered under ion bombardment, and the resulting super saturated solution had no effect on the mixing process. The presence of an impurity/native oxide layer considerably reduced the mixing efficiency. The thermochemical effects played a major role in ion mixing of Ni/Pt and René N4/Pt with the clean interface, as the rates predicted by the Equation 3 based on the thermochemical properties of interacting species were close to those observed.

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