

Some characteristics of first-order phase transformations

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Abstract. The distinction between first-order and second-order phase transformations is brought out. The general characteristics of first-order transformations are described. The salient features of transformations controlled by long-range diffusion, short-range diffusion and by (diffusionless) shear mechanisms are discussed. Martensitic transformations, which belong to the shear category, occur in many metallic and non-metallic systems and deserve an intensive study.

1. Introduction

Many metallurgical phase transformations are first-order, in contrast to the second-order phase transitions that form the subject matter of most papers discussed in this meeting.* The kinetics and crystallography of metallurgical transformations have been studied in great detail, in view of the practical importance of such transformations in determining the mechanical strength of engineering alloys. In this short presentation, the essential characteristics of first-order transformations will be discussed briefly. For a more detailed discussion, the reader is referred to recent reviews (Christian 1975; Raghavan and Cohen 1975).

2. Order of a phase transition

Thermodynamic parameters can be used to distinguish between first-order and second-order transitions. In all phase transitions, the Gibbs free energy G of a material varies continuously through the transition occurring at the equilibrium temperature and pressure. A first-order transition is characterised by discontinuities in the first derivatives of G with respect to temperature and pressure :

$$(\partial G/\partial T)_P = -S, \quad (1)$$

$$(\partial G/\partial P)_T = V, \quad (2)$$

where S and V are the molar entropy and the molar volume of the material. As illustrated schematically in figure 1, there are abrupt changes in the slope of the free energy curves during a first order transition.

* Phase transitions in solids, June 1978, Indian Academy of Sciences, Bangalore.

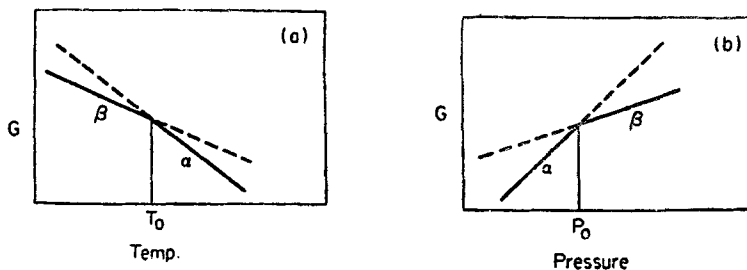


Figure 1. Abrupt changes in the slopes of the G - T and G - P curves occur at the $\alpha \rightarrow \beta$ first-order transition.

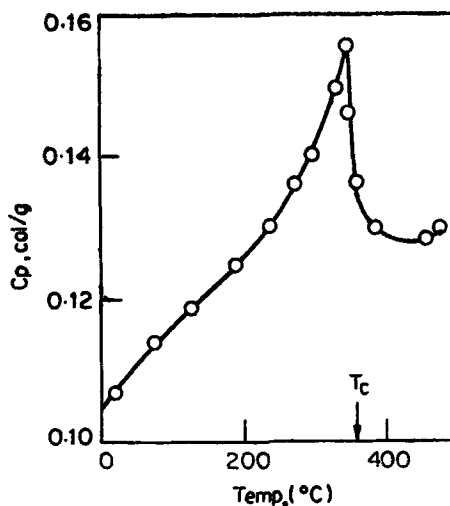


Figure 2. The variation in the specific heat c_p of nickel through the Curie temperature T_c .

A second order transition is one in which the Gibbs free energy G and its first derivatives change continuously through the equilibrium transition temperature T_c and pressure P_c . The second derivatives, however, have discontinuities :

$$(\partial^2 G / \partial T^2) = (-\partial S / \partial T)_P = c_p, \quad (3)$$

$$(\partial^2 G / \partial P^2) = (\partial V / \partial P)_T = \chi, \quad (4)$$

$$(\partial^2 G / \partial T \partial P) = (\partial V / \partial T)_P = a_v. \quad (5)$$

These discontinuities represent abrupt changes in specific heat c_p , isothermal compressibility χ and the volume coefficient of thermal expansion a_v . Figure 2 illustrates the variation in specific heat of nickel through the ferromagnetic-paramagnetic transition temperature T_c . The specific heat increases continuously as the temperature increases, reaching a maximum at the critical temperature T_c . On further heating, it falls abruptly to a lower value.

