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It will be shown, in the framework of a general statistical (atomic) treatment, that segregation inhibited grain coarsening in binary nanocrystalline alloys can be described by analytical expressions, if the effect can be attained with highly saturated grain boundaries. Relatively simple relations describing the temperature dependence of the stabilized grain-boundary fraction will be derived. The validity conditions of the relation proposed very recently by R. Kirchheim [Acta Mater. **50**, 413 (2002)] are also analyzed. Our conclusions are compared with experimental results and the reliability of the few experimental data, known at present, will be discussed as well. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1688461]

I. INTRODUCTION

It is known that in nanocrystalline binary alloys, with strongly segregating solute, there could exist a certain grain size, for which the free energy of the system has a minimum.[1–3] This segregation induced grain stabilization is due to the gain of the (chemical) energy related to the increased amount of segregated atoms: for small grain sizes this can be larger than the increase of the free energy caused by the enlarged number of the grain boundaries. This phenomenon, since the stabilization of different nanostructures is a crucial problem in many applications, can have high technological importance as well.

Weissmüller[2] made an attempt at the theoretical description of the above problem in the Langmuir–McLean approximation for a dilute solution. He has shown that indeed a minimum could exist on the free energy curve in the nanocrystalline region. Recently, using similar considerations, Kirchheim[1] also treated the effect of the simultaneous action of solute segregation and precipitation. He found that, if the precipitation is kinetically hindered, a metastable equilibrium with certain grain size can be attained. Furthermore, he proposed a simple formula for the temperature dependence of the equilibrium grain size as well. These issues have also been investigated in our group[3–5]—using a more general statistical (atomistic) treatment—in the Fowler–Guggenheim approximation. Confirming the conclusions of Weismüller, it was, e.g., shown from numerical calculations[3] that the same grain size can be stabilized at two different surface coverage's and temperatures. It was also found that, below a certain surface/grain-boundary fraction, the minimum is possible only with low surface coverage.

We present the results of our previous calculations in analytical forms and analyze the validity conditions of the relations obtained in dilute solutions from more heuristic considerations by Kirchheim.[1] We will show that indeed a relatively simple relation can be obtained for the limit when the minimum could exist with highly saturated grain boundaries (i.e., for $c_s \cong 1$, where c_s is the surface/grain-boundary atomic fraction, defined as the ratio of the number of solute atoms and lattice sites in the boundary layer) even in concentrated alloys. Considerations for more general cases (i.e., for nonideal solutions) will also be presented.

II. BASIC EQUATIONS

Consider a slab of an AB alloy with m lattice planes, normal to the y axis.[5,6] The lateral and vertical coordination numbers are z_l and z_v, respectively, and $Z = z_l + 2z_v$. Let n be the number of lattice sites in each atomic plane and n_{iA} the number of A atoms in the ith plane. The fraction of component A in the ith layer is denoted by $c_i = n_{iA}/n$. $X = N_A/N$ is the average concentration (N_A and N are the number of A atoms and the lattice sites in the system, respectively) and $\xi = 2/m$ is the surface fraction. Then f, the free energy per atom, in nearest neighbor approximation can be written[3] as the function of the above parameters as well as the V_{AA}, V_{BB} nearest neighbor pair interaction parameters ($V_{AA}, V_{BB} < 0$) and the regular solution parameter, V, defined as

$$V = V_{AB} - \frac{V_{AA} + V_{BB}}{2}. \tag{1}$$

In monolayer limit (i.e., assuming that the concentrations of the bulk layers, c_b, are the same, and only the surface layers have different compositions, c_s) f has the following form:[3]

$$f = \frac{Z}{2}[V_{BB}(1-X) + V_{AA}X] - z_v\frac{\xi}{2}[c_s V_{AA} + (1-c_s)V_{BB}]$$

$$+ V\left\{ ZX - \xi c_s z_v - \xi z_l\left[c_s^2 + (1-\xi)\frac{c_b^2}{\xi} \right] \right.$$

