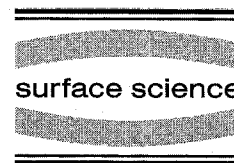




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Phase separation and finite size: from symmetry to asymmetry

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Abstract

We studied the influence of surface segregation and finite size effects on a phase diagram of a thin film. The tight binding Ising model within a mean field approximation was applied to the popular Fe–Cu system. Cu surface segregation leads to a pre-phase separation at the surface and then reduces the stability range of the solid solution on the Fe-rich side of the phase diagram. At the opposite side, the free energy cost of the interphase boundaries leads to an increase of the domain of the solid solution on the Cu-rich side.

Keywords: Alloys; Copper; Equilibrium thermodynamics and statistical mechanics; Iron; Metallic films; Surface segregation; Surface thermodynamics

1. Introduction

Finite size systems such as bimetallic clusters or thin films are increasingly used due to their technological applications. The influence of the finite size on the phase diagram has been investigated, mainly on small clusters. For alloys that show phase separation in the bulk, the general rule is that for small systems the range of stability of the solid solution is *extended* on both sides of the phase diagram due to the interface free energy [1,2]. However, this result is obtained without taking into account surface segregation phenomenon. On the other hand surface segregation can produce a pre-phase separation, which *decreases* the domain of stability of the solid solution for a semi-infinite system relatively to an infinite one, at least on one side of the phase diagram [3].

In this paper we present results on the theoretical

phase diagram for a thin film, taking into account within the same model the surface segregation and the interface free energy cost. To illustrate our calculations, we chose the Fe–Cu system, which was largely studied because of its technological interest when depositing Fe on Cu [4]. However, the thermal stability of these thin films is not well known and we hope that the present study will suggest new experiments.

2. Theoretical model

This study pointed out the influence of the finite size on the whole concentration range of copper. Although the copper is fcc, we considered a bcc $\text{Cu}_c\text{Fe}_{1-c}$ thin film of a given thickness (here 21 atomic planes) limited by two (110) free surfaces at temperature T . We assumed that the main results presented here do not depend on the structure and can be considered as generic.

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We minimized the free energy of the system using the tight binding Ising model (TBIM) [5] and a mean field approximation. This allowed us to obtain the equilibrium concentration profile c_p , where c_p is the Cu concentration (assumed homogeneous) in the p th (110) layer parallel to the surfaces ($p=0$ and $p=20$).

Let us briefly recall the three main energetic factors occurring in the TBIM [6] and their values for the Cu–Fe system:

- the difference in surface energy between Cu and Fe for the (110) face in the bcc structure, $\Delta\tau=272$ meV at $^{-1}$ [7], favours the Cu segregation
- the alloying effect, which is at the origin of the miscibility gap in the bulk, can be expressed in terms of effective pair interactions between nearest (V_1) and next-nearest (V_2) neighbours. Tight binding calculations show that V_2 is roughly equal to $V_1/2$ in the bcc structure [8]. A good agreement with the experimental solubility limit for Fe-rich alloys [9] is obtained for $V_1=2$ and $V_2=36$ meV
- the size effect, which takes into account the difference in size between the components, can be neglected in the present case ($r_{\text{Cu}}/r_{\text{Fe}}=1.001$, where r_A is the atomic radius of the element A).

3. (110) $\text{Cu}_c\text{Fe}_{1-c}$ semi-infinite crystal

Before studying the thin film behaviour, we present the result for the semi-infinite (110) crystal to discriminate the effect of surface segregation and the finite size effect. The results are obtained for $T=750$ K, which is a sufficiently high temperature to reach equilibrium during experiments. At this temperature the bulk solubility limits, which obviously are symmetric for the model, are equal to $c_\alpha=2.24 \times 10^{-3}$ and $c_\beta=1-c_\alpha=0.99776$.

In the Fe-rich part of the phase diagram ($c \ll 1$), the surface energy effect leads to a strong Cu surface segregation. Due to the alloying effect, we observe a first-order surface phase transition [10] for $c=1.7 \times 10^{-4}$, the surface concentration changing from $c_0=0.10$ to $c_0=0.90$. When the bulk concentration increases towards the limit of solu-

bility, there is an infinite succession of first-order layering transitions [3,10]: the concentration of the layers below the surface changes successively from $c_p=0.07$ to $c_p=0.93$ (Fig. 1). This leads to the wetting of the majority phase (rich in Fe) by the minority one (rich in Cu), the thickness of the last one diverging logarithmically with $c_\alpha - c$ [11]. In other words, for Fe-rich solid solutions, the surface segregation leads to a pre-phase separation: an equilibrium interphase boundary appears near the surface before reaching the bulk solubility limit.

