Spinodal Structures

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Spinodal structures are fine-scale, homogenous two-phase mixtures 
resulting from a phase separation that takes 
place under certain conditions of temperature and composition. The conjugate phases 
produced by the spinodal decomposition of a 
supersaturated solid solution differ in composition 
from the parent phase, but have 
especially the same crystal structure. Precipitation 
by spinodal decomposition may occur 
in conjunction with an ordering reaction, as 
discussed below.

The simplest phase transformation that 
can produce a spinodal reaction product is 
decomposition within a stable or metastable 
miscibility gap, as shown in Fig. 1. If a solid 
solution of composition $C_0$ is solution 
treated in the single-phase field at a temperature $T_0$ 
then aged at an intermediate temperature $T_A$ 
(or $T_A$), the single-phase alloy tends to separa-
rate into a two-phase mixture. At the tem-
perature $T_A$, the compositions of the conjugate 
phases $n_1$ and $n_2$ under equilibrium conditions 
are $C_1$ and $C_2$, respectively. However, 
the supersaturated solid solution may decom-
pose into two phases along two different reaction 
paths.

At small undercoolings or low supersatura-
tions ($T_A$), the solution is metastable; appearance 
of a second phase requires relatively largelocalized composition fluctuations. This is 
the classical nucleation process, giving rise 
to "critical nucleus," which can grow sponta-
eously. As the particles of the new phase 
grow by diffusion, the matrix composition 
adjusts toward equilibrium. At large supersa-
trations ($T_A$), the solution is unstable, and 
the two-phase mixture gradually emerges by 
the continuous growth of initially small am-
plitude fluctuations (see Fig. 2). The rate of 
reaction is controlled by the rate of atomic 
migration and the diffusion distances in-
volved, which depend on the scale of decom-
position (undercooling). Therefore, spinodal 
structures refer to phase mixtures that derive 
from a particular kinetic process governing 
the initial stages of phase separation. The 
"spinodal line" shown in Fig. 1 is not a phase 
boundary but a demarcation indicating a differ-
ence in thermodynamic stability.

![Fig. 1 Schematic showing miscibility gap in the solid state and spinodal lines (chemical and coherent)](image)

Theory of Spinodal Reactions

The spinodal reaction is a spontaneous un-
mixing or diffusional clustering distinct from 
classical nucleation and growth in metastable 
solutions. This different kinetic behavior, 
which does not require a nucleation step, was 
first described by Gibbs in his treatment of 
the thermodynamic stability of undercooled 
or supersaturated phases. The spinodal line 
in Fig. 1 indicates a limit of metastability 
with respect to the response of the system to 
compositional fluctuations. The locus, called 
the "chemical spinodal," is defined by the in-
flexion points of the isothermal free energy 
($G$) composition curves ($\partial^2G/\partial C^2 = 0$). 
Within the spinodes where $\partial^2G/\partial C^2 < 0$, the 
supersaturated solution is unstable and spin-
oidal decomposition can occur. Spinodal de-
composition or continuous phase separation 
involves the selective amplification of long 
wave-length concentration waves within the 
supersaturated state resulting from random 
fluctuations. The transformation occurs 
homogeneously throughout the alloy via the 
gradual buildup of regions enriched in solute, 
resulting in a two-phase modulated structure. 
The continuous amplification of a quasi-
sinusoidal fluctuation depicted in Fig. 2 is 
rather general, because this sinusoidal com-
position wave may be viewed as a Fourier 
component of an arbitrary composition vari-
ation that grows preferentially.

The essential features of the spinodal pro-
cess can be understood by considering this 
diffusional clustering as the inverse of the ho-
mogenization of a nonuniform solid solution 
exhibiting a sinusoidal variation of composi-
tion with distance. In metastable solutions, 
the small deviations from the average concen-
tration, $C_0$, will decay with time according to 
the equation $\Delta C = \Delta C_0 \exp (-t/\tau)$, where

![Fig. 2 Schematic illustrating two sequences for the formation of a two-phase mixture by diffusion processes: nucleation and growth and spinodal decomposition. (Ref 1)](image)
the relaxation time \( \tau \approx \lambda^2 / D \); \( \lambda \) is the wavelength of the fluctuation and \( D \) is the appropriate diffusion coefficient. In a binary system \( D \propto \partial G / \partial C^2 \), and within the spinodes \( \partial G / \partial C < 0 \); that is, the curvature of the free energy-composition curve is negative. Therefore, in an unstable solid solution \( D \) is negative, and “uphill” diffusion occurs. The amplitude of the concentration wave grows with time, that is, \( \Delta C = \Delta C_0 \exp (+R(\beta) \tau) \), where the amplification factor \( R(\beta) \) is a function of the wave number \( \beta = 2\pi / \lambda \). The factor \( R(\beta) \) is a maximum for intermediate wavelengths. Long wavelength fluctuations grow sluggish because of the large diffusion distances; short wavelength fluctuations are suppressed by the so-called gradient or surface energy of the diffuse or incipient interfaces that evolve during phase separation. Therefore, the microstructure that develops during spinodal decomposition has a characteristic periodicity that is typically 2.5 to 10 nm (25 to 100 Å) in metallic systems.

