

Spinodal Decomposition and Continuous Ordering

D. E. Laughlin, K. B. Alexander and L. L. Lee

Metallurgical Engineering and Materials Science
Carnegie-Mellon University, Pittsburgh, PA 15213

Introduction

In this paper we will discuss continuous transformations in which a supersaturated solid solution decomposes into two phases, one of which is an ordered crystallographic derivative (1) of the parent solid solution. Continuous transformations proceed with no significant thermodynamic barrier, other than that of diffusion. They are homogeneous, in that they occur uniformly throughout the material. Thus, the alloy cannot be separated into transformed regions and untransformed regions.

The existence of concomitant atomic ordering and decomposition has been demonstrated by several investigations in alloys such as Cu-Ti, Ni-Al, Cu-Ni-Sn and Ni-Ti (See Reference 2 for a recent review). Richards and Cahn (3,4) demonstrated that these types of transformations could be understood in terms of an atomic interaction model which includes both first and second neighbor interactions. Their model thus demonstrated that both clustering and ordering could occur in the same system. Early solution models which only took into account first neighbor interactions could not account for the coexistence of both ordering and clustering in the same system.

Below, we shall review a thermodynamic model for the free energy of the solid solution of alloys in which both clustering and ordering occurs. Three dimensional free energy/order parameter/composition diagrams will be utilized to describe the decomposition process. Finally, we will present and review some of the experimental evidence for these processes in two alloys: Cu-Ti and Fe-Be.

Thermodynamic Modelling

A proper free energy expression is all that is needed to predict the equilibrium state of an alloy. To account for atomic ordering, the order parameters η_i have to be included within the free energy expression of an alloy. At a fixed pressure $F(c_i, \eta_i) = E(c_i, \eta_i) - TS(c_i, \eta_i)$ where E is the configurational energy and S is entropy. An approximation has to be used in order to express E and S in terms of composition c_i and order parameter η_i .

For a binary BCC based alloy which only has B2 type ordering (i.e. - only two sublattices are considered), Ino (5) has written the configurational energy and entropy in zeroth approximation as:

$$E(c, \eta) = NZ_1 V_1 [c(1-c) + \eta^2/4] + NZ_2 V_2 [c(1-c) - \eta^2/4] \quad (1)$$

$$S(c, \eta) = -kN/2 [(1-c+\eta/2)\ln(1-c+\eta/2) + (c-\eta/2)\ln(c-\eta/2) \\ + (1-c-\eta/2)\ln(1-c-\eta/2) + (c+\eta/2)\ln(c+\eta/2)] \quad (2)$$

where:

- V_1 and V_2 are the interchange energies between first and second nearest neighboring atoms and $V_1 = (V_{AA}^i + V_{BB}^i)/2 - V_{AB}^i$
- Z_1 and Z_2 are the coordination numbers of the first and second nearest neighboring atoms, with $Z_1 = 8$, $Z_2 = 6$ for BCC

- N is the total number of atoms in the system, k is the Boltzman constant
- η is the long range order parameter. ($\eta = c_\beta - c_\alpha$, where c_α and c_β are the concentrations of B atoms in α and β sublattices respectively)

At a given temperature and specific ratio of V_1 and V_2 , the free energy F can be plotted as a function of both c and η . A three dimensional plot of F is shown in Figure 1. Constant η curves are drawn on the surface to show the perspective. ABC is the $F(c, \eta)$ curve which will be derived and explained later. Note that η can never be greater than 2c due to the definition of the long range order parameter. Knowledge of this $F(c, \eta)$ allows the state with the lowest free energy (i.e., equilibrium state) to be obtained.

Since the order parameter cannot be controlled freely, it is not a thermodynamic degree of freedom(6). It seems reasonable to assume that the order parameter will always be able to adopt a value which minimizes the free energy of the system. That is

$$\left. \frac{\delta F(c, \eta)}{\delta \eta} \right|_{\eta = \eta_e} = 0 \quad (3)$$

Now $F(c, \eta)$ can be minimized with the above equation as a constraint to obtain the equilibrium state. A curve of $F(c, \eta)$ vs c for $T = 0.7T_c$ and $V_2/V_1 = -16/3$ (with V_1 negative) is plotted in Figure 2. This curve is a projection on the F-c plane of the three dimensional curve ABC of Figure 1. It is the free energy of the thermodynamically constrained homogeneous solid solution. The order parameter (η) vs. c of this homogeneous phase is plotted by the dotted line in the same figure. Note that the free energy curve has inflection points (spinodal points) and a local maximum. Also note that the homogeneous solid solution that is unstable with respect to spinodal decomposition is ordered, viz $\eta_e > 0$. The equilibrium compositions of the decomposed phases can be obtained by the "common tangent" criterion. By repeating this scheme for a series of temperatures, a phase diagram can be obtained. The ordered and disordered curves are shown in Figure 3 and are equivalent to the ABC and ABD curves, respectively, of Figure 1. It can be seen that the disordered alloy must first homogeneously order to reduce its free energy, after which it becomes unstable with respect to spinodal decomposition. During the spinodal decomposition process, the solute-rich phase increases its order parameter, while the solute-poor phase decreases its order parameter and can eventually disorder (Figure 2).

