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On the surface composition of intermetallic compounds: the case of MgNi$_2$

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Abstract

Basic factors governing surface segregation in “size-factor” intermetallics are introduced and applied to the case of Mg segregation in MgNi$_2$ thin films reported recently. The calculations, based on a Bragg–Williams-type approximation, are in agreement with the experimental results, and indicate a preferential population of surface Ni antisites by the larger Mg atoms from the nearby underlayers. The resultant increase in the equilibrium concentration of Mg with temperature is associated with entropy-driven enhancement of compositional disorder at the surface region of the intermetallic compound. © 1998 Published by Elsevier Science B.V. All rights reserved.

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Surface segregation of metallic constituents in solid solutions has been studied extensively since the advent of AES and XPS in the late sixties. In comparison, much less work has been devoted to surface segregation in ordered alloys or intermetallics [1], where the situation can be somewhat more diverse and complex. Simple thermodynamical considerations show that whereas in a randomly disordered alloy, segregation should always be exothermic and accompanied by a decrease in the configurational entropy, in ordered alloys, the segregation can be either endothermic or exothermic, depending primarily on the energy balance of near-surface broken bonds. In the case of endothermic segregation, bulk-terminated surface composition is energetically more favorable, but entropy-driven segregation can create partially disordered regions near the surface (or interface). Several studies revealed local disorder close to the grain-boundaries in Ni$_3$Al [2,3], and competition between surface segregation and bulk ordering can cause formation of metastable states with anti-phase boundaries, as calculated for model thin films of binary intermetallics [4]. An example for exothermic monolayer segregation process was reported recently for Au at the Au$_3$Cu(001) surface [5].

The simplistic Langmuir–McLean equation for segregation in a binary AB solid-solution has often been applied successfully to the description of the temperature dependence:

$$c_A^S = c_B^S \exp \left(-\frac{\Delta H}{RT}\right),$$  \hspace{1cm} (1)

where $c_A$ and $c_A^S$ are, respectively, the surface and
bulk concentrations of element A, and $\Delta H_s$ is the segregation enthalpy. A significant deviation from this law, namely the observation of increasing segregation levels with temperature, has been recently reported for Al in Ni-9\%Al solid solution, and attributed to short-range order (SRO) effects [6]. Depending on the solute-solvent interactions and other energetic parameters, SRO can suppress segregation, especially at relatively low temperatures, whereby anomalous temperature dependence (opposite to the Langmuir-McLean prediction) becomes possible [6,7]. Similarly to the case of SRO effects in disordered solid-solutions, an increase in equilibrium segregation levels with temperature can be expected for intermetallics due to the predominant enhancement of compositional disorder that disrupts the long-range order (LRO) and is associated with increased configurational entropy, especially when the enthalpic driving-force for segregation is weak or absent. Indeed, the anomalous temperature dependence of Si segregating at grain-boundaries in Fe-12.9\%Si [8] and the Al segregation at surfaces of Ni-10\%Al [9,10] and at Ni-48\%Al [11] were tentatively attributed to LRO effects. However, the anomalous temperature dependence observed recently for Mg segregation in MgNi$_2$ thin films [12,13] was analyzed according to the Langmuir-McLean equation. Obviously, an erroneous “segregation enthalpy” can be expected from an application of this procedure to ordered alloys exhibiting such a temperature dependence. Therefore, in the present work, the reported data are re-analyzed on the basis of a more appropriate model introduced below.