On the other side of the phase diagram (Cu-rich alloys), there is no such effect. Only a very slight Cu surface segregation exists in the solid solution domain.

In the miscibility gap, the equilibrium profile is obtained by locating the Cu-rich phase near the surface and the Fe-rich one in the core.

4. (110) $\text{Cu}_c\text{Fe}_{1-c}$ thin film

We have studied the equilibrium concentration profile for a (110) thin film (with two free surfaces) of 21 layers of $\text{Cu}_c\text{Fe}_{1-c}$ at $T=750$ K. In the following we distinguish the average concentration, c , from the core concentration c_c , which is the

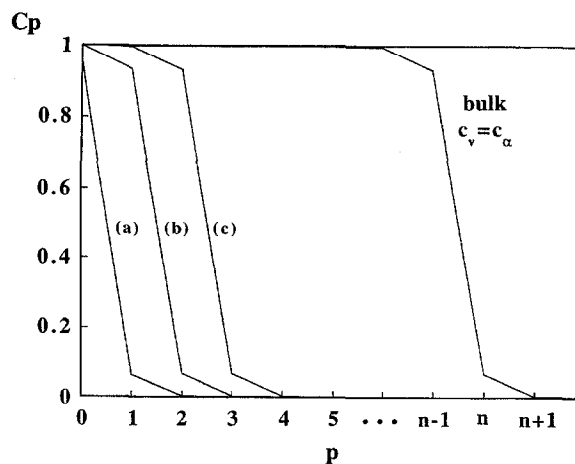


Fig. 1. Depth profile of c_p for $\text{Cu}_c\text{Fe}_{1-c}$ (110) at $T=750$ K. (a) $c=1.9 \times 10^{-4}$, (b) $c=2.20 \times 10^{-3}$, (c) $c=2.2370 \times 10^{-3}$. With increasing c up to $c_\alpha=2.2378 \times 10^{-3}$, the interphase boundary goes into the bulk and is located at $n=\infty$ for $c=c_\alpha$.

concentration in the central planes and which can be compared to the bulk concentration of the infinite (or semi-infinite) case.

Starting from the pure Cu film and lowering the Cu concentration, we can distinguish the following domains:

- for $0.937 < c < 1$ (corresponding to $0.927 < \underline{c} < 1$) the homogeneous profile (with a small Cu surface segregation) is the stable one. This is illustrated by the profile (d) in Fig. 2
- for $0.923 < c < 0.937$ (corresponding to $0.900 < \underline{c} < 0.927$) the homogeneous profile still exists (this allows us to define \underline{c}) but is only metastable. The most stable one is an inhomogeneous profile with a strong Cu depletion in the core, illustrated by the profile (c) in Fig. 2. This means that on this side of the phase diagram the limit of solubility, defined as the bulk (or the core) concentration for which there is a transition between an homogeneous profile and an inhomogeneous one, is equal to 0.927, largely smaller than the one for the infinite crystal ($c_\beta = 0.998$). This is obviously due to the free energy cost of the interphase boundaries. Two points should be noted at this stage:

(i) the concentration of the Cu-rich “phase” (a misused term to describe the concentration of the almost homogeneous region between the

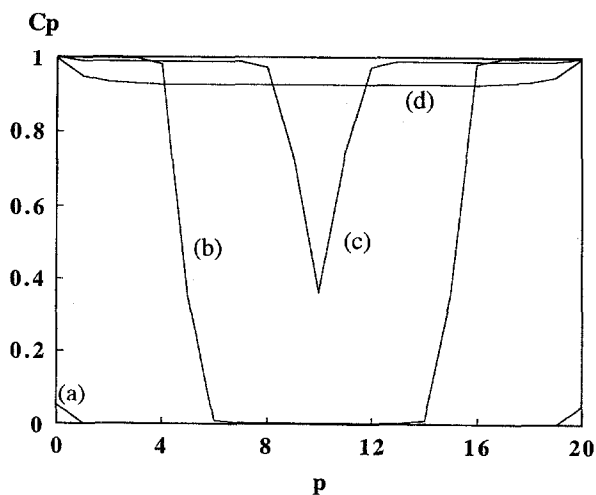


Fig. 2. Typical concentration profiles in the 21 (110) layers film for $\text{Cu}_x\text{Fe}_{1-x}$ at $T = 750$ K. (a) $c = 0.05$, (b) $c = 0.5$, (c) $c = 0.936$, (d) $c = 0.938$.

surface and the core) is very similar to c_β . This means that, contrary to the infinite case, we must distinguish the limit of solubility, defined as above, from the value of the homogeneous “phase” in the phase separation regime