$$\left. - \xi z_v\left[2c_s c_b + (2-3\xi)\frac{c_b^2}{\xi} \right] \right\}$$

$$+ kT\{\xi[c_s \ln c_s + (1-c_s)\ln(1-c_s)]$$

$$+ (1-\xi)[c_b \ln c_b + (1-c_b)\ln(1-c_b)]\}. \tag{2}$$

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Here k and T are the Boltzmann factor and temperature, respectively. Furthermore, according to the conservation of matter, the following relation holds:

$$c_b = \frac{X - \xi c_s}{1 - \xi}. \tag{3}$$

Allowing the redistribution of matter in the closed system, the minimum of the free energy should be found from the condition

$$\frac{\partial f}{\partial c_s} = 0, \tag{4}$$

while if the change of the film thickness is also allowed the

$$\frac{\partial f}{\partial \xi} = 0 \tag{5}$$

condition should be satisfied simultaneously.

From Eqs. (4) and (5) the following implicit equations can be derived[3] for the segregation isotherm:

$$\frac{V}{kT} = \frac{-\lambda \gamma(\xi, c_s, X)}{\alpha(\xi) + \lambda \beta(\xi, c_s, X)}, \tag{6}$$

and for the equilibrium surface fraction

$$\frac{V_{BB}}{V} = \frac{2}{z_v} \left[\frac{\epsilon(c_s)}{\lambda} + \phi(\xi, c_s, X) + \frac{kT}{V} \eta(\xi, c_s, X) \right], \tag{7}$$

respectively, with

$$\alpha(\xi) = \frac{\xi z_v}{2},$$

$$\beta(\xi, c_s, X) = \frac{\xi}{(1-\xi)^2} [2 z_l (1-\xi)(X - c_s)$$
$$- z_v (1 - 2\xi)(1 - 2X) - \xi^2 z_v (1 - 2 c_2)],$$

$$\gamma(\xi, c_s, X) = -\xi \ln \left[\frac{(1 - c_s) c_b}{c_s (1 - c_b)} \right],$$

$$\epsilon(c_s) = z_v \frac{c_s}{2},$$

$$\phi(\xi, c_s, X) = -\frac{1}{(1-\xi)^3} \{ z_l (1-\xi)(X - c_s)^2 + z_v (1 - 3\xi)[X^2$$
$$+ c_s (1 - 2X)] + \xi^2 c_s z_v (1 - c_s)(3 - \xi) \},$$

$$\eta(\xi, c_s, X) = c_s \ln \left(\frac{c_s}{c_b} \right) + (1 - c_s) \ln \left(\frac{1 - c_s}{1 - c_b} \right),$$

$$\lambda = \frac{V}{V_{BB} - V_{AA}}.$$

[Note that the expression according to Eq. (7) contains two misprints in our pervious article.[3]]

Now from Eq. (6) one can write

$$\frac{E_s - V\beta/\xi}{kT} = \ln \left[\frac{c_s (1 - c_b)}{c_b (1 - c_s)} \right] = \ln \left[\frac{c_s (1 - \xi - X) + \xi c_s^2}{X - c_s (\xi + X) + \xi c_s^2} \right], \tag{8}$$

where Eq. (3) was also used and the segregation energy E_s is defined as $E_s = z_v (V_{AA} - V_{BB})/2$. Furthermore, from Eq. (7)

$$\frac{\gamma_B - c_s E_s + V\phi}{kT} = (1 - c_s) \ln \left[\frac{c_s (1 - c_b)}{c_b (1 - c_s)} \right] - \ln \left(\frac{c_s}{c_b} \right)$$

$$= c_s \ln \left[\frac{X - \xi_0 c_s}{(1 - \xi_0) c_s} \right] - (1 - c_s) \ln(1 - c_s)$$

$$+ (1 - c_s) \ln \left[1 - \frac{X - \xi_0 c_s}{1 - \xi_0} \right], \tag{9}$$

where ξ_0 is the surface fraction belonging to the minimum of f and the surface energy (per atom) of the solvent (in eV units) is denoted by $\gamma_B = -z_v V_{BB}/2$.