Examples of Concomitant Ordering and Clustering

In this section we review the transformation sequences which occur in Cu-Ti (fcc based) and Fe-Be (bcc based) alloys. Both alloys exhibit concomitant spinodal decomposition and ordering subsequent to a homogeneous ordering of the solid solution as described above.

(a) Cu-Ti

It has been established by several investigators (7-12) that supersaturated copper rich Cu-Ti alloys decompose spinodally into a metastable mixture of α and an ordered phase with the D1a structure. The ordering to the D1a phase occurs during the phase separation. (11,12) Another ordering reaction occurs in this alloy, namely that to the $\{1\frac{1}{2}0\}$ state. Laughlin and Cahn (9,10) showed that a Cu-5w/o Ti alloy had $\{1\frac{1}{2}0\}$ reflections present in the diffraction pattern of the as quenched alloy. Thus, the diffraction pattern had diffuse scattering intensity around the fundamental reflections (satellites, due to spinodal decomposition) as well as SRO $\{1\frac{1}{2}0\}$ intensity and LRO D1a reflections. With aging, the $\{1\frac{1}{2}0\}$ intensity decreased but the D1a reflections increased. Recently, Woychik et al. (13) have shown that a Cu-15w/o Ti can be rapidly quenched from the liquid state to obtain a supersaturated fcc solid solution. The solid solution has diffuse intensity maxima only at the $\{1\frac{1}{2}0\}$ positions. From this and from the aforementioned works we can conclude that the Cu-Ti alloy passes through the following decomposition sequence.



where β is the metastable D1a phase. Equation (5) represents concomitant spinodal decomposition and long range ordering, following the suggestions of Biehl and Wagner (11,12). Thus, the Cu-Ti

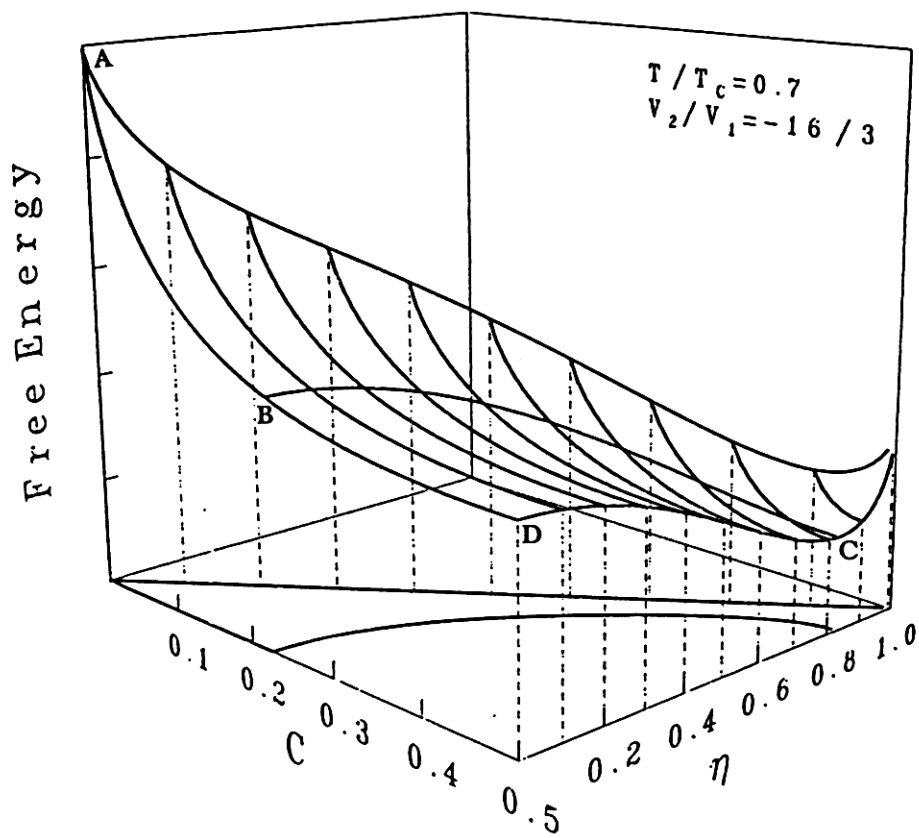


Figure 1: Free energy vs. composition and order parameter for a bcc based solid solution, calculated by the model described in the text

