

## Early Stage of Phase-Separation Processes in FeCr and AlZn Alloys

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Phase-separation processes in FeCr and AlZn alloys were studied by a small-angle scattering instrument installed at the KENS pulsed neutron source. Two stages were found in the decomposition process. In the late stage, after annealing time  $t$ , dynamical scaling holds for the scattering function  $S(q, t)$  which exhibits  $q^{-4}$  dependence for high  $q$  values. At the earlier stage  $S(q, t)$  cannot be described by the same scaling law, and  $q^{-2}$  dependence appears at high  $q$ . This relation can be well described by the nonlinear theory of Langer, Bar-on, and Miller.

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The kinetics of the phase separation of solid mixtures quenched into the miscibility gap is the subject of many theoretical and experimental investigations as a typical example of nonequilibrium phenomena.<sup>1-9</sup> Recent interest has been focused on the dynamical scaling behavior in the late stage of the process. Marro, Lebowitz, and Kalos<sup>5</sup> and Furukawa<sup>6</sup> pointed out independently that the scattering function  $S(q, t)$  in the late stage, after annealing time  $t$ , can be scaled as

$$F(q/q_1) = q_1^3 S(q, t), \quad (1)$$

where  $q_1$  is the first moment of the scattering function. Such a scaling has been found to hold in actual phase-separation processes in liquid mixtures,<sup>10</sup> a glass system,<sup>11</sup> and a number of binary alloys.<sup>12-15</sup> It has also been found that  $S(q, t)$  in this stage satisfies the Porod law;  $q^{-4}$  dependence for larger  $q$  values, corresponding to the situation that in this stage the precipitates have definite interfaces with the matrix.

The very early stage of the phase-separation process has also been studied extensively, because it is this stage where the most typical characteristics of spinodal decomposition—homogeneous buildup of fluctuations—should appear. Although many efforts have been made to verify Cahn's linear theory of spinodal decomposition,<sup>1</sup> no definitive experimental results have ever been provided to support the theory. Cahn's theory was improved by Cook<sup>2</sup> and Langer, Bar-on, and Miller (LBM)<sup>3</sup> to include the effects of thermal fluctuations and higher-order (nonlinear) terms, respectively, and a part of the discrepancy between the theory and observations was removed.<sup>3</sup> The nonlinear theory also gave reasonable agreement with Monte Carlo simulation calculations.<sup>16</sup> Critical comparison of the theory and observations is, however, not easy for the early stage, partly because of the experimental difficulty in distinguishing this stage from the late stage. Furthermore, the measurements should be extended over a wide range of  $q$  values because of the spreading of the fluctuations in this stage. One such wide- $q$  measurement was carried out by Spooner,<sup>17</sup> by changing the sample-to-detector distance. In his report, an early stage when the scaling

law does not hold is pointed out, but only a qualitative discussion is provided.

We have installed a neutron small-angle scattering instrument SAN<sup>18</sup> at the KENS spallation neutron source, which enables us to make simultaneous measurements of small-angle scattering over a  $q$  range more than twice as wide as conventional spectrometers. This paper provides the experimental results for our distinguishing the early stage of the phase-separation process from the late ones. The experiments have been performed for FeCr and AlZn alloys, both of which are known as ideal alloys for the study of the spinodal decomposition because of the small elastic strains involved in the separation process. The FeCr alloys are particularly suitable for the study of the very early stage because the diffusion rate is rather low compared with the AlZn alloys. Therefore, the experiments were initiated with FeCr alloys and then extended to AlZn alloys to show the universality of the features. This paper discusses briefly the results obtained for Fe<sub>60</sub>Cr<sub>40</sub> and Al<sub>93.2</sub>Zn<sub>6.8</sub> alloys. The details will be published separately.

The Fe<sub>60</sub>Cr<sub>40</sub> alloy was made from 99.99% materials in an arc furnace and was homogenized at 1000 °C for more than 24 h, followed by a quench in ice water. The sample was then annealed at a temperature  $T_a$  below the spinodal line ( $T_s = 550$  °C), in a tin bath for short periods ( $t < 60$  min) or in an evacuated Pyrex glass in a conventional furnace for longer periods. The variation of scattering functions  $S(q)$  with time of annealing was measured with SAN at room temperature after the sample was quenched in ice water. Scattering functions of the sample annealed for increasing times at 540 °C are presented on a log-log scale in Fig. 1(a), which shows that  $S(q)$  exhibits  $q^{-4}$  dependence for high  $q$  values when the annealing time exceeds 3 h. The scaled functions  $F(q/q_1(t))$  defined by Eq. (1) are plotted against  $q/q_1(t)$  in Fig. 1(b). It is apparent from Figs. 1(a) and 1(b) that the scaling law holds when  $S(q)$  exhibits  $q^{-4}$  dependence at large  $q$ . At shorter annealing times,  $S(q)$  shows  $q^{-2}$  dependence for high  $q$  values, and a clear deviation from the scaling law was also found.

