Crossover Phenomenon in Dynamical Scaling of Phase Separation in Fe-Cr Alloy

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A neutron-scattering study of phase separation in the Fe-Cr alloy system clearly indicates dynamical scaling. The results are compared with the predictions of recent scaling theories. Both the time evolution of the characteristic wave vector and the scaling function of the structure factor show crossover phenomenon. The crossover is attributed to a transition from a coagulation to a condensation process at a late stage of phase separation in alloy systems.

The kinetics of phase separation of quenched alloys in a two-phase region has received great attention from both theoretical and experimental points of view. One of the most significant results is dynamical scaling behavior in the late stages of the process. The idea of the scaling was implicit in the cluster diffusion-reaction theory proposed by Binder and Stauffer[1] and in the condensation theory developed by Lifshitz and Slyozov.[2] Recently the scaling of the structure factor has been discussed by Furukawa in the analysis of the kinetic equation[3,4] and by Marro and co-workers in computer simulations on the spin-exchange model.[5,6] They proposed that the structure factor $S(q,t)$ for an isotropic d-dimensional system obeys the scaling relation

$$S(q,t) = [q_1(t)]^{-d} F[q/q_1(t)], \qquad (1)$$

where the scaling function $F[q/q_1(t)]$ is independent of time. The characteristic wave vector $q_1(t)$, which is in inverse proportion to the average cluster size $R(t)$, shows a simple power law behavior

$$q_1(t) \propto t^{-a}. \qquad (2)$$

The value of the exponent a has been derived by several authors. On the basis of the cluster diffusion-reaction model, Binder and Stauffer,[1] and subsequently Binder,[7] arrived at $a = 1/(d+3)$ for low temperatures, $a = 1/(d+2)$ for intermediate temperatures at intermediate times after the complicated initial stage, and $a = \frac{1}{3}$ for these temperatures at late times. Furukawa predicted $a = 1/(d+2)$ or $1/(d+3)$ according to the different mobility in the analysis of the asymptotic behavior of the kinetic equation.[3,4] From a time-dependent Ginzburg-Landau model, Langer, Bar-on, and Miller obtained $a \simeq 0.2$.[8] Marro and co-workers showed in the computer simulations that the exponent changes from $a \simeq 0.2$ near the center of the miscibility gap to 0.28 near the coexistence line.[5,6]

The validity of the scaling of the structure factor was indicated in experiments on liquid mixtures,[9-11] a glass system,[12] and a binary alloy.[13]

In order to investigate the scaling property in alloy systems further, we chose the Fe-Cr alloy for the following reasons. (i) The phase diagram is simple and phase separation takes place within a wide concentration range. (ii) Since Fe and Cr atoms have similar size, the elastic strain generated by phase separation should be small. (iii) The time constant involved is fairly long. (iv) Phase separation does not occur at ordinary temperatures. Recently we investigated the kinetics of phase separation in FeCr alloys containing from 5 to 50 at.% Cr at intervals of about 4 at.% over a wide temperature range.[14-16] In these works, it was indicated that for the aging times up to 20 h the exponent a of the alloys containing high Cr concentration (larger than about 30 at.% Cr) aged around 500 °C agrees well with the value of $1/(d+3)$ predicted by Binder and Stauffer[1] and that the structure factor of these alloys under these conditions shows typical behavior in the unstable state as calculated by Langer, Bar-on, and Miller[8] and Lebowitz, Marro, and Kalos.[6] To observe further time evolution, we selected the alloy containing 34 at.% Cr aged at 500 °C. This sample has a reasonable time constant for observation, and shows typical properties of the high-Cr-concentration alloys. In this paper we report that the experimental results for this alloy system indicate the crossover in the scaling relation predicted by Binder.[7] It is found that the exponent a changes its value at a certain aging time and, moreover, that the form of the scaling function $F(q/q_1)$ also changes.[17]

The Fe-Cr alloy was prepared by melting 99.99% pure Fe and 99.999% pure Cr in an argon-arc furnace. The ingot was homogenized at 1100 °C for 5 days, and quenched in iced brine. Aging was done

at 500 °C up to 500 h. After aging, the specimen was quenched. Small-angle neutron scattering was measured at room temperature with use of a triple-axis spectrometer in the diffraction arrangement with a neutron wavelength of 2.35 Å. Soller slits with a horizontal divergence of 20 min of arc were used between monochromator and specimen and between specimen and counter. The geometrical cross section of the incident beam was 6×6 mm². The wave vector resolution was about 0.01 Å^{-1}. The counting times were long enough to obtain good statistics for most of the data shown later. The time evolution of the scattered intensity was obtained by subtracting the intensity of the as-quenched specimen from that of the aged one. Since it is known that magnetic and nuclear scattering show almost the same patterns and differ only by a scale factor,[18] magnetic and nuclear scattering were not distinguished.

Figure 1 shows the time evolution of the structure factor $S(q,t)$ ($q = 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle) at 500 °C for aging times (a) up to 20 h and (b) from 20 to 500 h. With increasing aging times, the structure factor becomes sharp with the maximum position shifting towards small wave vector and with the peak intensity increasing rapidly.

