

# 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 essentially the same crystal structure. Precipitation by spinodal decomposition may occur in conjunction with an ordering reaction, as discussed below.

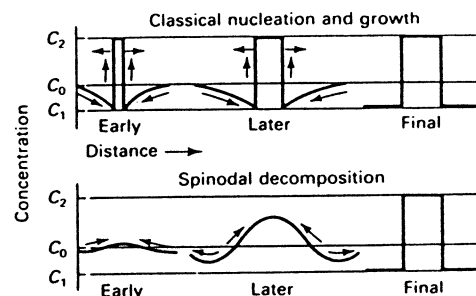
The simplest phase transformation that can produce a spinodal reaction product is decomposition within a stable or metastable miscibility gap, as shown in Fig. 1. If a solid solution of composition  $C_0$  is solution treated in the single-phase field at a temperature  $T_0$ , then aged at an intermediate temperature  $T_A$  (or  $T_A$ ), the single-phase alloy tends to separate into a two-phase mixture. At the temperature  $T_A$ , the compositions of the conjugate phases  $\alpha_1$  and  $\alpha_2$  under equilibrium conditions are  $C_1$  and  $C_2$ , respectively. However,

the supersaturated solid solution may decompose into two phases along two different reaction paths.

At small undercoolings or low supersaturations ( $T_A$ ), the solution is metastable; appearance of a second phase requires relatively large localized composition fluctuations. This is the classical nucleation process, giving rise to "critical nuclei," which can grow spontaneously. As the particles of the new phase grow by diffusion, the matrix composition adjusts toward equilibrium. At large supersaturations ( $T_A$ ), the solution is unstable, and the two-phase mixture gradually emerges by the continuous growth of initially small amplitude fluctuations (see Fig. 2). The rate of reaction is controlled by the rate of atomic migration and the diffusion distances involved, which depend on the scale of decomposition (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 difference in thermodynamic stability.

## Theory of Spinodal Reactions

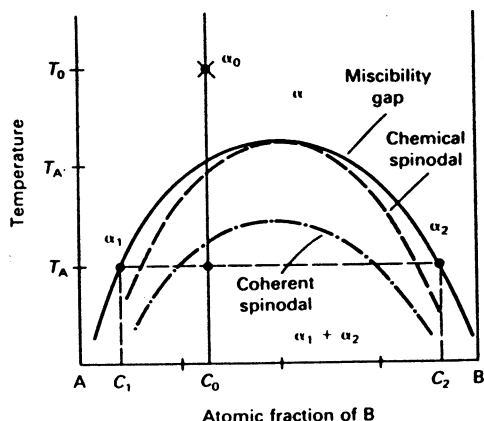
The spinodal reaction is a spontaneous unmixing or diffusional clustering distinct from classical nucleation and growth in metastable solutions. This different kinetic behavior, which does not require a nucleation step, was first described by Gibbs in his treatment of the thermodynamic stability of undercooled 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-



**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)

flexion points of the isothermal free energy ( $G$ ) composition curves ( $\partial^2 G / \partial C^2 = 0$ ). Within the spinodes where  $\partial^2 G / \partial C^2 < 0$ , the supersaturated solution is unstable and spinodal decomposition can occur. Spinodal decomposition or continuous phase separation involves the selective amplification of long wavelength 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 composition wave may be viewed as a Fourier component of an arbitrary composition variation that grows preferentially.

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



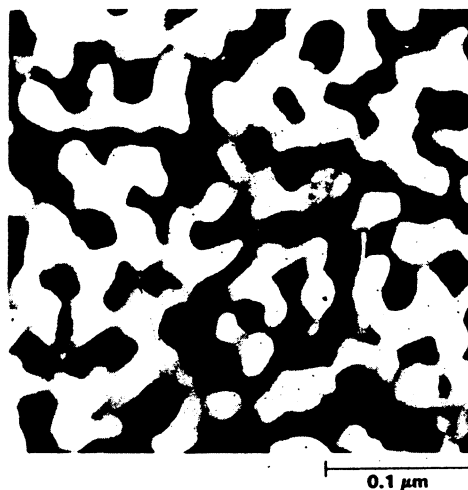
**Fig. 1** Schematic showing miscibility gap in the solid state and spinodal lines (chemical and coherent)

