

## Part V. Solid-solid transformations II

### Module 2 : Order-disorder transformation

## Spinodal decomposition

### 2.1 Motivation

In the previous module, we considered a system with  $\Omega > 0$ . In such systems, at lower temperatures, the free energy develops a concave curvature leading to a phase separation into mechanical mixture. Now, consider a system with  $\Omega < 0$ , that is, the AB bonds are preferred over AA/BB bonds. What happens to such systems at low temperatures?

### 2.2 Ordered phases

In systems with  $\Omega < 0$ , that is, systems in which AB bonds are preferred over AA/BB bonds are preferred, at lower temperatures, the system becomes ordered. This ordering is over and above the crystallographic ordering. In the crystalline lattice, specific lattice positions are occupied by specific atoms, thus leading to more of the preferred unlike bonds.

Consider for example a bcc lattice occupied by A and B atoms. If it is disordered, then, the probability of the cube corners and cube centers are occupied by the A or B atoms is 50% (that is, the same as the alloy composition in at%). However, when this system orders, the cube corners preferentially occupy one of the positions, say, cube corners while the other preferentially occupies the cube centers. That is, the bcc lattice now can be considered to be consisting of two interpenetrating cubic lattices. Such a structure is known as B2. Notice that in the (ideal) B2 structure, there are only AB bonds and no AA/BB bonds. NiAl is a system in which, for example, such B2 ordered structure is known. There are also fcc based ordered structures such as L1<sub>2</sub> (example: Ni<sub>3</sub>Al) and L1<sub>0</sub> (example: CuAu). In Fig. 9, we show these three ordered structures.

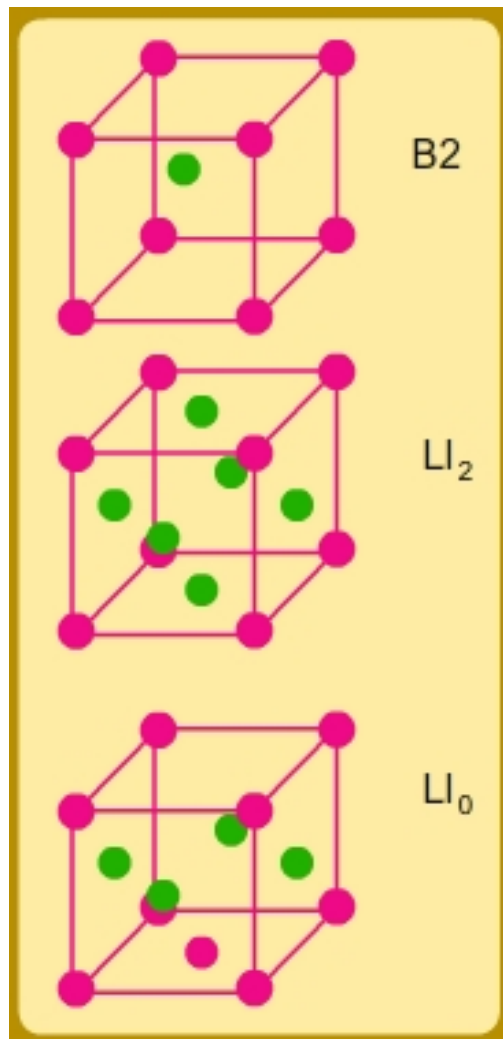


Figure 9: Ordered structures: three examples.

### 2.3 Long range and short range order parameters

There are two different order parameters that one can define. The first is the short range order parameter ( $s$ ) which is defined as follows:

$$s = \frac{P_{AB} - P_{AB}(\text{random})}{P_{AB}(\text{max}) - P_{AB}(\text{random})} \quad (15)$$

Here,  $P_{AB}(\text{max})$  and  $P_{AB}(\text{random})$  refer to the maximum number of bonds that can exist and the number of bonds in a random solution. As one can see, the short range order parameter is closely related to the  $\Omega$ , regular solution parameter; this type of ordering is possible in alloys of all compositions.