Note that relation (8) is the general form of the well-known Fowler–Guggenheim isotherm for nanosystems: for $\xi \to 0$ it transforms to the familiar surface segregation isotherm obtained for a semi-infinite bulk sample with one free surface.[5] Indeed, in this case the energy term in the nominator on the left hand side of Eq. (8) has the form

$$E_s - 2V[z_l(c_s - X) - z_v(X - \tfrac{1}{2})]. \tag{10}$$

III. RELATIONS FOR THE ANALYSIS OF THE EXPERIMENTAL DATA

A. General relations for the temperature dependence of the equilibrium (stabilized) interface fraction

In order to get an expression similar to that obtained by Kirchheim[1] we have to combine Eqs. (8) and (9)

$$\frac{[\gamma_B - E_s + (V\beta/\xi_0)(1 - c_s) + V\phi]}{kT} = \ln \left(\frac{X/c_s - \xi_0}{1 - \xi_0} \right)$$

$$= \ln \left(\frac{c_b}{c_s} \right). \tag{11}$$

Substituting the solutions of Eq. (8) for c_s into Eq. (11) an implicit expression for the $\xi_0(T)$ function can be obtained.

Before doing so, it is worth considering simpler cases, also treated in Ref. 1. Assuming that the surfaces (or grain boundaries) are always saturated (the reliability of this supposition will be analyzed later) one can put simply $c_s = 1$ into Eq. (11) and

$$\frac{\gamma_B - E_s + V\phi}{kT} = \ln c_b = \ln \left(\frac{X - \xi_0}{1 - \xi_0} \right), \tag{12}$$

with

$$\phi = -\frac{(1 - X)^2}{(1 - \xi)^3} [z_l (1 - \xi) + z_v (1 - 3\xi)] \tag{13}$$

is obtained.

B. Comparison with the relation derived by Kirchheim[1]

Relation (12) has to be compared with Eq. (20) in Ref. 1

$$\frac{\gamma_0 / \Gamma_{0A} + H_s}{RT} = \ln x_{gA} = \ln \left(x_A - \frac{3 \Gamma_{0A} V_M}{g_0} \right), \tag{14}$$

where R is the gas constant, γ_0 is the grain boundary energy of the pure solvent (in J/m^2 units), g_0 is the equilibrium grain diameter, Γ_{0A} is the excess amount of the saturated solute atoms at the boundary in mol/m^2, V_M is the molar volume, and H_s is the enthalpy of segregation per mole (defined to be negative for solute enrichment at the boundary). It is worth mentioning that in Ref. 1 the relation between $X \equiv x_A$ and x_{gA} [defined as the ratio of the solute atoms in the bulk and N, i.e., $x_{gA} = (1 - \xi)c_b$] had the form

$$x_A = X = 3\Gamma_{0A}V_M/g_0 + x_{gA}. \tag{15a}$$

Thus

$$\xi c_s \cong \xi = 3\Gamma_{0A}V_M/g_0 \tag{15b}$$

and Eq. (14) can be written as

$$\frac{\gamma_0/\Gamma_{0A} + H_s}{RT} = \ln(X - \xi_0). \tag{16}$$

Comparing relations (12) and (16), it can be seen that

(i) On the left hand side of Eq. (12) the first two terms are similar to the left hand side of Eq. (16): H_s/R corresponds to $-E_s/k = -z_v(V_{AA} - V_{BB})/2k$, which is indeed negative for an enrichment of A atoms ($|V_{AA}| < |V_{BB}|$), and γ_0/Γ_{0A}, the boundary energy per mole, is proportional to the surface energy per atom of the solvent ($\gamma_0/R\Gamma_{0A} = -z_v V_{BB}/2k$). Furthermore, while Eq. (16) has been derived for $c_s \cong 1$ and for dilute alloy, deriving Eq. (12) the latter assumption was not made. Assuming that $X \ll 1$, ϕ in Eq. (12) will have the following form:

$$\phi = -\frac{1}{(1 - \xi_0)^3}[z_l(1 - \xi_0) + z_v(1 - 3\xi_0)]. \tag{17}$$

(ii) Obviously—taking into account comment (i)—a relation similar to Eq. (16) can be obtained from Eq. (12) only for ideal solutions (i.e., if $V = 0$, which was indeed supposed in Refs. 1 and 2).