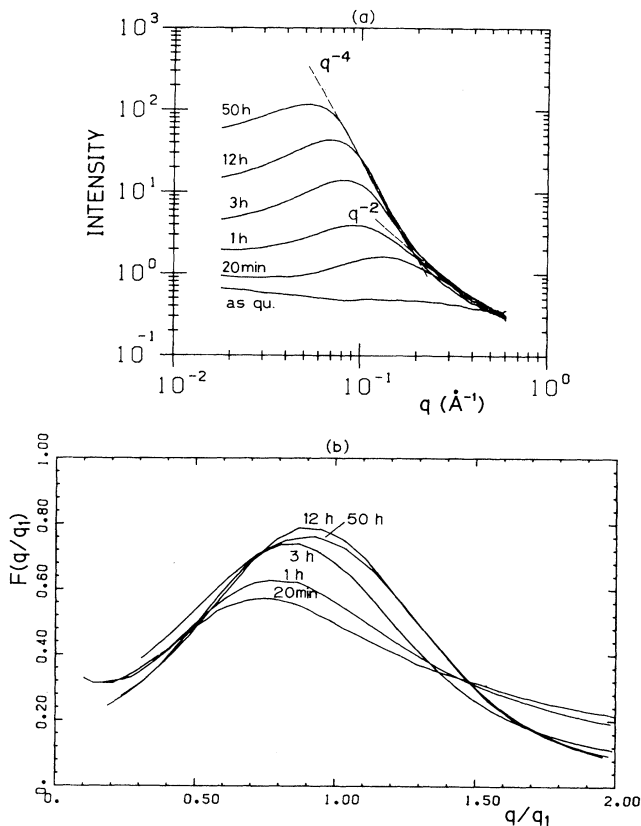


FIG. 1.  $\text{Fe}_{60}\text{Cr}_{40}$ ;  $T_a = 540^\circ\text{C}$ , at the late stage of decomposition. (a) Log-log plot. (b) Scaled function [ $F(q/q_1) = q_1^3 S(q, t)$ ].

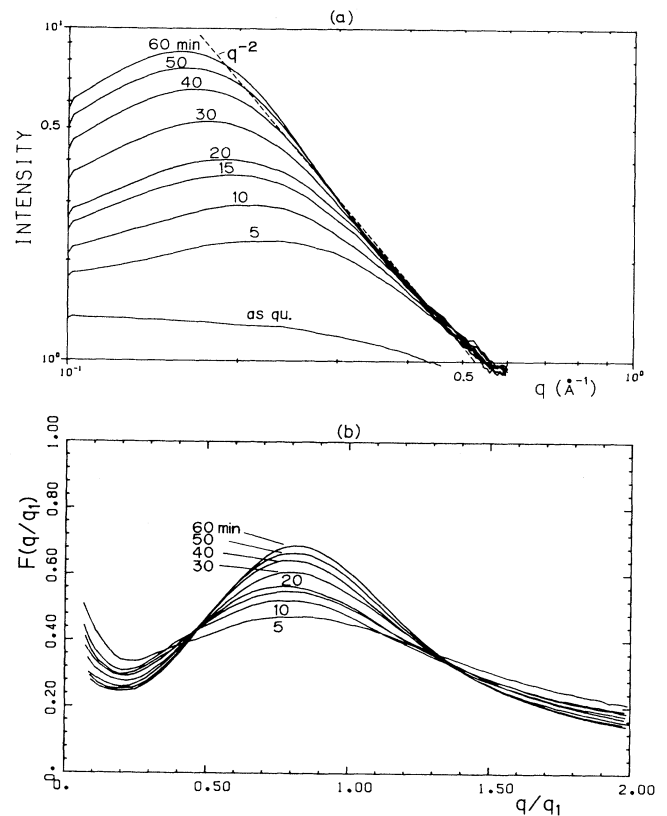


FIG. 2.  $\text{Fe}_{60}\text{Cr}_{40}$ ;  $T_a = 515^\circ\text{C}$ , at the early stage of decomposition. (a) Log-log plot. (b) Scaled function [ $F(q/q_1) = q_1^3 S(q, t)$ ].

The situation is more clearly seen in Fig. 2(a), where log-log plots of the scattering functions are displayed for lower-temperature annealing ( $T_a = 515^\circ\text{C}$ ). The scattering functions for annealing times between 5 and 60 min exhibit a clear  $q^{-2}$  dependence for high  $q$  values, suggesting that the  $q^{-2}$  dependence is a characteristic of the early stage of phase separation. In Fig. 2(b) are plotted the scaled functions  $F(q/q_1)$  against  $q/q_1$ , and they clearly indicate the breakdown of the scaling law of Eq. (1) in this stage.

