PHYSICAL REVIEW B VOLUME 46, NUMBER 21 1 DECEMBER 1992-I

Rapid Communications

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** *should be no longer than four printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

Nucleation and growth in Al-Zn: A test of the Langer-Schwartz model

G. Sundar and J. J. Hoyt
Department of Mechanical and Materials Engineering, Washington State University, Pullman, Washington 99164-2920

S. Spooner
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

(Received 27 July 1992)

Small-angle x-ray scattering has been used to monitor the decrease in supersaturation with time in Al-Zn alloys following quenches into the metastable miscibility gap. The results demonstrate that the Langer-Schwartz model of nucleation and growth is accurate provided a time-dependent nucleation rate is included.

The nearly 60 year old classical theory of nucleation[1,2] predicts that the rate of formation of minority phase droplets depends strongly on the quench position within the miscibility gap of a phase-separating solution. The dependence is in fact so strong that one can define a unique, critical undercooling, or cloud point, where the nucleation rate increases by many orders of magnitude from a near zero value. An obvious test of classical nucleation theory would be the comparison of measured and predicted values of the cloud point. Somewhat surprisingly, past experiments on liquid systems have demonstrated serious discrepancies between theory and experiment.[3-6]

That the negative result of experiments need not indicate a fundamental flaw in classical nucleation theory was pointed out by Binder and Stauffer (BS).[7] These authors argue that, since the nucleation rate depends very strongly on supersaturation (or undercooling), one cannot overlook another mechanism, besides the formation of stable nuclei, which depletes available solute from the matrix phase. The second competing mechanism is the growth of droplets. Since growth and nucleation cannot be viewed as independent mechanisms, BS point out that the meaningful quantity with which to test theory is the time dependence of the decrease in matrix supersaturation.

The ideas of BS were placed on a quantitative footing by Langer and Schwartz[8] (LS) in 1980. The main results of their computation are presented in Fig. 1. The quantity τ_c denotes the time required for the supersaturation to decrease to one-half its initial value. The solid line of Fig. 1 shows the LS prediction for the half completion time versus the initial supersaturation and the dash-dotted curve depicts the classical theory result. The latter curve being nearly vertical illustrates the cloud point phenomenon alluded to above.

The quantities plotted in Fig. 1 are in fact scaled parameters. In the LS treatment, the time τ is given by

$$\tau=(Dx_0^3/24\xi^2)t \tag{1}$$

where D is the solute diffusion coefficient, ξ is the correla-

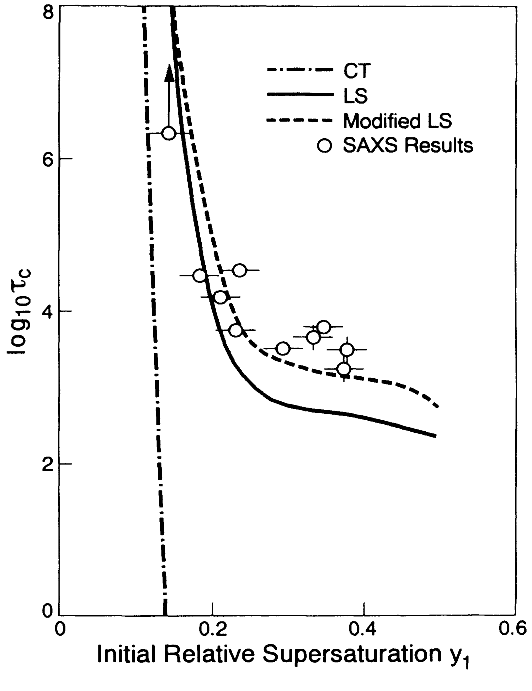

FIG. 1. Log of the half completion time τ_c vs y_1 as predicted by classical theory (CT), the Langer-Schwartz model (LS), and the LS model modified to include a time-dependent nucleation rate (dashed line). The data points are results from Al-Zn alloys using small-angle x-ray scattering.

tion length, and t is the real time. Also, y denotes the scaled supersaturation and is written as

$$y = 2\delta c / \beta x_0 \Delta c \tag{2}$$

where β is the critical exponent associated with the shape of the miscibility gap, Δc is the width of the miscibility gap at the aging temperature, and δc is the real supersaturation. The quantity x_0, which is nearly unity for most systems, is given by

$$x_0 = 4(\sigma \xi^2 / k T_c)^{1/2} \tag{3}$$

with σ denoting the the surface energy, T_c the critical temperature, and k Boltzmann's constant.