(iii) The $\xi_0(T)$ function is different [see the $(1 - \xi_0)$ in the denominator of the right hand side of Eq. (12)].

(iv) For $V = 0$, in the framework of a simple broken bond model, the left hand side of Eq. (12) should be equal to the surface energy of the solute: $\gamma_B - E_s = \gamma_A$. This would mean however that the condition

$$\gamma_B - E_s < 0 \tag{18}$$

[i.e., the left hand side of Eqs. (12) or (16) should be negative] would never be fulfilled and thus segregation inhibited grain coarsening could not be observed. However in more realistic estimations of γ_B and E_s (see e.g., Refs. 7–9) it could be assumed that Eq. (18) is fulfilled. Indeed it is well know that estimations of surface energies from $\gamma_i = -z_v V_{ii}/2$ give overestimated E_s values[10] (e.g., due to structural relaxations in the surface layer). Furthermore in more sophisticated calculations of the segregation energies—besides the broken bonds—e.g., the size mismatch terms can also be important.[9,11] Thus there could exist systems obeying Eq. (18) and having a grain stabilization effect in the nanocrystalline state even in this simple (ideal solution) limit.

(v) it can be seen from Eqs. (12) and (13) that for phase separating systems (where $V > 0$) the condition

$$\gamma_B - E_s + V\phi < 0 \tag{19}$$

is more easily fulfilled because $\phi < 0$. In more sophisticated treatments (see e.g., Ref. 11) it is assumed that the pair interaction energies, and thus the values of V, are different at the surface and in the bulk. It can also be supposed that $V_{Bulk} = 0$ but $V_{surf} \neq 0$: nevertheless these refinements do not modify the qualitative conclusions drawn above.

(vi) Due to the supposition of $c_s = 1$, Eq. (12) [or (16)] has a very restricted validity, i.e., for large ξ_0 ($\xi_0 > X$) it will not be applicable. This is the consequence of the finite size of the sample: with increasing ξ there will not be enough solute to saturate at the surfaces[3] [see also the right hand side of Eq. (11)] and the more general form (i.e., Eq. (11) with $\ln[(X/c_s - \xi_0)/(1 - \xi_0)]$) has to be investigated, where X/c_s stands instead of X.

IV. DISCUSSION

A. Ideal, dilute solution with $c_s = 1$

Let us first consider the simplest case (investigated by Kirchheim[1]) i.e., take ideal dilute solution ($V = 0$, $X \ll 1$) with $c_s = 1$. Before analyzing the validity of Eq. (12) [in contrast to Eq. (16)], it is important to note that, for comparison with experimental findings, Kirchheim,[1] starting from Eq. (14), proposed the following form [see Eq. (21) in Ref. 1]:

$$\frac{d(1/g_0)}{d \ln T} = \frac{x_{gA} \ln x_{gA}}{3\Gamma_{0A}V_M}, \tag{20}$$

with the comment: "the right hand side depends on the temperature too, because changes in g_0 give rise to changes in x_{gA}. Nevertheless Eq. (21) turns out to be useful for a comparison with experimental results." But this latter problem is more serious as it can be seen from the rewritten version of Eq. (20):

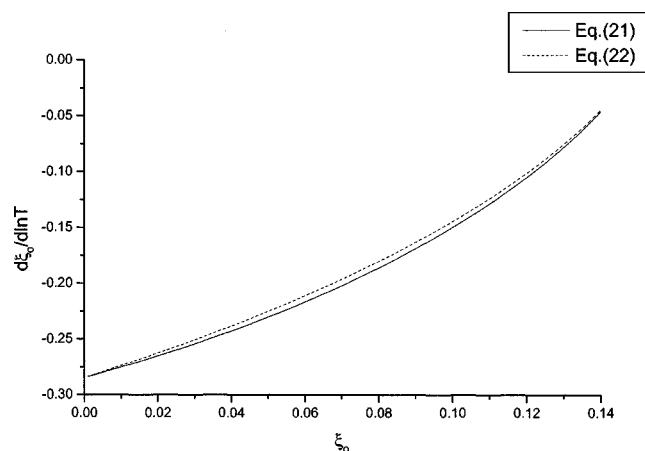$$\frac{d\xi_0}{d(\ln T)} = (X - \xi_0)\ln(X - \xi_0), \tag{21}$$