The factors controlling the spinodal reaction and resultant structures are clarified by examining the energetics of small-amplitude fluctuations in solid solutions. The free energy of an inhomogenous solution expressed as an integral over the volume, \( V \), of the crystal can be written as:

\[
G = \int \left( f(C) + K \nabla C^2 + E_0 \right) dV
\]

where \( f(C) \) is the free energy per unit volume of a uniform solution of composition \( C \), \( K \) is the gradient energy parameter, and \( E_0 \) is a strain energy term that depends on the elastic constants and misfit (difference in lattice parameter) between the solute-enriched and solute-depleted regions. For a sinusoidal composition fluctuation \( C = C_0 \sin \beta x \) (where \( \lambda \) is the amplitude of the sine wave), the gradient or surface energy term varies as \( K \beta^2 \) and prohibits decomposition on a finite scale. The wavelength of the dominant concentration wave that essentially determines the scale of decomposition varies as

\[ K^{1/2}(\Delta T)^{-1/2}, \] where \( \Delta T = T_S - T_S \) in which \( T_S \) is the spinodal temperature. The coherency strain energy term is independent of wavelength, but can vary markedly with crystallographic direction in elastically anisotropic crystals. Therefore, the dominant concentration waves will develop along elastically “soft” directions in anisotropic systems. For most cubic materials, the \( \langle 100 \rangle \) directions are preferred, although \( \langle 111 \rangle \) waves are predicted in certain alloys, depending on the so-called anisotropy factor. The strain energy can also stabilize the system against decomposition and effectively displaces the spinodal curve (and the solvus), thus defining a “coherent spinodal” (Fig. 1).

Periodic composition fluctuations in the decomposing solid solution cause diffraction effects known as “satellites” or “sidebands.” The fundamental reflections in reciprocal space are flanked by satellites or secondary maxima, and the distance of the satellites from the fundamental varies inversely with the wavelength of the growing concentration wave. This diffuse scattering arises from the periodic variation of the lattice parameter and/or scattering factor. The strain effects are negligible around the origin of reciprocal space. Small-angle x-ray and neutron scattering can be used to study quantitatively the kinetics of the reaction by monitoring the changes in the intensity distribution around the direct beam due to changes in the structure factor modulations. The electron diffraction pattern of a spinodally decomposed copper-titanium alloy shown in Fig. 3 reveals the dominant \( \langle 100 \rangle \) concentration waves that develop during the early stages of phase separation.

Microstructure

If the strain energy term in the free energy expression is negligible (small misfit) or if the elastic modulus is isotropic, the resultant microstructure will be isotropic, similar to the morphologies evolving in phase-separated glasses. In Fig. 4, an isotropic spinodal structure developed in a phase-separated iron-chromium-cobalt permanent magnet alloy is clearly revealed by transmission electron microscopy. The two-phase mixture is interconnected in three dimensions and exhibits no directionality. The microstructure is comparable to the computer simulation of an isotropically decomposed alloy shown in Fig. 5 (Ref 1).

Fig. 5 Computer simulation of an isotropically decomposed microstructure. (J.W. Cahn and M.K. Miller)

Fig. 6 Spinodal microstructure in a 51.5Cu-32.5Ni-15Fe (at.%) alloy aged 15 min at 775°C (1425 °F) revealed by transmission electron microscopy. Foil normal is approximate [001], and the orientation angle along the [100] microdirections is apparent. The wavelength of the modulated structure is approximately 25 nm (250 Å). 70000X. (G. Thomas)
supersaturated phase spinodally decomposes into two phases, one or both of which are ordered. A transmission electron micrograph of a spinodally decomposed iron-beryllium alloy is shown in Fig. 8, and a corresponding field-ion micrograph is shown in Fig. 9. The brightly imaged phase in the electron micrograph (Fig. 8) is the ordered phase (B2 superstructure), whereas the brightly imaged phase in the field-ion micrograph (Fig. 9) is the iron-rich disordered phase. The microstructure is periodic and aligned along the “soft” (100) directions.

The spinodal mechanism provides an important mode of transformation, producing uniform, fine-scale, two-phase mixtures that can enhance the physical and mechanical properties of commercial alloys. Spinodal decomposition has been particularly useful in the production of permanent magnet materials, because the morphologies favor high coercivities. The structure can be optimized by thermomechanical processing, step aging, and magnetic aging. Continuous phase separation or spinodal decomposition appears to be important in the classic Alnicos and copper-nickel-iron alloys, as well as in the newly developed iron-chromium-cobalt materials.

REFERENCES


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