In case the alloy composition is in simple ratios of the constituent atoms, then, one can define the so-called long range order parameter  $L$  in terms of the alloy composition  $x$  as follows:

$$L = \frac{p - x}{1 - x} \quad (16)$$

where  $p$  is the probability of occupancy of the given site by the right kind of atom.

At absolute zero, the system will choose a state with  $L = 1$ ; however, as temperature increases, the effects of configurational entropy come into play; so the value of  $L$  decreases from unity and eventually reaches zero. The temperature at which this change of LRO from unity to zero takes place is known as the critical temperature ( $T_c$ ) for the order-disorder transformation.

In Fig. 10 we show the variation of  $L$  and  $s$  with temperature in two systems, namely, one that undergoes an order-disorder transformation from B2 to disordered bcc and another that undergoes an order-disorder transformation from  $L1_2$  to disordered fcc. As is clear from the figures, the changes are of two different types; in the equiatomic case of B2 to bcc (NiAl type), the variation is continuous; however, in the case of  $L1_2$  to fcc ( $\text{Ni}_3\text{Al}$  type), the variation is abrupt. These differences in the behaviour is a consequence of the differences in atomic configurations in the two ordered lattices.

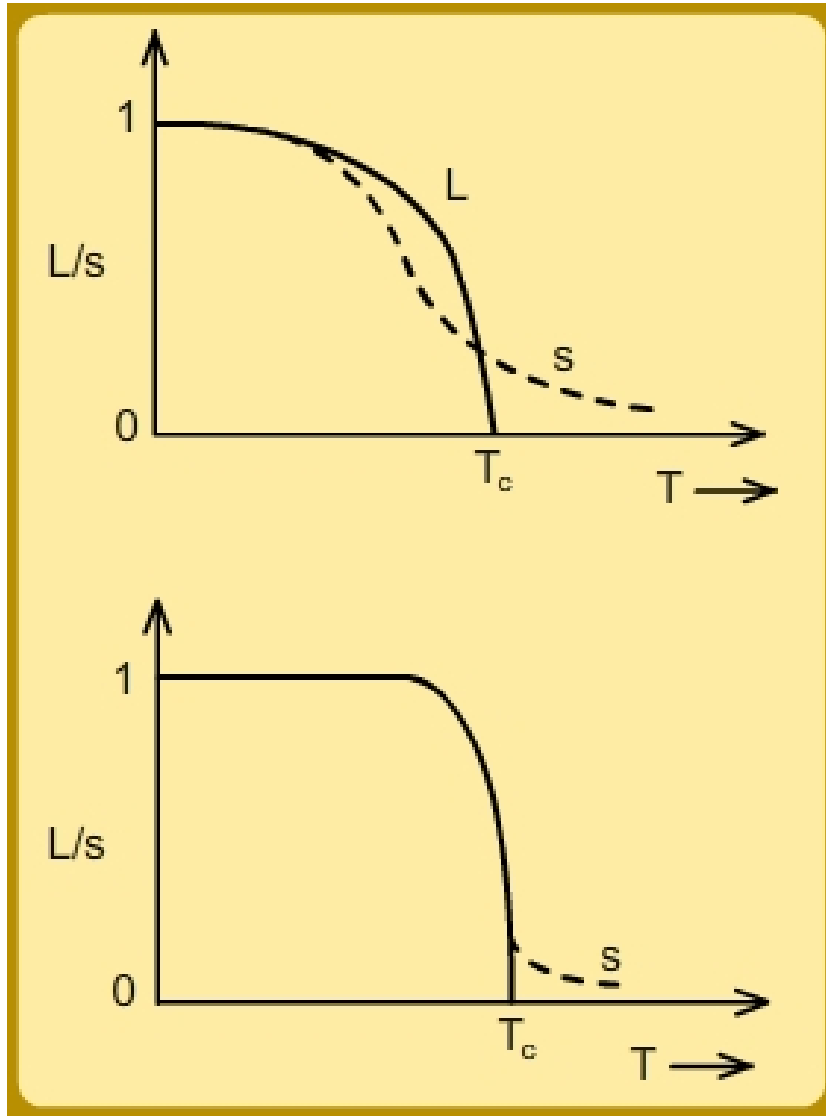


Figure 10: Order parameter variation with temperature: continuous (B2 type) and abrupt ( $L1_2$ ).