or form the relation obtained from Eq. (12) with $V = 0$ and $X \ll 1$

$$\frac{d\xi_0}{d(\ln T)} = (X - \xi_0)\ln\frac{X - \xi_0}{1 - \xi_0}. \tag{22}$$

One can see from relations (21) or (22) that the slope of the $1/g_0$ (ξ_0) versus $\ln T$ function should have considerable temperature dependence (because of the temperature dependence of ξ_0), and thus in general such a plot should not be linear. For the illustration of this, one has to know the proportionality factor between ξ_0 and $1/g_0$. In fact one can read it out from Eq. (15b) but on the other hand, assuming nearly spherical grains,[1] the $\xi_0 = 3\delta/g_0$ relation should also be valid [$\delta(= \Gamma_{0A}V_M)$ is the boundary width].

Figure 1 shows the right hand side of Eqs. (21) and (22) versus ξ_0 for $X = 0.15$, corresponding to the experimental data in RuAl(Fe) system[12] analyzed also by Kirchheim.[1] It can be seen that these functions are not constant in accor-
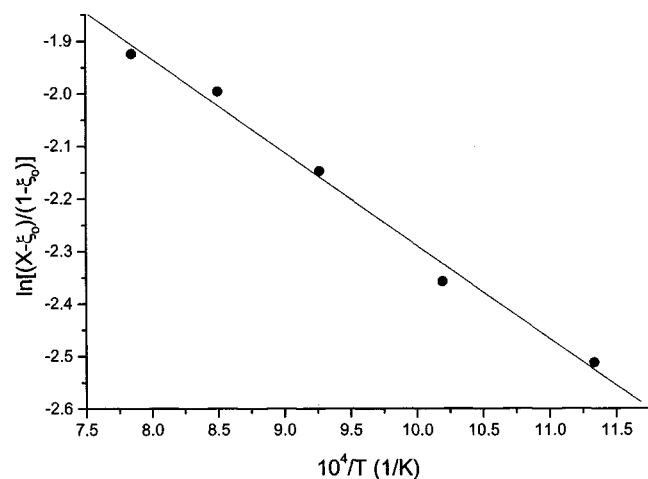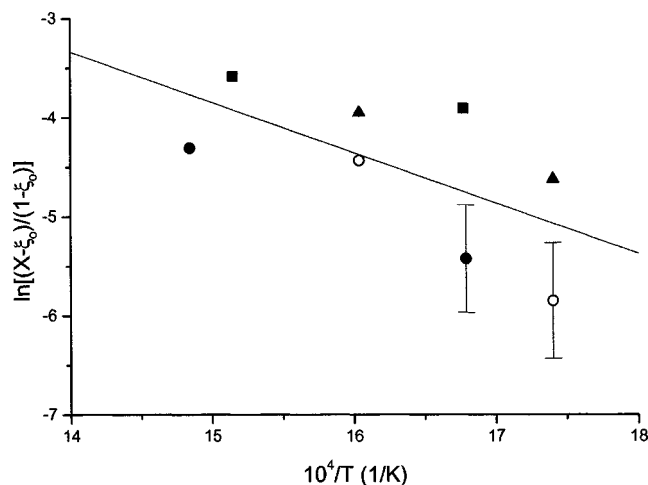
FIG. 1. The right hand side of Eqs. (21) and (22) vs ξ_0.