3. General characteristics of first-order transformations

A number of second-order transitions discussed in this meeting involve a change in the vibrational mode or they are electronic transitions. In contrast to this, many first-order transformations require movement of atoms over considerable distances within the solid. Depending on the nature and the extent of such movement, first-order transformations may be classified as follows :

- (i) those involving atom movements over a large number of interatomic distances;
- (ii) those with atom movements over one or two interatomic distances; and
- (iii) those with atom movement over a fraction of an interatomic distance.

The atom movements in the first two categories above are brought about by the process of diffusion. Diffusion is the mass flow process in which the atoms (or molecules) change their positions relative to their neighbours by "random-walk". A net flow occurs, when there is a gradient. This gradient is essentially a free energy gradient that can arise from the superimposition of an electric or magnetic field or a stress field. In many metallurgical transformations, the gradient arises from the variation in concentration of an atomic species within a solid solution or from a free energy difference on the two sides of an interface.

In the first category above, where the atoms move over a large number of interatomic distances, the process is called long-range diffusion. When the atom movement is over one or two interatomic distances, the process is known as short-range diffusion. In the last category, where the atom displacement is only over a fraction of the interatomic distance, the process is a deformation or distortion (shear or dilatation or both).

A homogeneous transformation occurs simultaneously in all parts of the assembly. A heterogeneous transformation starts from tiny regions in the parent phase in the form of nuclei and these nuclei in turn grow into larger regions of the product phase by the outward movement of the interface that separates the nucleus and the parent phase. Figure 3 illustrates the difference between two transformations, both requiring long-range diffusion, but one occurring homogeneously and the other heterogeneously. In the homogeneous case, the transformation starts as a small composition fluctuation about the mean composition c_m spread over a large volume of the material. Initially, there is no sharp boundary between the parent and the product phases. The composition fluctuation grows in intensity with time to yield finally the equilibrium phases of composition c_p and c_a . In the heterogeneous case, small particles or nuclei of the same composition as the product phase c_p first form. A sharp boundary separates the particle and the parent phase. The particle grows until the composition of the parent phase falls to the equilibrium value c_a .

It is tempting to associate transformations that involve changes in the vibrational mode or electronic rearrangements, which can occur very rapidly, with second-order and those that need the relatively slow movement of atoms by diffusion with the first order. Such a classification is largely true; however, there are exceptions to this. For example, the martensitic transformation in steels, which occurs very rapidly by a shear mechanism, is of the first order, involving nucleation and growth. Other transformations having the characteristics of martensitic transformations are

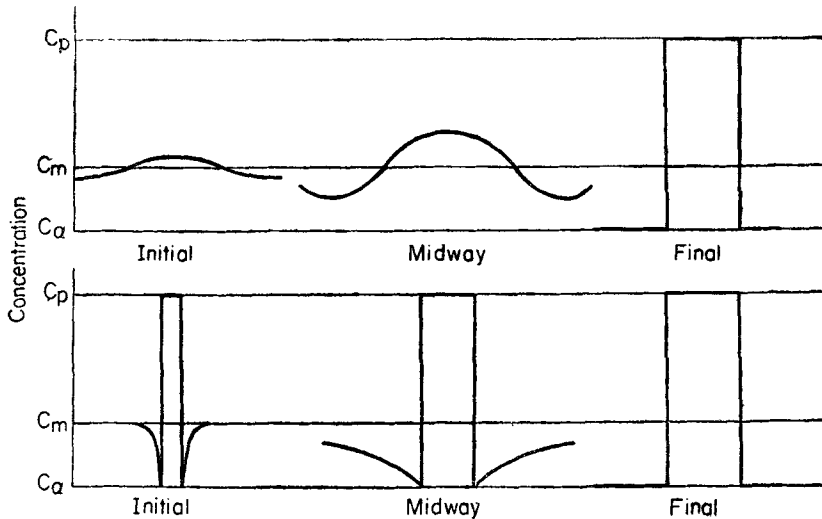


Figure 3. Comparison of a homogeneous and a heterogeneous transformation.

known to be of the second order. Another exception is the spinodal decomposition, which requires long-range diffusion, but is a second-order transformation occurring homogeneously.