## 2.4 Microstructural features

The order-disorder transformation can take place both through the nucleation and growth mechanism and spinodal mechanisms. In spinodal mechanism there is continuous increase in  $s$  homogeneously all through the crystal leading to the transformation. In the nucleation and growth mechanism, small regions form overcoming an energy barrier and these regions grow.

In ordered alloys, the two phases have near-identical lattice parameters and the interfacial energies between the ordered and disordered phases is very low. Hence, the barrier for nucleation is very small. Hence, order-disorder transformation, when takes place through the nucleation and growth mechanism, takes place through homogeneous nucleation.

The surface defects that come about in ordered alloys is known as anti-phase boundaries (APB). These come into existence due to accidents of nucleation and growth. For example, in bcc-B2 transformation, since the two sites in B2 are completely equivalent, at some nuclei, the cube corner is occupied by A while in some nuclei the cube corner is occupied by B. Hence, as these nuclei grow and the ordered regions impinge, there is predominant AA or BB bonds (unpreferred bonds). Such defects are known as APBs and in Fig. 11 we show, schematically, the formation of APBs. In Fig. 12 we show a schematic ordered microstructure in B2 and  $L1_2$  alloys. As is clear from the figures, the nature of APBs and hence the microstructures are different in these two cases.

## 2.5 Tutorial problems and questions

- Consider NiAl which prefers to order into B2 structure. Suppose the crystal structure deviates slightly from 50 at.%. What happens?

### Solutions to the tutorial

- The alloys with exact 50 at.% composition are known as stoichiometric. The off-stoichiometry, in ordered alloys, can lead to point defects. One

