Evidence for Significant Short-Range Order Effects on Surface Segregation in Ni-Al Solid Solution

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(Received 16 July 1996)

Aluminum surface segregation in Ni-9% Al as studied by low-energy Auger electron spectroscopy is characterized by quite low equilibrium levels that increase with temperature, in contrast to predictions of Bragg-Williams–type theories. The free-energy cumulant expansion approach, adapted for surface segregation, reveals that short-range order can induce significant suppression of solute segregation, depending mainly on the solvent-solute interaction strength. The diminution of the effect with increasing temperature leads to anomalous increase of equilibrium segregation, in agreement with the Ni-Al experiments. [S0031-9007(97)02329-6]

PACS numbers: 64.60.Cn, 64.75.+g, 68.35.Dv, 82.80.Pv

The intrinsic deviation of a solid-vacuum interfacial composition from the bulk value is quite a common physical phenomenon in metallic alloys [1], affecting diverse macroscopic properties (adhesion, catalytic activity, surface magnetism [2], etc.). Yet, usually somewhat simplistic theoretical models of equilibrium surface segregation in binary alloys have been used so far. Thus, the most common statistical-mechanical approach to the problem is based on the classical mean-field theory, which is equivalent to the Bragg-Williams (BW) approximation, assuming random distribution of atoms at identical lattice sites. Effects of correlations between atoms (short-range order, SRO) have been usually ignored in theoretical calculations of surface segregation in binary A_cB_{1-c} solid solutions, although usually A atoms tend to be preferentially surrounded by B atoms ("mixing" tendency, exothermic alloying), or by A atoms ("demixing" tendency, endothermic alloying). Such interatomic correlations play an important role in several bulk properties, especially at temperatures not much higher than the phase-transition temperature, and likewise, correlations are expected to have some effect on surface segregation phenomena. Direct observation of surface short-range order has been found, for example, in Pt segregated $\mathrm{Pt}_{0.25}\mathrm{Ni}_{0.75}$ (111) surface by means of scanning tunneling microscopy [3], in agreement with Monte Carlo calculations using the embedded-atom method [4]. The few previous studies that went beyond the ordinary mean-field theory used quasichemical or cluster variation approaches [5–7] with the main purpose of evaluating relationships between surface segregation and order parameters. However, choosing a specific cluster representation for certain alloy surface structures restricts the general applicability of the theory and involves quite complicated equations with more SRO parameters than for the bulk [6]. Therefore, as will be outlined briefly below and derived in detail elsewhere, a different approach has been chosen, yielding explicit formulas for quantification of SRO effects that furnish better physical understanding of surface segregation phenomena.

This Letter presents clear experimental evidence for dominant effects of short-range order on surface segregation in a solid solution. Thus, as measured by low-energy Auger electron spectroscopy (AES), aluminum segregation in Ni-9% Al is significantly weaker than anticipated according to the BW-type pair-bond model, including elastic strain-energy contributions [8], and its equilibrium levels *increase* with temperature between ~500 and 750 °C (Fig. 1). This deviation from the usual temperature dependence is reported for the first time for a solid solution subjected to adequate equilibration. In some previous segregation studies (e.g., Pt-Rh [9–11] and Cu-Mn [12]) the apparent increase in segregant concentration with temperature was due to kinetic effects, whereas comparing the present data to calculations based on a segregation-kinetics model [13] with experimental diffusion coefficients of Al in Ni [14] show that real equilibrium conditions have been achieved even at the lowest annealing temperature. The distinct segregation trend, occurring at approximately the same temperature range for which significant short-range order was found to exist in Ni-Al solid solutions [15], has stimulated our attempt to unravel the general role of SRO in surface segregation. For this goal we adapted

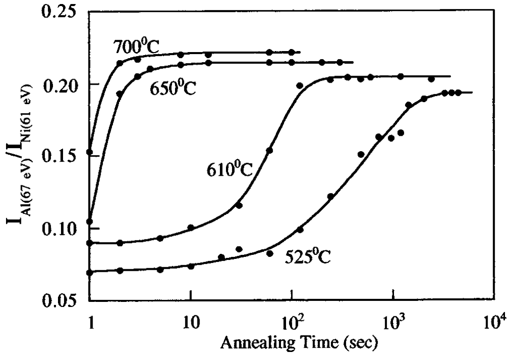

FIG. 1. Representative segregation curves of aluminum at Ni-9% Al (110) surface as reflected by variations in AES relative intensities. ($I_{\mathrm{Al}}/I_{\mathrm{Ni}} = 0.165$ for the alloy bulk composition).