In transformations where atom movement is appreciable, elastic strain energy may play an important role in the transformation process. The volume change or the shape change that may accompany a transformation has to be accommodated in the form of elastic strains (or plastic deformation) in the product phase and the matrix. When large strains are involved, considerable hysteresis effects may occur. For example, in the martensitic transformation in steels, a shape strain of 0.2 is to be accommodated elastically and this gives rise to a temperature hysteresis of several hundred degrees between the forward and the reverse transformations.

In addition, a sharp interface between the parent and product phases in the nucleation-and-growth type transformations has a surface energy. If there is a one-to-one correspondence in atom positions on either side of an interface, it is said to be coherent and has a low energy in the range of 5–25 erg/cm². If there is no correlation whatever between the atom positions on the two sides of the interface, the boundary is incoherent with a high energy, about 500 erg/cm². Intermediate interfacial structures are also known exhibiting partial coherency and are called semicoherent interfaces. The interfacial energy plays an inhibiting role on the transformation especially in the nucleation stage.

4. First-order transformations occurring by long-range diffusion

In many metallurgical transformations, a single phase decomposes into two phases of differing composition and crystal structure. The eutectoidal transformation in steels belongs to this category. Austenite, the high temperature FCC solid solution

of carbon in iron, decomposes below the eutectoid temperature into ferrite, a BCC solid solution with a greatly reduced solubility for carbon, and cementite (Fe_3C):

austenite	→	ferrite	+	cementite
FCC		BCC		orthorhombic
0.8% C		0.02% C		6.67% C

The initial uniform carbon content of 0.8% is redistributed during the transformation to 0.02% in ferrite and 6.67% in cementite. Such redistribution requires the long-range diffusion of carbon. The carbon may diffuse either through the austenite ahead of the advancing interface or along the interface itself. The product nuclei grow in the form of a colony, with alternate lamellae of ferrite and cementite, as sketched in figure 4. Such a morphology indicates that the diffusion direction is perpendicular to the lamellae and is about half of the width of a pair of platelets. Depending on the temperature of the transformation, the width of a pair of lamellae varies from about 1 μm to 0.1 μm . Thus the carbon diffusion distance is hundreds or thousands of interatomic spacings. The kinetics of the transformation as a whole is controlled by the rate at which the carbon can diffuse and bring about the required redistribution. Once the nucleation has occurred, all other steps in the transformation process such as the reshuffling of atoms to bring about the new crystal structure in the ferrite and the cementite regions are faster than the diffusion process.

The eutectoidal transformation in steels described above belongs to the category called discontinuous precipitation. Continuous precipitation is the process in which precipitates of a different crystal structure from the matrix, usually richer in solute, form by the depletion of the solute in the matrix. This kind of precipitation occurs in several aluminium alloys of commercial importance. The formation of CuAl_2 precipitates in duralumin, an alloy of Al with about 4.5% copper, is an example:

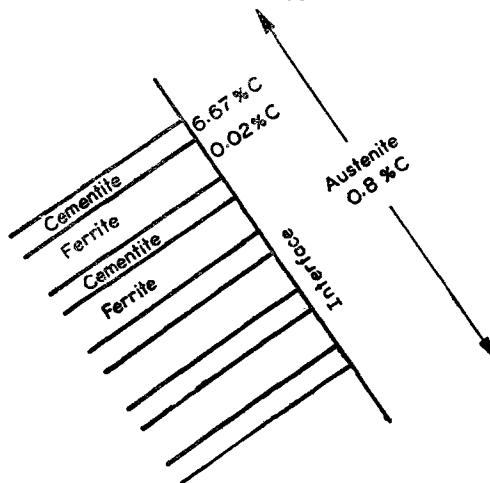
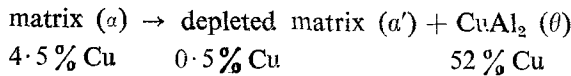