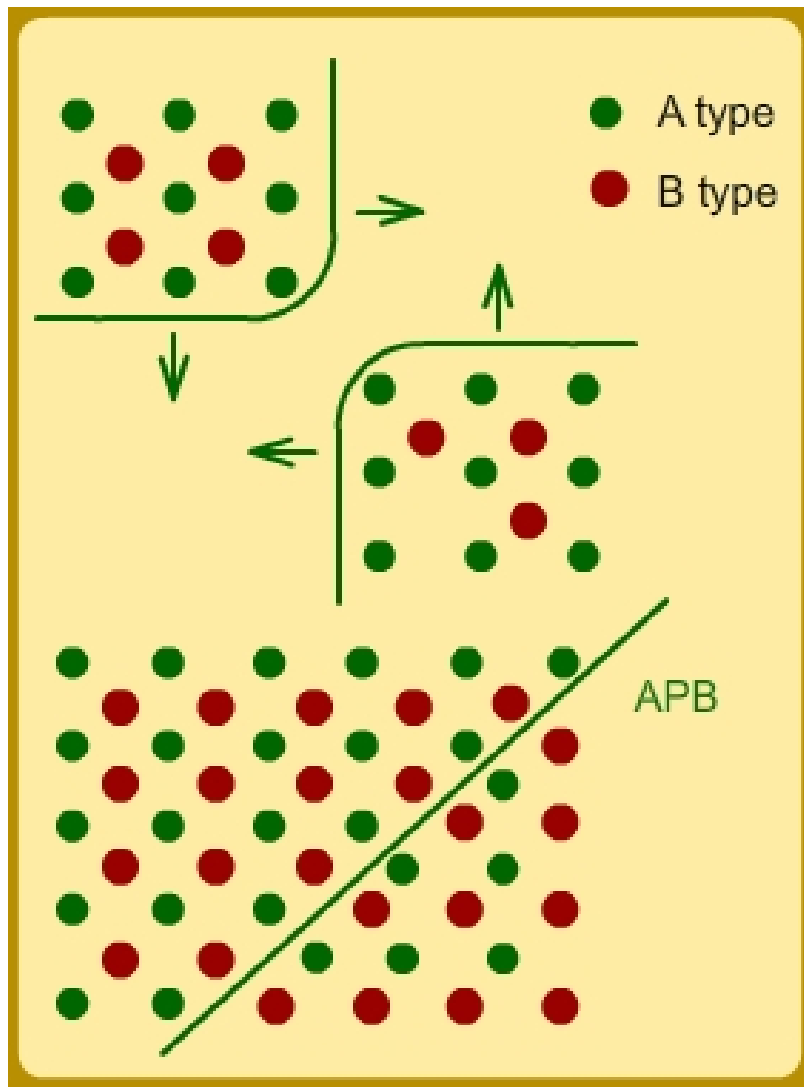


Figure 11: Formation of APBs.

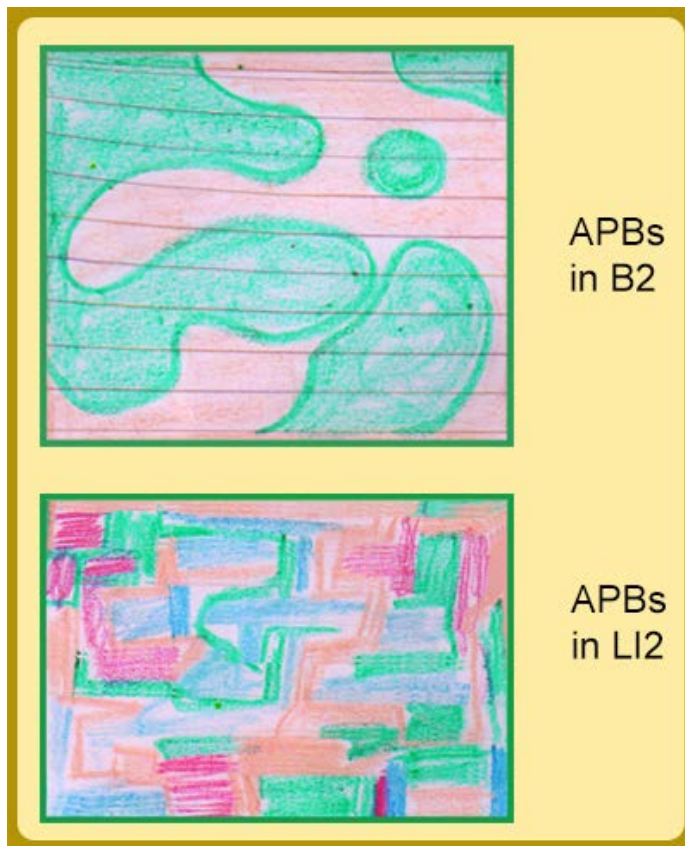


Figure 12: Schematic domain structures in ordered systems.

type of point defect is known as anti-site defect. In this case, the off-stoichiometry is accommodated by the excess atoms occupying the lattice position of the other atoms; these atoms are thus at wrong sites and hence the name. In some cases (for example, excess Al in NiAl), this can also lead to vacancies which are twice the off-stoichiometry value. This is because the excess atoms still occupy their own lattice positions (say cube corners); since there is shortage of atoms of the other type, the corresponding sites in the other sublattice (cube centres in this case) are left vacant. Note that off-stoichiometry can also lead to two phase order+disorder coexistence regions if the defects are not accommodated by such point defects.

## 2.7 Supplementary information

The ordered structures can be quite complex. For relatively more complex but often seen ordered structures see the  $DO_3$  and  $DO_{19}$  structures shown in [1]. As noted in the previous part, in shape memory alloys, the martensitic transformation takes place between two ordered structures. In the case of Ni-base superalloys, the precipitates are ordered. Thus, ordered structures are not only interesting from the scientific point of view but also from an application point of view.



## References

- [1] David A. Porter, Kenneth E. Easterling, and Mohamed Y. Sherif, Phase transformations in metals and alloys, CRC press, Third edition, 2009.
- [2] V Raghavan, Solid state phase transformations, Prentice-Hall India Pvt. Ltd., First edition, 1992.