In order to examine the scaling property, we investigated the time dependence of the characteristic wave vector $q_1(t)$, which is defined as the first moment of the structure factor

$$q_1(t) = \sum_q q S(q,t) / \sum_q S(q,t) \tag{3}$$

and is proportional to the maximum wave vector $q_m(t)$. In Fig. 2, $q_1(t)$ is plotted as a function of aging time on a logarithmic scale. It is of interest to see how the result can be fitted by the power law (2), which is a straight line on this figure. As is clearly seen, the entire time evolution cannot be expressed by a single power law. Then it is pertinent to restrict the time range of fitting to the initial and final stages. By choosing appropriate data points we could fit the respective ranges by straight lines as shown in the figure. The striking feature of the result is that the exponent changes from 0.17(± 0.02) to 0.33(± 0.03) around 30 h. This is the crossover predicted by Binder for alloy systems. According to him, the exponent a changes from $1/(d+3)$ at intermediate aging times to $\frac{1}{3}$ at late times because of a transition in the phase-separation mechanism. The former value is predicted for the coagulation process in which clusters diffuse by the evaporation of atoms from the cluster surface and their reimpingement and consequently clusters coalesce. The latter is obtained in the condensation process in which clusters grow by the diffusion of single atoms one after the other from one stationary cluster to the other [the Lifshitz-Slyozov (LS) process].[19] The reasonable agreement of the exponents indicates that the kinetics of phase separation is governed by the processes predicted by Binder. The crossover time between these two processes, t_{cr}, and the cluster radius at that time, r_{cr}, were estimated by Binder roughly as $t_{cr} \simeq 10^{-2}$ sec and $r_{cr} \propto (10^4 t_{cr})^{1/3} \simeq 5$ lattice spacings with the diffusion constant $D = 10^{-10}$ cm²/sec. Since $t_{cr} \propto D^{-1}$ and $r_{cr} \propto D^{1/3}$ according to his theory, supposing the diffusion constants of Fe and Cr in Fe-Cr alloys around 500 °C to be 10^{-17} cm²/sec,[20,21] one gets $t_{cr} \simeq 10^5$ sec $\simeq 30$ h and $r_{cr} \propto (10^{-3} t)^{1/3} \simeq 5$ lattice
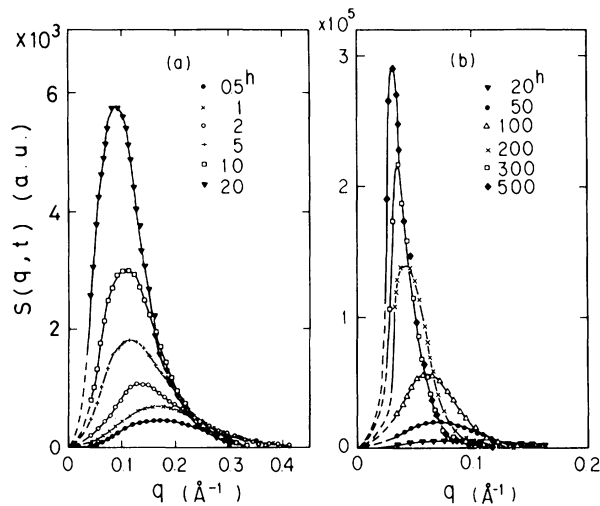

FIG. 1. Time evolution of the structure factor of Fe-Cr alloy containing 34 at.% Cr aged at 500 °C for aging times (a) up to 20 h and (b) from 20 to 500 H.
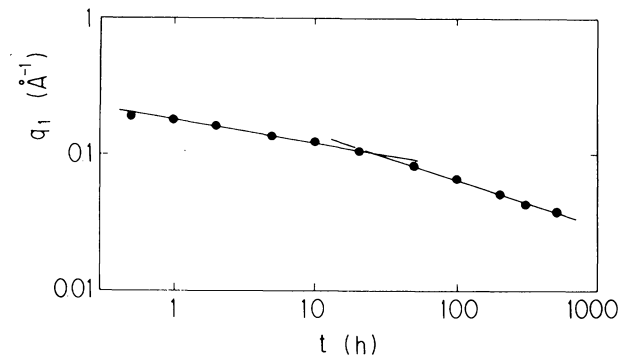

FIG. 2. Time dependence of $q_1(t)$. The full lines correspond to the exponent $a = 0.17$ at early times and 0.33 at late ones.

spacings. The experimental result indicates $t_{cr} \simeq 30$ h and $r_{cr}(= \pi/q_m) \simeq 40$ Å. If we take into account the rough nature of the theoretical estimate, the agreement of t_{cr} is good and that of r_{cr} is reasonable.

On the other hand, the computer simulations have not indicated the crossover of the scaling behavior of q_1. Lebowitz, Marro, and Kalos stated that the time evolution of $q_1(t)^{-3}$ follows $A + Bt$ for late times being consistent with the LS theory.[6] However, the same result also shows that q_1 changes according to the power law with a single exponent from early to late times. Therefore, the clear crossover as obtained here is not seen in the simulations.