FIG. 3. $\ln[(X-\xi_0)/(1-\xi_0)]$ vs $1/T$ for the Ni(P) system: (open circles) 2.3 at. % P (Ref. 13); (triangles) 2.8 at. % P (Ref. 14); (filled circles) 3.6 at. % P (Ref. 15); and (squares) 5.8 at. % P (Ref. 15); δ=0.1 nm.

dance with Eq. (12) and the temperature dependence of the slope of the $1/g_0$ (or ξ_0) versus $\ln T$ plot cannot be neglected (see also below). This also means that for the investigation of the effect of the surface fraction (or grain boundary diameter) on the segregation effects on nanoscale it is better to use c_s and X, and not the parameters corresponding to c_s and c_b (or x_{gA}).

Accordingly, we propose to use relation (12) for the analysis of the experimental data. Assuming again ideal solution, i.e., $V=0$, the $\ln[(X-\xi_0)/(1-\xi_0)]$ versus $1/T$ function has to be investigated. It is important to note that the assumption $X \ll 1$ should not be made.

Let us now see the examples analyzed by Kirchheim[1] as well. Figure 2 shows the $\ln[(X-\xi_0)/(1-\xi_0)]$ versus $1/T$ function for the RuAl(Fe) system.[12] For the calculation of ξ_0, δ=0.25 nm was taken for the boundary width, belonging to $\Gamma_{0A}=2.5\times10^5$ mol/m^2 and $V_M=10^{-5}$ m^3/mol.[1] It can be seen that a linear relation has been obtained with the slope yielding $Q=\gamma_B-E_s=-15$ kJ/mol.

Constructing a similar plot for the Ni(P) system, also analyzed in Ref. 1, $\delta=\Gamma_{0A}V_M=0.1$ nm was assumed ($\Gamma_{0A}=1.5\times10^{-5}$ mol/m^2,[1] and $V_M=6.6\times10^{-6}$ m^3/mol for Ni). It is important to note that the point, belonging to the largest
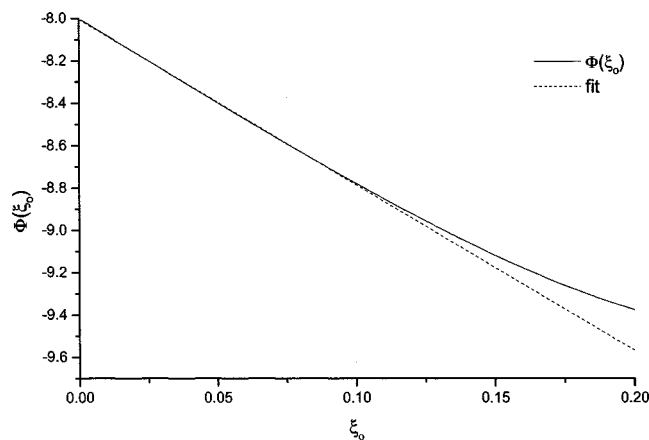
value of g_0, and obtained at $X=2.3$ at. %[13] (see also Fig. 2 of Ref. 1) cannot be plotted on our figure because the $X-\xi_0$ value is negative. This is probably related to the problem treated already in comment (vi) of Sec. III. It can also be seen in Fig. 3 that, although the scatter of points is large, different experimental points belonging to different X values are scaled together and a common straight line can be fitted to them. (The effect of 1 nm uncertainty in g_0 is shown for the illustration on the two points being very close to the $X \cong \xi_0$ limit.) Figure 3 has to be compared with Fig. 2 of Ref. 1 where these points could not be scaled together. The slope of the straight line yields $Q=-42\pm20$ kJ/mol which is in a reasonable agreement with $Q=-22$ kJ/mol, if we estimate it from the data $[\gamma_0/\Gamma_{0A}=(0.5/1.5\times10^{-5})$ J/mol$=33$ kJ/mol and $H_s=-55$ K J/mol] used in Ref. 1.