0031-9007/97/78(6)/1058(4)$10.00

the Kirkwood statistical-mechanical method, which was developed initially for describing atomic ordering in bulk substitutional alloys [16], and recently applied to the problem of surface magnetic order [2,17]. Advantages of this consistent approach, based on the free-energy cumulant expansion, include its general applicability to Ising systems, the relative simplicity of equilibrium equations, the convenient extension to non-nearest neighbor interactions, and its compatibility with the method of "area-preserving map" for quantitative evaluation of in-depth concentration gradients [18]. Most modern theories of surface segregation involve electronic structure calculations (e.g., Refs. [19,20]), and one can consider also possible contributions of atomic vibrations [21] and surface relaxation [21,22]. Yet, as will be shown below, the observed segregation behavior of aluminum can be fully accounted for in terms of the common pair-bond approach extended to include SRO effects.

Starting with the Ising model Hamiltonian for an A_cB_{1-c} alloy with a surface and effective pair interaction $V = (V^{AA} + V^{BB} - 2V^{AB})/2$, the free energy, expanded in inverse-temperature power series, is given in the nth order correlation approximation by

$$F_n = F_1 - kT \sum_{s=2}^{n} \frac{C_s}{s!}\left(-\frac{V}{kT}\right)^s, \tag{1}$$

where C_s are sth order cumulants, and F_1 denotes the alloy free energy in the BW-type approximation. Minimization of the free energy with respect to the p-plane concentration (c_p) leads to the following set of coupled equations describing the equilibrium composition profile extending from the top surface layer ($p = 0$) to the bulk (with concentration c),

$$\frac{c_p}{1 - c_p} = \frac{c}{1 - c}\exp\left(-\frac{\Delta H_p}{kT}\right), \tag{2}$$

ΔH_p is the sum of segregation energy in the BW approximation, $\Delta H_p^{(1)}$, and SRO related correction, $\Delta F_p^{\mathrm{SRO}}$, which involves both energy and entropy contributions and depends explicitly on temperature. For the case of first-neighbor interactions, the first term can be read

$$\Delta H_p^{(1)} = \Delta h_p + \Delta H_p^{se} + \sum_q V z_{pq}(2c_q - 1) - Vz(2c - 1), \tag{3}$$

and, limiting expansion (1) to the first (pairwise) correlation approximation, F_2, gives for the second term,

$$\Delta F_p^{\mathrm{SRO}} = \sum_q \frac{2V^2}{kT} z_{pq} c_q (1 - c_q)(2c_p - 1) - \frac{2V^2}{kT} zc(1 - c)(2c - 1). \tag{4}$$

In Eq. (3), according to the pair-bond approach, Δh_p corresponds to the difference in p-layer tensions between the pure constituents; ΔH_p^{se} is the difference of strain energy between a p-layer site and a bulk site. The bulk coordination number is denoted by z, and z_{pq} is the coordination number of a p-plane atom with respect to neighboring q-plane atoms. It should be noted that in the case of $V > 0$ (exothermic alloying), consecutive terms in the untruncated expansion [Eq. (1)] have alternating signs, and depending on the value of the V/kT parameter and on the crystal structure, convergence can be sluggish. For the truncated series used here, a better approximation is to use summation by arithmetic means [23], namely to calculate $\overline{F}_2 = (F_1 + F_2)/2$ instead of F_2. Its validity has been verified in case of weak segregation in a dilute alloy by comparing Eq. (4) with an exact formula for the correlation correction based on the infinite expansion. {This formula coincides with Eq. (4), except that $2V^2/kT$ is replaced by $[\exp(-2V/kT) + 2V/kT - 1]kT$}.