the relaxation time  $\tau \approx \lambda^2/\bar{D}$ ;  $\lambda$  is the wavelength of the fluctuation and  $\bar{D}$  is the appropriate diffusion coefficient. In a binary system  $\bar{D} \propto \partial^2 G/\partial C^2$ , and within the spinodes  $\partial^2 G/\partial C^2 < 0$ ; that is, the curvature of the free energy-composition curve is negative. Therefore, in an unstable solid solution  $\bar{D}$  is negative, and "uphill" diffusion occurs. The amplitude of the concentration wave grows with time, that is,  $\Delta C = \Delta C_0 \exp(+R(\beta)t)$ , 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 sluggishly 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 inhomogeneous solution expressed as an integral over the volume,  $V$ , of the crystal can be written as:

$$G = \int \{f(C) + K \nabla^2 C + E_s\} dV$$

where  $f(C)$  is the free energy per unit volume of a uniform solution of composition  $C$ ,  $K$  is the gradient energy parameter, and  $E_s$  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  $C - C_0 = A \sin \beta x$  (where  $A$  is the amplitude of the sine wave), the gradient or surface energy term varies as  $K\beta^2$  and prohibits decomposition on a fine scale. The wavelength of the dominant concentration wave that essentially determines the scale of decomposition varies as



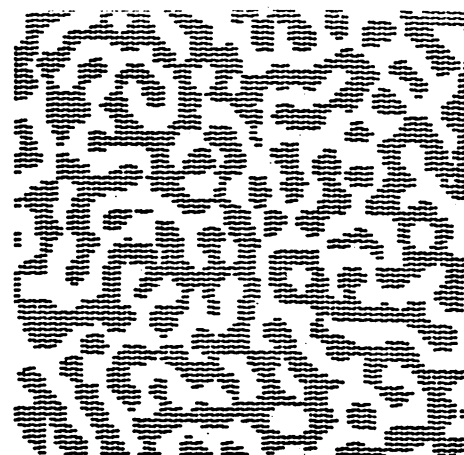
**Fig. 4** Transmission electron micrograph of isotropic spinodal structure developed in Fe-28.5Cr-10.6Co (wt%) alloy aged 4 h at 600 °C (1110 °F). Contrast derives mainly from structure-factor differences. 225 000 $\times$ . (A. Zellser)

$K^{1/2}(\Delta T)^{-1/2}$ , where  $\Delta T = T_s - T_A$ , 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 displace 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

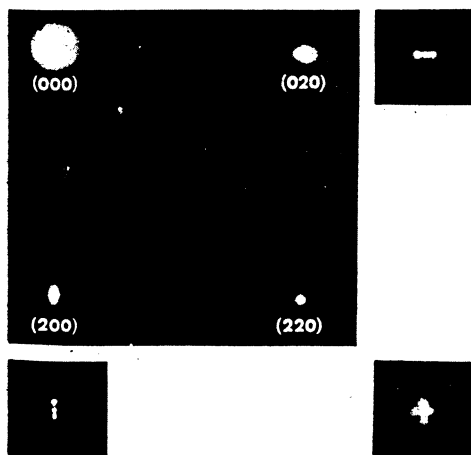
If the strain energy term in the free energy expression is negligible (small misfit) or if the elastic modulus is isotropic, the resultant mi-



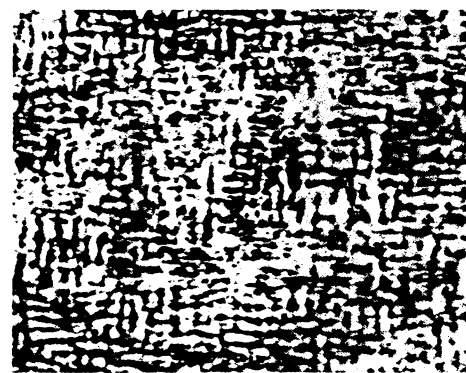
**Fig. 5** Computer simulation of an isotropically decomposed microstructure. (J.W. Cahn and M.K. Miller)

crostructure 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). In Fig. 6, the dominant composition waves have developed preferentially along the  $\langle 100 \rangle$  matrix directions to produce an aligned modulated structure in a copper-nickel-iron alloy. Because the homogeneous phase separation process is relatively structure-insensitive, the spinodal product is generally uniform within the grains up to the grain boundaries, as revealed in the copper-nickel-chromium spinodal alloy shown in Fig. 7.