The AlZn alloys have also been studied extensively as a typical spinodal decomposition system. It has been reported that the dynamical scaling of Eq. (1) really holds in the late stage of phase separation of these alloys.<sup>12-14</sup> In contrast with the FeCr alloys, the phase-separation process of the AlZn alloys occurs quite rapidly even at low temperatures. Therefore, a special furnace was designed which made it possible to anneal the sample *in situ* at a temperature above or below room temperature for a very short time ( $t > 1$  min). This is an image furnace system consisting of two infrared heaters and a nickel-coated parabolic mirror to focus the images of the heaters on the sample.

The sample was cooled rapidly from the annealing temperature to about 100 K by a flash of liquid nitrogen which was poured on the sample through a stainless-steel tube. The maximum cooling rate was  $200^\circ\text{C}/\text{min}$  for a bulk sample, and the neutron scattering measurements were carried out *in situ* at 100 K. The  $\text{Al}_{93.2}\text{Zn}_{6.8}$  sample was made by melting 99.999% materials in an HF furnace and was homogenized at  $400^\circ\text{C}$  for 12 h in the image furnace. The sample was then annealed in the same furnace at a temperature below the reported spinodal line ( $129^\circ\text{C}$ )<sup>19</sup> for a short time, followed by a quench to 100 K for neutron scattering measurements.

The temporal evolution of the scattering functions of the sample annealed at 116 and  $25^\circ\text{C}$  are shown on log-log scales in Figs. 3(a) and 3(b), respectively. The results indicate that  $S(q, t)$  for annealing at  $116^\circ\text{C}$  exhibits the  $q^{-4}$  dependence for high  $q$  values, if the annealing time exceeds 2 min. This suggests that the phase separation at  $116^\circ\text{C}$  is already in the late stage. Corresponding to this situation, the scattering functions for this annealing obey the dynamical scaling as displayed in Fig. 4(a), where the scaled functions  $F(q/q_1)$  are plotted against  $q/q_1$ .

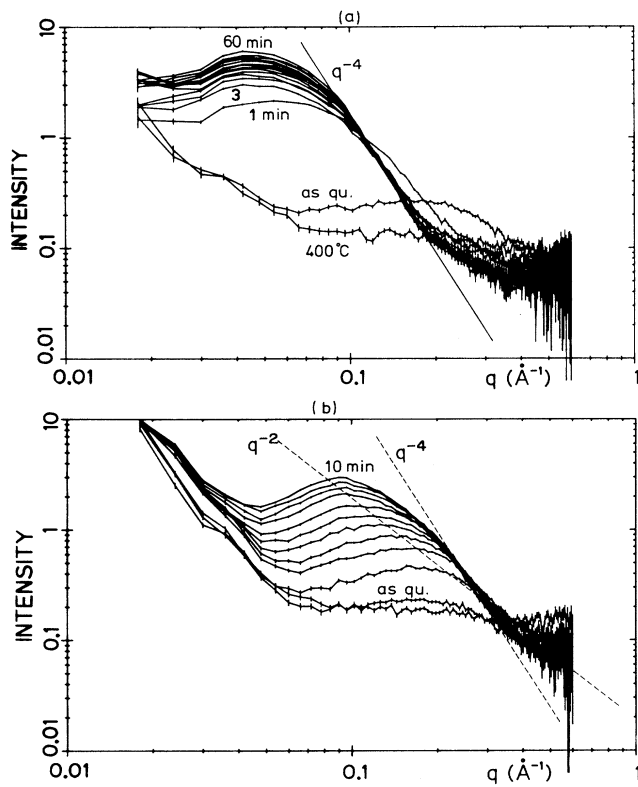


FIG. 3. Scattering function  $S(q,t)$  of  $\text{Al}_{93.2}\text{Zn}_{6.8}$  on a log-log scale, aged at (a)  $116^\circ\text{C}$  and (b)  $25^\circ\text{C}$ .

The situation is more clearly seen for annealing at  $25^\circ\text{C}$ . The dynamical scaling holds only for annealing longer than 7 min as seen in Fig. 4(b), for which the  $q^{-4}$  dependence appears for high  $q$  values [Fig. 3(b)], in good agreement with the results for the  $\text{Fe}_{60}\text{Cr}_{40}$  alloy. Although the  $q^{-2}$  dependence is not so evident for shorter annealing times at  $T_a = 25^\circ\text{C}$ , the scaling law does not hold in this regime. A clear  $q^{-2}$  dependence could be observed for  $T_a = -30^\circ\text{C}$ , indicating that the early stage in  $\text{Al}_{93.2}\text{Zn}_{6.8}$  can be observed only for anneals below room temperature.