Several factors, such as geometrical parameters, chemical bond strength or the energy band structure, determine the atomic arrangement in intermetallic phases [14]. Thus, the relative atomic dimensions in a binary alloy can affect characteristic structural properties. A considerable number of intermetallic compounds have been classified as “size-factor” phases formed by efficient packing together of atoms of significantly different sizes [15]. In particular, when the ratio of atomic diameters equals approximately 1.2 [15]. Laves phases, to which MgNi$_2$ belongs, are formed. Such compounds possess a narrow range of homogeneity and stoichiometric composition [15], and their bulk thermal disordering is prevented almost to the melting point due to the relatively high energetic barrier for penetration of the larger atoms into the smaller atom sites (“antisites”). However, size-related (“mismatch”) energy differences between near-surface sites of the larger atom and surface antisites should be significantly lower than for the bulk antisites (Fig. 1) due to the reduced coordination and possible surface relaxation and reconstruction. The corresponding site-antisite atomic exchange process can be further facilitated due to surface tension differences of the two con-

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**Fig. 1.** Schematics of the relative positions of energy-wells for endothermic disordering exchange processes of the larger atoms in a size-factor intermetallic between their equilibrium positions (open circle) and a bulk antisite (filled circle) or a surface antisite (grey circle).
Fig. 2. Schematics of the atomic arrangement in a Laves phase structure with larger atoms, e.g. Mg (open circle) and smaller atoms, e.g. Ni (filled circle): (a) side view of the (KTTTK) five-layer sandwich; (b) top view of the two outermost layers used in the calculation (K₁ and T₂ ~1.4 Å apart).

stituents, so that the resultant segregation can become exothermic leading to the normal ("Langmuir–McLean") temperature dependence. Nevertheless, significant transfer of the larger atoms from bulk sites to surface antisites is expected even in case of endothermic segregation (depicted in Fig. 1), and the entropy-driven exchange process should be enhanced with increasing thermal energy.

The intermetallic compound MgNi₂ has the ordered C36 hexagonal Laves phase structure formed by packing together Mg and Ni atoms in separate (0001) layers of a simple triangular arrangement (T) and a "Kagome" network of triangles and hexagons (K-layers in Fig. 2) [15]. Bulk coordination numbers are 12 for the smaller (Ni) and 16 for the larger (Mg) atomic sites, including interatomic distances less than 3 Å [16]. The intermetallic compound MgNi₂ has the ordered C36 hexagonal Laves phase structure formed by packing together Mg and Ni atoms in separate (0001) layers of a simple triangular arrangement (T) and a "Kagome" network of triangles and hexagons (K-layers in Fig. 2) [15]. Bulk coordination numbers are 12 for the smaller (Ni) and 16 for the larger (Mg) atomic sites, including interatomic distances less than 3 Å [16]. The surface composition was calculated as function of temperature for a symmetric slab (relative to the middle layer) composed of an even number of sandwiches, s, and a total odd number of layers, 4s + 1, assuming that the outermost layer is the dense, pure Ni, K-layer (Fig. 2b). Since the hexagonal lattice constant, c, of the unit cell containing four sandwiches is 15.8 Å long, the number of sandwiches in the 60 Å MgNi₂ film studied experimentally [12,13] was assumed to be s = 16 (the total number of layers is 65).

Elaborate theoretical approaches to surface segregation, such as Monte-Carlo simulations using an appropriate semi-empirical interatomic potential, have been applied to several intermetallics (Pt₀.₈Fe₀.₂ [17] and Cu₃Au [18], for example). Yet, for the purpose of elucidating the segregation characteristics in MgNi₂, an analysis based on the Bragg-Williams approximation, assuming simple Boltzmann configurational entropy contribution, constant interactions and constant layer-related bond energies in a rigid lattice, seems to be sufficient. Within this framework, and taking into account the above-mentioned size-mismatch energy contributions, the free-energy is given by:

\[
F = kT \sum \limits_{p} N_p \ln c_p + (1 - c_p) \ln (1 - c_p)
\]

\[
+ \frac{1}{2} \sum \limits_{p} N_p (\Delta H_p + \Delta H_p^{\text{m}})(2c_p - 1) + \frac{1}{2} \sum \limits_{\{mn\}} V_{\text{nn}} (2c_m - 1)(2c_n - 1), \tag{2}
\]