Figure 4. Austenite of 0.8% carbon transforms to alternate lamellae of ferrite (0.02% C and cementite (6.67% C) by long-range diffusion of carbon.

Long-range diffusion of solute atoms controls the transformation process. The concentration gradient required for diffusion is obtained by the composition profile that arises during the transformation, figure 5. At the interface between CuAl_2 and the matrix, local equilibrium is assumed to exist, i.e., the matrix of 0.5% copper is in contact with CuAl_2 of 52% copper. Copper atoms diffuse down the concentration gradient in the matrix that results from the local equilibrium at the interface. The rate of growth of a spherical precipitate particle of radius r with time t is given by

$$dr/dt = D_a (c_a - c_{a'})/r (c_\theta - c_{a'}), \quad (6)$$

where D_a is the diffusion coefficient of copper atoms in the matrix (a) and c is the concentration of copper atoms, with the subscripts indicating the appropriate values.

5. First-order transformations requiring short-range diffusion

In transformations which do not require a change in composition, nucleation and growth can occur by short-range diffusion with the transfer of atoms across the free energy gradient that exists at the interface. Many polymorphic transformations in metals are of this type. The new crystal nucleates as discrete particles in the matrix and has an incoherent interface with the matrix. The movement of the interface is brought by atom diffusion across the interface over a distance of one or two interatomic distances. Once nucleation has occurred, further growth is controlled by the kinetics of this short-range diffusion. The rate of growth of a spherical particle of radius r with time t is given by

$$dr/dt = \lambda v \exp(-Q/kT) [1 - \exp(\Delta g/kT)] \quad (7)$$

where λ is the jump distance, v is the lattice vibration frequency, Q is the activation energy for the jump and Δg is the free energy change per atom as the jump is executed.

If the cooling rate is very rapid, there is insufficient time even for short-range diffusion. Under such circumstances, a polymorphic transformation in metals can occur by a martensitic mechanism. Many polymorphic transformations in

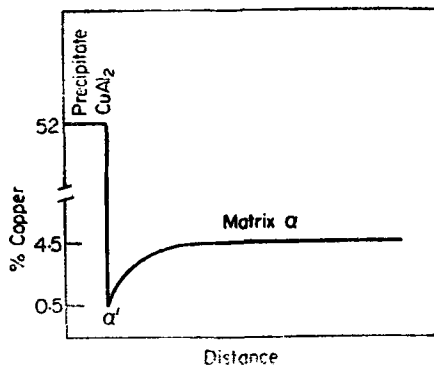


Figure 5. Composition profile arising during the growth of a CuAl_2 particle by continuous precipitation from a duralumin matrix.

compounds such as NaCl are also of the martensitic type (displacive transformations), discussed below.

6. Martensitic transformations

Atom movement over only a fraction of an interatomic distance implies that neighbours remain neighbours even after the transformation. Such a transformation cannot occur in an uncoordinated fashion that is characteristic of the "random-walk" diffusion process. In order to generate the product crystal structure, the atomic movements have to be coordinated or should be the "military type". When a steel is rapidly cooled (quenched), there is no time for the relatively slow process of diffusion to take place and to bring about the compositional changes indicated by the eutectoidal reaction. The austenite shears into a new crystal structure called martensite. There is no diffusion involved, either the short range or the long-range type. Such a shear transformation is called a martensitic transformation. The mechanism of this transformation has acquired a general meaning to cover all transformations that have the same essential characteristics.