The multilayer model described above enables us to take into account contributions to Auger line intensities from any number of atomic layers starting from the top surface, and it has been used to calculate Al segregation at the Ni-9% Al (110) surface and at the less open (100) surface. Values for Δh_0, ΔH_0^{se}, and V were obtained from the pure Al and Ni surface tensions, atomic sizes, and their heat of mixing [24,25], respectively, and it was assumed that $\Delta h_p = \Delta H_p^{se} = 0$ for $p \geq 1$. Since elastic strain energy can be estimated by different elasticity formulas, and possible contributions of accommodation energy at the surface [26] are ignored, the ΔH_0^{se} value used can be regarded as a rough estimate only. The effective pair interactions at an alloy surface may be enhanced [27] or reduced [28] relative to the bulk value [and then V is replaced by V_0 in terms corresponding to p or $q = 0$ in Eqs. (3) and (4)]. However, as shown by electronic structure calculations [20], in Ni-Al solid solutions the interactions are nearly uniform. The set of coupled equations in composition [Eq. (2)] was solved consecutively for the two surface orientations by a trial-and-error iterative procedure starting with a guessed c_0 value for the Al concentration in the top layer, and imposing the condition $c_5 = c$ (bulk concentration). The calculated compositional gradient changed only slightly when the truncation of the profile was imposed at a deeper layer. Since in the present experiment the quite surface-sensitive Ni(MVV) and Al(LVV) transitions at 61 and 67 eV, respectively, have been chosen for quantitation, it is sufficient to include calculated signals from the three upper atomic layers, which contribute to about 95% of the total intensities (effective escape depths, $\lambda_{\mathrm{Al}}^{\mathrm{eff}} = 2.7$ Å and $\lambda_{\mathrm{Ni}}^{\mathrm{eff}} = 2.6$ Å). Thus, based on the c_p values derived, the intensity ratio for the alloy can be calculated as

$$\frac{I_{\mathrm{Al}}}{I_{\mathrm{Ni}}} = \frac{I_{\mathrm{Al}}^0}{I_{\mathrm{Ni}}^0}\frac{(1 + r_{\mathrm{Ni}})}{(1 + r_{\mathrm{Al}})}\frac{[1 - \exp(-d/\lambda_{\mathrm{Al}}^{\mathrm{eff}})]}{[1 - \exp(-d/\lambda_{\mathrm{Ni}}^{\mathrm{eff}})]} \times \frac{\sum_{p=0}^{2} c_p \exp(-pd/\lambda_{\mathrm{Al}}^{\mathrm{eff}})}{\sum_{p=0}^{2}(1 - c_p)\exp(-pd/\lambda_{\mathrm{Ni}}^{\mathrm{eff}})}, \tag{5}$$

where d is the atomic layer thickness (2.38 Å), I^0_{Al} and I^0_{Ni} are the signal intensities measured for the pure elements under identical conditions, and r_{Al}, r_{Ni} are the corresponding electron backscattering terms. Figure 2 shows results of the calculations in the correlation (SRO) approximation and in the BW approximation together with experimental data (experimental procedures were described before [24]). Clearly, SRO diminishes aluminum segregation levels, and the calculated ratios are significantly closer to the experimental results, including the anomalous temperature dependence. As mentioned above, the ΔH_0^{se} value used in the calculations for the elastic energy contribution is a rough estimate, so in order to obtain a more accurate value, it was used as an adjustable parameter, improving the agreement between calculated and experimental ratios (graphs 3 in Fig. 2). Furthermore, as expected, the adjusted $\Delta h_0 + \Delta H_0^{se}$ absolute value for the more open (110) surface, 0.79 eV, is larger than the value (0.68 eV) obtained for the (100)-surface. Compositional variations with temperature in individual atomic layers, presented in Fig. 3, show anomalous temperature dependence over a certain range. The oscillatory concentration profile obtained at all temperatures is related to the tendency of increasing the number of Ni-Al pairs in this exothermic alloy. Compared to results of BW-type calculations, the inclusion of SRO leads to significantly damped profiles.

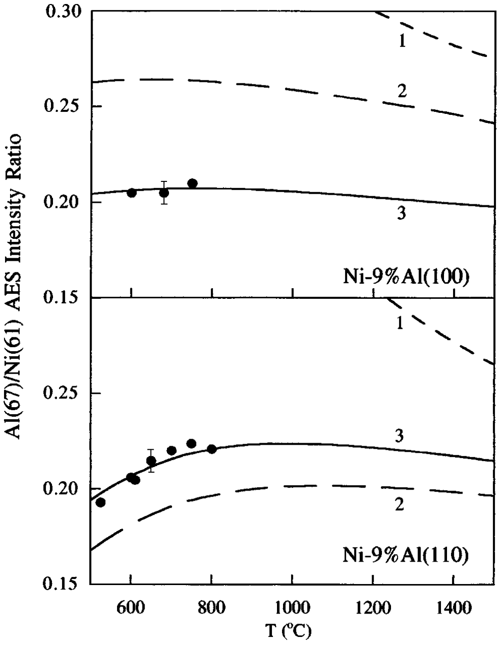

FIG. 2. Comparison of experimental (●) and theoretical Auger intensity ratios of Ni-9% Al as a function of equilibration temperature: 1, Bragg-Williams type approximation; 2, correlation (SRO) approximation, both with estimated $\Delta h_0 + \Delta H_0^{se} = -0.77$ eV [27]; 3, correlation approximation with fitted $\Delta h_0 + \Delta H_0^{se} = -0.68$ and -0.79 eV for (100) and (110), respectively (in all the calculations $V = 0.15$ eV).