The estimations above are based on the assumption that $V=0$ (or $V\phi\cong$const). Furthermore, the grain stabilization effect can be caused by other factors as well: see for example Ref. 12 where the inhibition of grain growth was interpreted as the result of the solute drag in the RuAl(Fe) system. In addition the linearity in Fig. 2 alone is not strong evidence for the solute segregation inhibited grain coarsening. Indeed, the RuAl(Fe) system is an ordering alloy based on the RuAl compound and only the RuAl–(Fe) quasibinary system could have a nearly ideal behavior. Nevertheless, if we assume—in accordance with Refs. 1 and 12—that the RuAl–Fe system is a nearly ideal solid solution, then Fig. 2 provides good evidence for the validity of Eq. (12) with $V=0$ (or with $V\phi\cong$ const). On the other hand, it is known that there is a strong phase separation tendency (precipitation) in the Ni(P) system[13,14] and thus, although the scatter of points is too large in Fig. 3, the $V=0$ assumption is a rough approximation only. Thus the investigation of the more general case ($V\neq0$) is necessary.

FIG. 2. $\ln[(X-\xi_0)/(1-\xi_0)]$ vs $1/T$ for the RuAl(Fe) system (Ref. 12) (δ=0.25 nm).

B. $c_s=1$, but $V\neq0$

In this case the right hand side of Eq. (12) also depends on ξ_0 through ϕ as shown by Eq. (13). Figure 4 shows the

FIG. 4. $\phi(\xi_0)$ vs ξ_0 for a fcc structure with $z_l=z_v=4$ and for $X=0$.

FIG. 6. $[T/(1-X)^2]\ln[(X-\xi_0)/(1-\xi_0)]$ vs ξ_0 for the Ni(P) system assuming $\delta=0.1$ nm: (open circles) 2.3 at. % P (Ref. 13); (triangles) 2.8 at. % P (Ref. 13); (filled circles) 3.6% P (Ref. 15); (filled squares) 5.8 at. % (Ref. 15); (open squares) if 4.5 at. % would be taken instead of 5.8 at. %. Fitting the straight line squares was not taken into account.

$\phi(\xi_0)$ function in an fcc structure with $z_l=z_v=4$ and for $X\ll 1$. Fortunately this function can be well approximated by a straight line in the (0–0.10) interval of ξ_0 and thus $\phi=-8(1+\xi_0)(1-X)^2$ can be taken. Using this estimate, Eq. (12) can be rearranged as

$$T \ln\frac{X-\xi_0}{1-\xi_0} = \frac{\gamma_B - E_s - 8V(1-X)^2}{k} - \frac{8V(1-X)^2}{k}\xi_0.$$

(23)

Figure 5 shows this function for the RuAl(Fe) system, and it can be seen that the slope has a positive sign, which underlines the warning already discussed above. The role of the choice of δ has to be mentioned as well, because the evaluation could be rather sensitive for this. In the analysis above we assumed that $\delta(=\Gamma_{0A}V_M)=0.25$ nm, which was obtained from data estimated by Kirchheim as well ($\Gamma_{0A}=2.5\times 10^5$ mol/m^2 and $V_M=10^{-5}$ m^3/mol).[1] The value of Γ_{0A} belongs to 1 monolayer on a dense packed (111) plane of an fcc structure. Thus this is the maximum that one can choose for δ. We determined that values less than δ_{max} would just increase the slope in Fig. 5. On the other hand, if X were smaller (e.g., if $X=0.12$, which could correspond to the case when about 20% of the Fe content is in precipitates, but the density of the precipitated particles is not high enough to
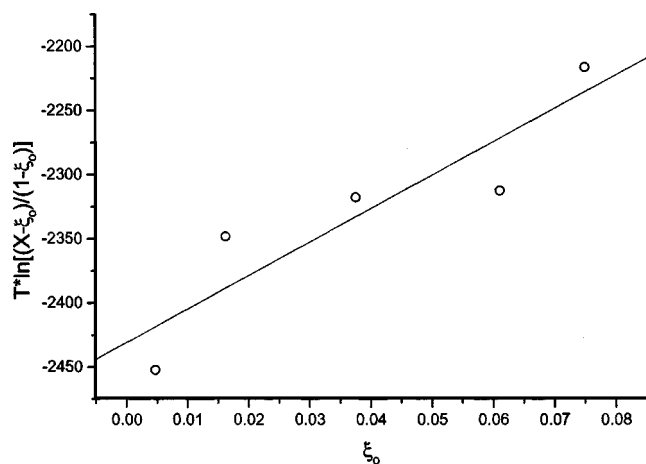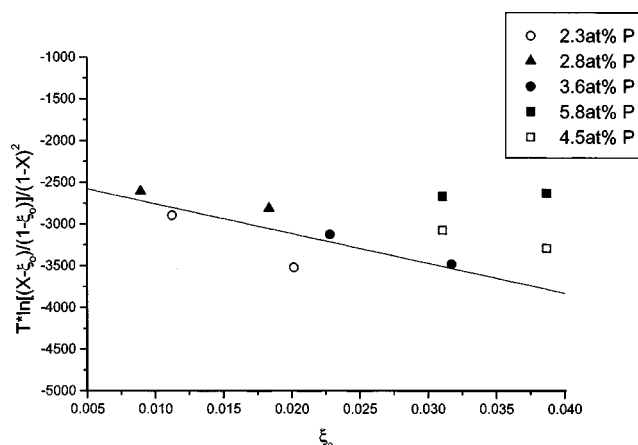
stabilize the small grain size), then the slope would be already approximately zero, indicating the sensitivity of such a plot for the value of X as well. At the same time this also means that for the RuAl–Fe system the second term in Eq. (23) is negligible (as it was discussed after Fig. 2.)