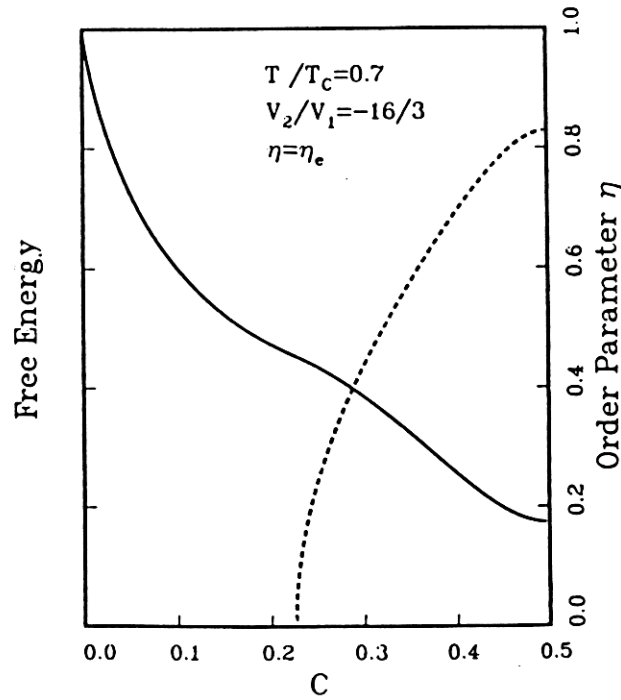


Figure 2: Projection of the free energy surface of minimum energy onto F-c plane (solid). The phase is constrained to be homogeneous. The order parameter, η of the homogeneous phase is shown as a dotted line.

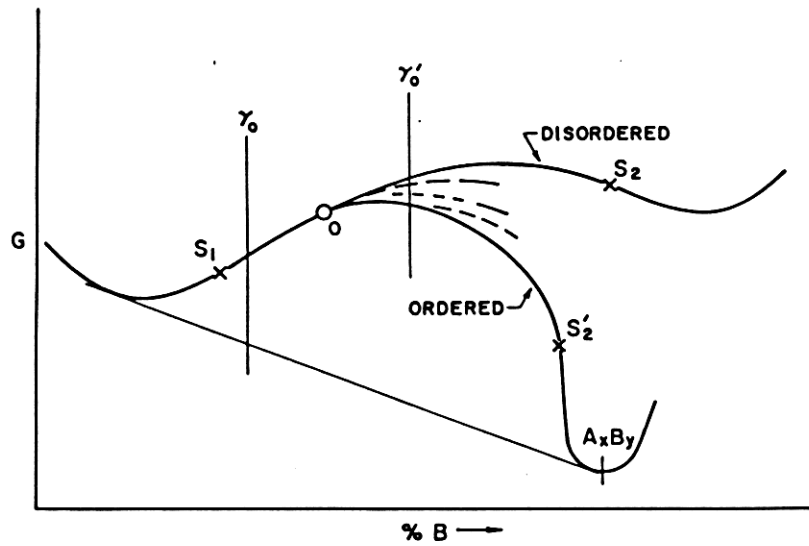


Figure 3: Schematic free energy vs. composition diagram, showing various possible paths of decomposition

system exhibits continuous homogeneous ordering (to the SRO state) prior to spinodal decomposition.

(b) Fe-Be

The Fe-Be system has been investigated by several authors (14,15). Recently, Miller et al. (16) have shown that a metastable phase with the B32 structure forms in addition to the metastable B2 phase. Combining the results of all these investigators, the following is the decomposition sequence in Fe-Be alloys:

1. Supersaturated solid solution (A2) orders continuously to B2 on quenching.
2. The B2 phase spinodally decomposes to $\alpha + B2$.
3. Another metastable phase (B32 - Fd3m) forms within the spinodally decomposed $\alpha + B2$ regions, replacing the B2 phase.
4. The equilibrium C14 phases forms at grain boundaries, replacing the B32 phase.

Ino (5), not being aware of the existence of the B32 phase in this alloy system, suggested that the Fe-Be system has a negative first nearest interaction energy (V_1) and a positive second nearest neighbor interaction energy (V_2), with $V_2/V_1 \approx -4$. This would account for the concomitant spinodal decomposition and B2 ordering, but can not account for the B32 phase, since, according to the ground state diagrams developed by Richards and Cahn (3,4), an alloy with this ratio of V_2/V_1 should not have B32 as a more stable phase than the B2 phase. Even including third neighbor interactions can not stabilize B32 in regimes where concomitant spinodal decomposition and B2 ordering occurs. Hence, it has been suggested (16) that magnetic interactions are important in this alloy. This also suggests that other Fe based systems with bcc derivative ordered structures may also have a phase with the B32 structure. Careful diffraction studies are necessary to elucidate if a phase with the B32 structure is present in an alloy that may have α , B2 and DO_3 phases present (see Ref. 16).

Conclusions

We have shown that in both Cu-Ti and Fe-Be, a homogeneous supersaturated alloy first lowers its free energy by a homogeneous ordering process. This process may be followed by concomitant spinodal decomposition and long range atomic ordering within the solute enriched phase. The sequence of reactions can be understood in terms of a thermodynamic model of the free energy of a solution that uses first and second neighbor interaction energies.

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