The observed (and calculated) suppression of solute surface segregation induced by short-range order can be simply understood in terms of atomic coordination considerations. SRO lowers the alloy energy by changing the atom surroundings, so that local ordered regions are formed. Such compositional fluctuations always attract solute atoms, and thus, in case of demixing (mixing) tendency, clusters of like (unlike) atoms are able to grow. In case of weak segregation and equal surface and bulk interactions, surface segregation of the solute is suppressed because of its stronger attraction to bulk fluctuations compared to fluctuations at surfaces, which have reduced coordination numbers [this can be deduced from the two terms having opposite signs in Eq. (4)]. Since this suppressing effect decreases with *increasing* temperature, anomalous increase in equilibrium segregation level becomes possible, as observed for Ni-Al. On the other hand, SRO intensifies with *decreasing* temperature, and in exothermic solid solutions long-range order (LRO) can appear with the formation of intermetallic compounds. Effects of LRO on surface segregation were treated theoretically before [7,29] and are similar in their general trends to those of SRO, namely the possibility of inducing suppression of surface segregation. The anomalous behavior of Si segregating at grain boundaries in Fe-12.9%Si [30], the Al segregation at surfaces of Ni-10% Al [31,20] and at Ni-48% Al [32] were tentatively explained by means of LRO effects.

Numerical calculations based on the derived equations have revealed quite subtle conditions for anomalous temperature dependence of equilibrium surface segregation in solid solutions. Thus, SRO-induced anomaly is expected to occur in case the segregation is relatively weak, and it depends critically on the magnitude of the segregation driving force relative to the solvent-solute interaction strength

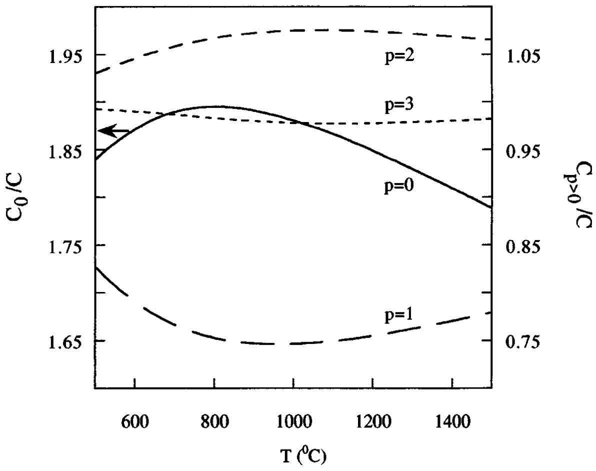

FIG. 3. Variations of Al relative enrichment (or depletion) at individual (100) atomic planes, as a function of temperature for Ni-9% Al with SRO (the outermost layer is denoted by 0; 1, 2, and 3 denote the 1st, 2nd, and 3rd underlayer, respectively). The plane concentrations were calculated in accordance with the adjusted $\Delta h_0 + \Delta H_0^{se} = -0.68$ eV value and $V = 0.15$ eV.

($|V|$). Only when this ratio is not too large ($<\sim 10$), significant SRO effects are expected, depending on the sign of V, the bulk concentration, the crystal structure, as well as on the surface orientation. Furthermore, in case of weak segregation in a dilute solid solution, a highly sensitive technique [e.g., secondary-ion mass spectroscopy (SIMS)] is essential in order to detect the segregant low levels in the anomalous segregation temperature range [33]. Another crucial factor is related to the interaction strength itself, since for alloys with relatively small V the anomalous range is expected to be well below temperatures required for achievement of surface segregation equilibration in reasonable annealing times. At higher temperatures, SRO effects become less and less significant. For example, this accounts for the very small deviations from the BW-type calculations reported previously for Ag-Au and Ag-Pd alloys [5,6], with interaction parameters nearly an order of magnitude smaller than in Ni-Al. It should be noted that in a certain number of other binary alloys solute-solvent interactions are quite strong, so that short-range order is expected to play a significant role in their surface segregation characteristics.

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