Figure 6 shows the plot according again to relation (23), but for the Ni(P) system. Furthermore—in order to "scale" the slopes together for all the points obtained at different X values—the $[T/(1-X)^2]\ln[(X-\xi_0)/(1-\xi_0)]$ function is plotted versus ξ_0. It can be seen that the points for $X=2.3$, 2.8, and 3.6 at. % P indeed fit approximately to the same line with negative slope as it is expected. The points belonging to $X=5.8$ at. % P do not fit to the tendency above. Whether this is simply due to the scatter of the experimental points or is related to the possible precipitation of the Ni$_3$P phase[1] (the point corresponding to about 660 K is close to 700 K above which precipitation already was observed)[13,15,16] is not clear at present. If we take—by the same arguments as for the RuAl(Fe) system—$X=0.045$, these points will be shifted as indicated by open rectangles in Fig. 6.

C. Cases for $V\neq 0$ and $c_s\neq 1$

This general problem of the existence of a minimum on the f versus ξ function was already investigated elsewhere.[3] No attempt was made there (as it was done by Kirchheim[1] or here above) to find a simple relation describing the temperature dependence of ξ_0. As it was illustrated above this is a rather complicated problem and will be analyzed in a separate article.

V. CONCLUSIONS

We have shown, from general statistical (atomistic) calculations, that a relatively simple analytical relation [see Eqs. (12) or (23)] can be obtained for the temperature dependence of the segregation stabilized boundary fraction (or grain

FIG. 5. $T \ln[(X-\xi_0)/(1-\xi_0)]$ vs ξ_0 for the RuAl(Fe) system (Ref. 12).

size). It was illustrated that Eq. (12) corresponds to Eq. (14), obtained by Kirchheim[1] in ideal ($V=0$) dilute ($X \ll 1$) solutions with saturated boundaries. It is important to note that in the derivation of relation (12) the $X \ll 1$ assumption was not made.

It is expected that in general the relation (20) [or (21)], obtained from Eq. (14) and proposed for the comparison with experimental findings in Ref. 1, cannot be fulfilled. Instead we propose using Eq. (12) with $V=0$ or Eq. (23) for the analysis of the experimental data. They are based on the only assumption that grain stabilization occurs with saturated boundaries. This, however, can be questioned (see the results of our previous article),[3] or at least can be fulfilled in very special cases only. Thus—taking also into account the eligible quantity of experimental evidence as well—further analyses of the general case(s) are desirable. Furthermore, more straightforward experiments (clearly distinguishable from other effects such as grain-boundary pinning caused by precipitations) for the verification of the segregation inhibited grain coarsening, and especially for the verification of the temperature dependence of stabilized grain size, are necessary. Nevertheless, it is illustrated that the RuAl–Fe and the Ni(P) system can be well described by relation (12) with $V=O$ and by Eq. (23), respectively.

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