(ii) the core concentration does not reach the value of c_α . This is essentially due to the lack of Fe atoms. With a very crude approximation for the concentration profile at the interface, we estimate that c must be lower than $18/21 = 0.857$ to eliminate this constraint and then to have a core concentration equal to c_α

for $0.85 < c < 0.923$ the behaviour is the same as above except that the homogeneous profile is no longer metastable but unstable. This allows us to define a spinodal limit (as the stability limit of the homogeneous profile) for the thin film as $\underline{c} = 0.900$, very near to the spinodal limit for the infinite case: $c_s = 0.910$

for $0.09 < c < 0.85$ the behaviour of the thin film is very similar to the one obtained for the semi-infinite crystal in the phase separation regime. The “ β phase” of concentration c_β exists on both sides of the film, with a small Cu surface enrichment relatively to c_β , and the “ α phase” of concentration $\underline{c} = c_\alpha$ is located at the core of the film (see profile (b) in Fig. 2). As c decreases, the interfaces between the α and β phases move towards the surfaces. In fact this is the domain of the layering transitions observed for the semi-infinite crystal (see Fig. 1):

(i) each displacement of one interlayer distance in the thin film corresponds to one layering transition in the semi-infinite crystal

(ii) for each displacement of the interface there is a small variation of the core concentration (around c_α) that is exactly the same as the variation of the bulk concentration for each layering transition

for $c < 0.09$ (profile (a) in Fig. 2) the core concentration is no more constant: \underline{c} becomes smaller than c_α . As for the Fe-rich solid solution in the semi-infinite case, there is a surface phase transition for $\underline{c} = 1.7 \times 10^{-4}$ (the same value as in Section 3). In this domain, the behaviour of the thin film is totally similar to the one observed for the semi-infinite crystal.

5. Discussion and further work

In view of our results, we can see that the coupling between surface segregation effects and finite size effects leads to spectacular differences between the phase diagram of thin films and infinite systems.

For thin films rich in the surface-segregating element (here Cu-rich films), the stability range of the solid solution is extended, due to the cost of the interface, whereas the spinodal limit is little affected by finite size effects. The nucleation of the minority phase occurs at the core of the thin film, imposing the existence of two interfaces.

For thin films rich in the non-surface-segregating element (here Fe-rich films), the minority phase nucleates at the surface, due to surface segregation. The behaviour is very similar to the semi-infinite case with the occurrence of a surface transition (pre-phase separation) followed by a wetting behaviour. The stability range of the solution is then reduced (if we consider the surface phase transition as a phase separation) or almost unchanged (if we consider only the other layering transitions).

Let us conclude on the preliminary character of this study. A systematic study of the influence of the temperature and the thickness of the film is under progress. Moreover, in order to take into account the different structures of the two elements we will compare these results with those obtained in an fcc structure (but this will not affect the main results, the finite size effect being at the origin of the solubility limit shift). Furthermore, the dependence of the behaviour on the surface energy effect must be also considered. In fact, for small surface segregation energy it is expected that the thin film becomes asymmetric with the A-rich phase on one side and the B-rich one on the other

side [12]. In this configuration (which has been found unstable in the case studied here) only one interface occurs instead of two. To follow this study further we could also consider a “pseudo” thin film limited by a surface and a boundary on the other side, in order to apply the results at sandwiches and multilayers. Finally, it would be useful to perform Monte-Carlo simulations, which include the effect of the heterogeneity in the planes parallel to the surface.

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References

- [1] D.F. Ollis, *J. Catal.* 23 (1971) 131.
- [2] A. Christensen, P. Stoltze and J.K. Nørskov, *J. Phys.: Condens. Matter* 7 (1995) 1047.
- [3] Y. Teraoka and T. Seto, *Surf. Sci.* 255 (1991) 209.
- [4] Th. Detzel and N. Memmel, *Phys. Rev. B* 49 (1994) 5599.
- [5] G. Tréglia, B. Legrand and F. Ducastelle, *Europhys. Lett.* 7 (1988) 575.
- [6] F. Ducastelle, B. Legrand and G. Tréglia, *Prog. Theor. Phys. Suppl.* 101 (1990) 159.
- [7] M. Aldén, H.L. Skriver, S. Mirb and B. Johansson, *Surf. Sci.* 315 (1994) 157.
- [8] F. Ducastelle, *Order and Phase Stability in Alloys* (North-Holland, Amsterdam, 1991).
- [9] G. Salje and M. Feller-Kniepmeier, *J. Appl. Phys.* 48 (1977) 1833.
- [10] B. Legrand, A. Saül and G. Tréglia, *Mater. Sci. Forum* 155/156 (1994) 165.
- [11] A. Saül, B. Legrand and G. Tréglia, *Surf. Sci.* 331–333 (1995) 805.
- [12] A.M. Lois and C.R. Mirasso, *Phys. Rev. B* 41 (1990) 8112.