In martensitic transformations, there is a correspondence between the crystal directions and planes of the parent and product crystal structures. The lattice correspondence between the FCC austenite and the BCT martensite in steels is illustrated in figure 6. A BCT unit cell is outlined within two adjacent unit cells of FCC

The corresponding crystal directions are :

$$[110] \text{ austenite} \rightarrow [010] \text{ martensite}$$

$$[\bar{1}\bar{1}0] \text{ austenite} \rightarrow [100] \text{ martensite}$$

$$[001] \text{ austenite} \rightarrow [001] \text{ martensite}$$

A similar correspondence between crystal planes in the two lattices can be inferred from figure 6.

The transformation is brought about by simply altering the dimensions of the outlined BCT cell (figure 6). Before the transformation, the axial ratio c/a of the BCT structure is $\sqrt{2}$. This ratio decreases, as the deformation occurs. The c axis contracts by about 20% and the a' axes expand by about 12%, to yield an axial

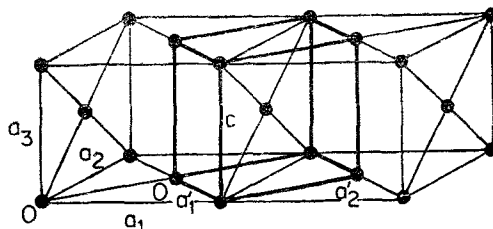


Figure 6. The lattice correspondence between FCC austenite and BCT martensite, a_1 , a_2 and a_3 are the axes of the cubic unit cell and a'_1 , a'_2 and c are the axes of the tetragonal cell. (For clarity, the atoms on the front and back face centres are not shown).

ratio slightly greater than unity, which is characteristic of the martensitic phase. This deformation is known as the Bain strain B .

In addition to the Bain deformation, another important condition still remains to be satisfied. The two crystal structures must be matched at the common interface without building up an unduly high elastic strain energy in the material. Then only the plate-like particle of martensite can grow into the austenite at very high speeds approaching the speed of sound in the solid, as is found experimentally. This requires that the interface plane called the habit plane remains undistorted and unrotated during the transformation. Using this criterion and the lattice correspondence, it is possible to predict the indices of the habit plane.

The classical theories of martensite crystallography are those due to Weschler *et al* (1953) and Bowles and Mackenzie (1954). The elements of these theories, which are essentially equivalent, are the following : The Bain strain B , with the minimum atomic displacements, converts the austenite lattice into the martensite lattice. A second shear ensures that the distortions on the habit plane introduced, by the Bain strain, are removed in a macroscopic sense. The second shear is called the lattice invariant shear P , as it does not change the lattice. It, however, introduces fine twins in the transformation product or slip dislocations at the interface. The rotation effect of the Bain strain on the habit plane is nullified by a third operation which is a rigid body rotation R . These three operations together constitute an invariant plane strain S :

$$S = RBP. \quad (8)$$

Some ferroelectric transitions are known to be of the martensitic type (DiDomenico and Wemple 1967). The atom displacements in ferroelectric transformations are usually smaller than those in the steel transformation. Also, some of them are clearly second order. Participants in this meeting may find it worthwhile to devote some of their attention to the martensitic transformations.

7. Conclusions

- (i) Thermodynamic parameters can be used to distinguish between first-order and second-order transformations.
- (ii) Many metallurgical transformations are first-order. They have typical characteristics such as being the nucleation-and-growth type, having appreciable strain energy generated during the transformation and having a sharp interface between parent and product phases.
- (iii) Transformations that occur with a compositional change require long-range diffusion for the process to occur.
- (iv) Many polymorphic transformations in metals are of the nucleation-and-growth type, with an incoherent interface separating the parent and product phases and requiring short-range diffusion of atoms across the interface.
- (v) Coordinated movements of atoms (unlike in diffusion) characterise a martensitic transformation. The high speed with which interfaces move in martensitic transformations have led to the concept of an invariant plane strain. Ferroelectric transitions and polymorphic transitions in compounds such as NaCl are of the martensitic type.

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