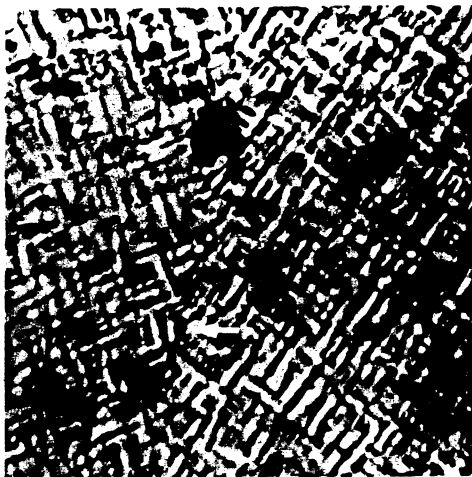
Atomic ordering and spinodal clustering can occur concomitantly in a precipitation system (see Ref 2 for a review of ordering and spinodal decomposition). In these systems, a



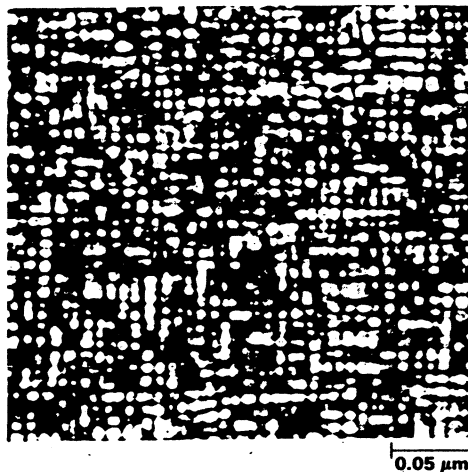
**Fig. 3** [001] electron diffraction pattern from spinodally decomposed Cu-4Ti (wt%) alloy aged 100 min at 400 °C (750 °F) showing satellites flanking the matrix reflections. (A. Datta)



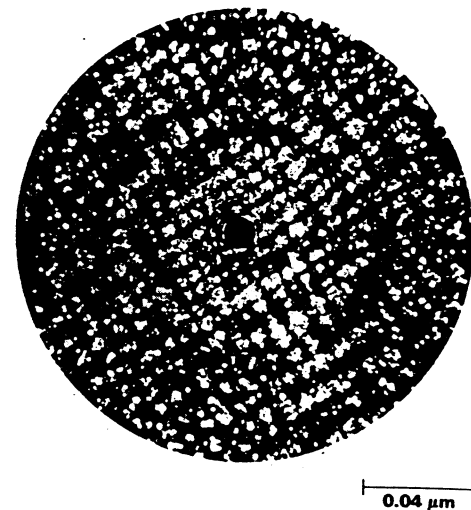
**Fig. 6** Spinodal microstructure in a 51.5Cu-33.5Ni-15Fe (at.%) alloy aged 15 min at 775 °C (1425 °F) revealed by transmission electron microscopy. Foil normal is approximately [001], and the alignment along the  $\langle 100 \rangle$  matrix directions is apparent. The wavelength of the modulated structure is approximately 25 nm (250 Å). 70 000 $\times$ . (G. Thomas)



**Fig. 7** Transmission electron micrograph of spinodal microstructure developed in a 66.3Cu-30Ni-2.8Cr (wt%) alloy during slow cooling from 950 °C (1740 °F). The microstructure is homogeneous up to the grain boundary indicated by the arrow. 35 000 $\times$ . (F.A. Badia)



**Fig. 8** Spinodal structure aligned along  $\langle 100 \rangle$  directions of decomposed Fe-25Be (at.%) alloy aged 2 h at 400 °C (750 °F). The bright phase is the Be-enriched ordered B2 structure revealed by dark-field imaging using a superlattice reflection; the dark phase is the Fe-rich disordered (or weakly ordered) transformation product. The TEM foil normal is approximately  $[001]$ . 200 000 $\times$ . (M.G. Burke)



**Fig. 9** Field-ion micrograph of spinodally decomposed Fe-25Be (at.%) alloy aged 20 min at 400 °C (750 °F). The axis of the needle-like specimen is  $[001]$ . The iron-rich phase images brightly because of the different contrast mechanism operating in the field-ion microscope. 375 000 $\times$ . (M.K. Miller)

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"  $\langle 100 \rangle$  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.

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