In order to extend the comparison with the scaling theory we have calculated the normalized scaling function $\tilde{F}$ according to the definition given by Marro and co-workers[5,6]:

$$\tilde{F}[q/q_1(t)] = [q_1(t)]^3 \tilde{S}(q,t), \tag{4}$$

where the normalized structure factor $\tilde{s}(q,t)$ is defined as

$$\tilde{S}(q,t) = S(q,t)/\sum_q q^2 S(q,t)\delta q, \tag{5}$$

and δq is the wave-vector increment in the observation. The plots of $q_1^3 \tilde{S}(q,t)$ for different times are shown in Fig. 3. It is found that the scaling of the structure factor is satisfied separately in earlier times and later ones and that the scaling function $\tilde{F}(q/q_1)$ changes in correspondence with the crossover of the scaling behavior of q_1, although the change of the scaling function takes place in a rather broad time range in comparison with the sharp change in the case of q_1. The scaling function is independent of time up to 20 h, but around 50 h $\tilde{F}$ starts to deviate from this scaling function and then after 200 h the function assumes another form which is fairly sharp compared with the earlier one.

In this figure the dashed line shows the scaling function obtained by the computer simulations for a concentration near the center of the miscibility gap.[6] This is in good agreement with our result at late times. Since the result of the simulations at late times has been pointed out to be consistent with the LS process,[6] the agreement of the scaling function at this stage supports our interpretation that the process after the crossover is the condensation (LS) one. At the earlier times, however, the function $\tilde{F}$ in the simulation is dependent on time, while our result shows the existence of another scaling function in the region assigned to the coagulation process. This discrepancy may be related to the fact that the simulations do not apparently indi-
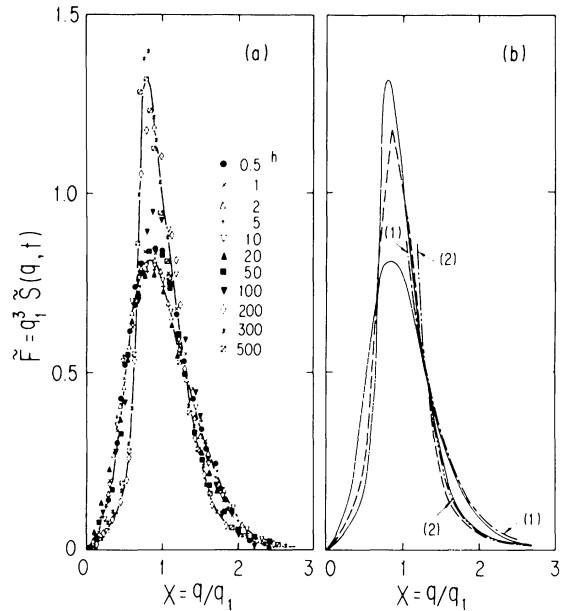

FIG. 3. (a) Scaling of the normalized structure functions. The full lines are guides to the eye. (b) The dashed line is the result of computer simulations for the concentration near the center of the miscibility gap (Fig. 7 in Ref. 6). The broken lines 1 and 2 represent x^{-4} and x^{-6} dependence, respectively.

cate the crossover of $q_1(t)$ but our experiment clearly shows it. It is natural that the scaling function changes in correspondence to the crossover of the scaling behavior of q_1.

The form of the scaling function is important, because it should be determined by the factors such as the cluster shapes and correlations between clusters. Furukawa discussed the x dependence of the scaling function for large x, where $x = q/q_1$.[4] He obtained an $x^{-(d+1)}$ dependence for smoothly curved surfaces and an x^{-2d} dependence for extremely tangled surfaces. As shown in Fig. 3, our result indicates an x^{-4} dependence (line 1) at early times and an x^{-6} dependence at late ones (line 2).[22] Since it is considered that the cluster surfaces are smooth at the early stage and become tangled at the late one,[23] our result is explained by the discussion of Furukawa. Recently Rikvold and Gunton derived the scaling function for phase separation.[24] However, as their model is limited to low concentrations and based on the Lifshitz-Slyozov process only, a simple comparison with our experiment is impossible. A more advanced theory is required to understand the scaling function in the coagulation process and the change of the scaling function obtained here.

In conclusion, the result of the Fe-Cr alloy con-

taining 34 at.% Cr shows that the dynamical scaling of phase separation holds well. Moreover, a crossover occurs in the exponent, which is accompanied by a change in the scaling function. This crossover is caused by the transition from the coagulation process to the condensation one in alloy systems.

We would like to thank H. Furukawa for valuable comments and J. Marro and P. Guyot for informing us of their results.

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[23]A. R. Forouhi showed also that in the first stage the microstructure of Al-Zn-Mg alloy consisted of spherical clusters and in the second, platelets (Ref. 19). In the case of Fe-Cr alloy also, this kind of transmission electron microscopy study would be very useful.

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