where \(N_p\) and \(c_p\) denote, respectively, the number of sites and the Mg concentration in the p-plane parallel to the surface. In the structure under consideration, every site of odd atomic layers belongs to the Ni sublattice, whereas sites of even layers belong to the Mg sublattice, so that no additional summation within the layers is necessary in Eq. (2). \{mn\} denotes a pair of lattice sites, and \(V_{\text{nn}}\) is the interatomic I–J interaction. From the MgNi₂ enthalpy of formation −4.4 kcal g-atom⁻¹ [19] and the coordination numbers, an effective pair interaction, \(V_{\text{nn}} = 0.064 \text{ eV}\), is obtained for the nearest neighbors (more remote interactions are neglected). \(\Delta H_p\) is the commonly used segregation driving force corre-
The XPS study of MgNi$_2$ [12,13] was based on the intensity ratios of the Mg 1s and Ni 2p lines corresponding to relatively shallow probing-depths especially at grazing angles, and it was concluded that the segregation was confined to the surface layer. Considering this and the crude quantification procedure used in that study, calculation of the average composition of the first and second atomic layers (see Fig. 2b) seems to be adequate for comparison with the experimentally derived composition (no significant signal attenuation is expected in the two-layer open structure). Thus, in order to take into account also the relative abundance of the corresponding two sites ($K_1/T_2 = 3:1$), the average was calculated as $c_s = (3c_1 + c_2)/4$, where $c_1$ and $c_2$ are the individual layer concentrations. Furthermore, in view of the shallow compositional variations in the film, it is sufficient to include in the calculation of the segregation profile only the external and first internal sandwiches (eight layers from each side of the slab). The other internal sandwiches were supposed to be identical to the first internal sandwich.

The minimization was performed with respect to the eight variables mentioned above. The mismatch energy for the first (and the last) surface layer, $\Delta H^{\text{sm}}_1$, was the only parameter adjusted in order to improve the agreement between the calculated and the experimental surface concentrations (Fig. 3), yielding a value of 0.32–0.38 eV. (It is considerably lower than the mismatch energy of Mg dissolved in the bulk of Ni, estimated on the basis of a simple linear elasticity theory.) As can be seen, the net main atomic exchange processes between layers leading to Mg segregation are:

\[ \text{MgNi}_2 \rightarrow \text{MgNi}_1 + \text{Ni}, \]

with the number of Mg atoms segregated to the first layer from the non-nearest neighbour fourth layer being somewhat larger than the Mg originated from the nearest neighbour second layer. The former process is energetically more favorable since, in this alloy structure, the second layer has some broken bonds, and hence, the surface-tension-related gain upon atomic exchange with the first layer is smaller.

Additional calculations revealed significant effects of the film thickness on the surface composi-
tion. Thus, the segregation levels increase with increasing thickness, and the effect of temperature becomes stronger, without changing the general trends. These sample dimension (size) effects are clearly related to variations in the overall reservoir available for Mg surface segregation, which becomes smaller for thinner films.

To summarize, the simple approach used in this work accounts for the segregation characteristics reported for MgNi$_2$, and it can be applied to size-factor intermetallics in general. Insight into the basic factors governing the segregation has been gained by inspecting the two contributions, energy and entropy, whose balance determines the minimal value of the free-energy. In particular, the constant bond-energy calculations show that the non-segregated, fully ordered state of MgNi$_2$ is energetically preferable, so the segregation process is expected to be endothermic in this system, leading to the observed anomalous temperature dependence. The negative entropy contribution increases with temperature when the layer concentrations deviate progressively from 0 or 1. Thus, Mg segregates to the outermost (Ni) layer as a result of entropy driven preferential surface disordering. It can occur, but to a lesser extent, even in the hypothetical case of absence of any surface-energy related contribution, namely $\Delta S_p=0$ for all p. The relatively low size-mismatch energy at the surface antisites allows exchange of the smaller atom at the surface by the larger atom from the nearby layers, yielding a shallow segregation profile, as was measured experimentally [12,13]. In fact, this energy factor limits the segregation/disordering process at the MgNi$_2$ surface region, as does the finite supply of Mg atoms from the film interior. Clearly, surface segregation phenomena in intermetallics deserve further experimental and theoretical studies concerning mainly the competition with the tendency for atomic order.

References