The  $q^{-2}$  dependence of the scattering function can be derived directly from the kinetic equation of the LBM nonlinear theory,<sup>3</sup>

$$\partial S(q)/\partial t = -2M\kappa q^2[q^2 + A(t)/\kappa]S(q) + 2Mk_B T q^2, \quad (2)$$

where  $M$  is the mobility and  $\kappa$  is the energy gradient coefficient. The term  $A(t)$  includes both the usual linear and the nonlinear terms. If  $A(t)/\kappa$  is a slowly varying function of time, or if  $q^2$  is much greater than  $A(t)/\kappa$ , the kinetic equation has an approximate solu-

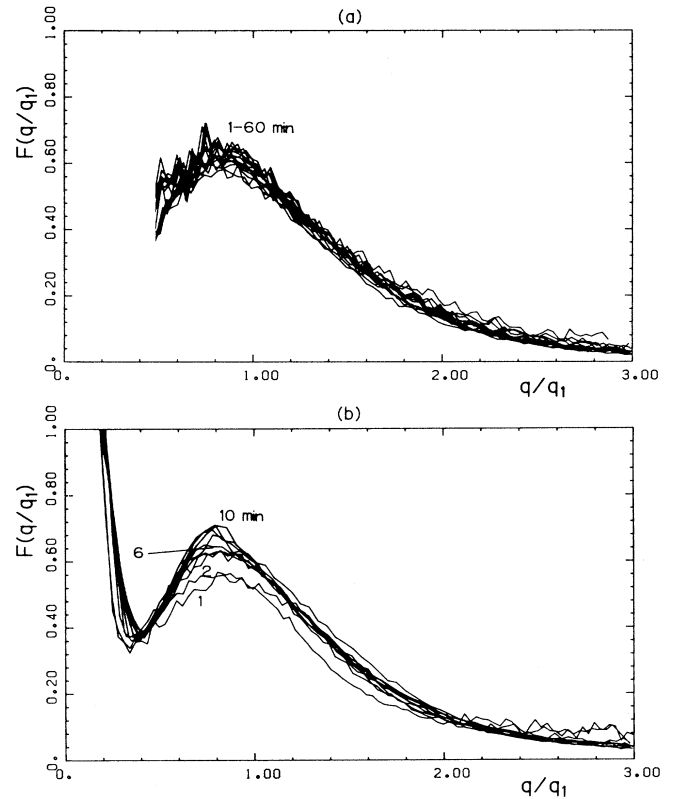


FIG. 4. Scaled function  $[F(q/q_1) = q_1^3 S(q,t)]$  for  $\text{Al}_{93.2}\text{Zn}_{6.8}$ , aged at (a)  $116^\circ\text{C}$  and (b)  $25^\circ\text{C}$ .

tion of the form

$$S(q,t) = [S(q,t=0) - S_{st}(q,t)]\exp(\omega t) + S_{st}(q,t), \quad (3)$$

with

$$\omega(q) = -2M\kappa q^2[q^2 + A(t)/\kappa]. \quad (4)$$

The quasistationary solution  $S_{st}(q,t)$  is given by

$$S_{st}(q,t) = \frac{k_B T/\kappa}{q^2 + A(t)/\kappa}. \quad (5)$$

We have found that the scattering function  $S(q,t)$  of  $\text{Fe}_{60}\text{Cr}_{40}$  annealed at  $500$  and  $515^\circ\text{C}$  (the early stage of phase separation) can be described by Eq. (3) over a wide  $q$  range<sup>20</sup> ( $0.02 \text{ \AA}^{-1} \leq q \leq 0.6 \text{ \AA}^{-1}$ ) with  $A(t)/\kappa$  slowly varying in time. The value  $A(t)/\kappa$  determined experimentally decreases monotonically with time, tending to zero for longer annealing time. This tendency is in good agreement with what the LBM theory predicts.<sup>3</sup> Therefore, the early stage of the phase separation can be well described in terms of the LBM nonlinear theory.

In conclusion, we have found that the early stage of spinodal decomposition can clearly be distinguished from the late stage by its different  $q$  dependence of  $S(q)$  for high  $q$  values. The dynamical scaling holds only for the stage where the  $q^{-4}$  dependence appears and the precipitates have a definite interface with the matrix. We have also shown that the kinetics of spinodal decomposition in the early stage is well described by the LBM nonlinear theory with the  $q^{-2}$  dependence of  $S(q, t)$  for high  $q$  values. The dynamical scaling of Eq. (1) does not hold in this stage which corresponds to the situation that the precipitates are still in the form of composition fluctuations. Finally, we should also remark that none of our results for the very early stage of the phase-separation process exhibits the characteristics of spinodal decomposition predicted by Cahn's linear theory. This is partly because the alloys that we employed have off-critical concentration and the experiments were performed near the spinodal temperature where the nonlinear effect plays a significant role.

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