Although the basic ideas of the LS model have been confirmed in liquid systems,[9-12] to date, few conclusive studies on solids or alloy systems have been performed.[13,14] In 1984 Simon, Guyot, and Ghilarducci de Salva[14] tested the LS theory on Al-Zn alloys using small-angle x-ray scattering (SAXS). The results of τ_c vs y_1 showed serious discrepancies with theory including one data point which seemed to confirm the classical prediction. Inclusion of the effects of heterogeneous nucleation into the LS computation does not appear to explain the difference between the model and the Simon, Guyot, and Ghilarducci de Salva results.[15] The purpose of the present work is to further investigate nucleation and growth kinetics in Al-Zn alloys and provide a more accurate test of the LS model.

Alloys of five average compositions (17, 17.5, 18, 18.5, and 19 at. % Zn) were rolled and strain annealed to produce an average grain size of $\simeq 1$ mm. The grain size was approximately the same as the beam spot size used in the subsequent SAXS experiments and thus all complicating effects due to the presence of grain boundaries were negligible. Disks of 3 mm diam were punched from the rolled material and further thinned by electropolishing to an ideal thickness corresponding to the reciprocal of the linear absorption coefficient.

SAXS experiments were performed at the 10-m line at the National Center for Small Angle Scattering Research located at the Oak Ridge National Laboratory. The system features a rotating anode source (operated at 100 mA and 60 kV in this experiment) and an area detector. A complete description of the apparatus can be found elsewhere.[16] The x-ray energy used was Cu $K\alpha$.

The samples were heated and cooled by adjusting the current which passed through a steel ring in thermal contact with the specimen disks. Temperatures were calibrated with the known boundary of the metastable miscibility gap.[17] Each sample was solutionized for approximately 0.5 h at 340 °C and subsequently quenched to a temperature in the vicinity of 260 °C ($\simeq 0.9 T_c$). The duration of the quench was about 30 sec, which is slow compared to other studies of phase separation in alloys[18] but is, in this instance, must faster than the kinetics being observed. Also the relatively slow quench rate has the desirable effect of helping to eliminate the high-temperature nonequilibrium concentration of vacancies. Excess vacancies are known to have a significant effect on the measured nucleation kinetics.[19]

SAXS is the ideal experimental technique with which to test the LS model because the supersaturation as a function of time can be measured directly. Gerold[20] has shown that the integrated intensity in the small-angle region is given by

$$I(t) = [\delta c_1 - \delta c(t)][c_B - c(t)] \Delta Z^2 / V_a \ , \tag{4}$$

where δc_1 is the initial supersaturation, c_B is the solute concentration within the nuclei, $c(t)$ is the matrix concentration, ΔZ is the difference in atomic numbers of the two species in solution, and V_a is the atomic volume. To a good approximation the $c_B - c(t)$ term can be replaced by Δc, independent of time, and I becomes directly proportional to the supersaturation. It is then a simple matter to extract the half completion times from the *in-situ* SAXS data.

Figure 2 shows the integrated intensity in arbitrary units vs the aging time for three different quench temperatures for the Al–18 at. % Zn sample. The increase in intensity from zero ($\delta c = \delta c_1$) to a constant value ($\delta c = 0$) is consistent with the Gerold result, Eq. (4). The vertical lines in Fig. 2 show the half completion times for each run. Naudon and Caisso[21] included a contribution to the integrated SAXS intensity at high values of the scattering vector k. The procedure employs a Porod extrapolation of the spherically averaged intensity and, since the intensity in the present case is anisotropic (see below), such an averaging procedure was impossible. Nevertheless, we have assumed that the high-k contribution is small and that the change in integrated intensity with time due to this correction is small compared to the time dependence of the measured intensity in the small-k region.

To convert from the real times of Fig. 2 to the scaled time and supersaturation of Fig. 1 one must obtain the various material parameters given in Eqs. (1)–(3). Both the correlation length ξ and the critical temperature T_c have been measured in a study of Schwann and Schmatz.[22] The diffusion coefficient for Zn in Al is fairly well known,[23] as is Δc at any temperature.[17] It should be noted that, of the above parameters, the diffusion

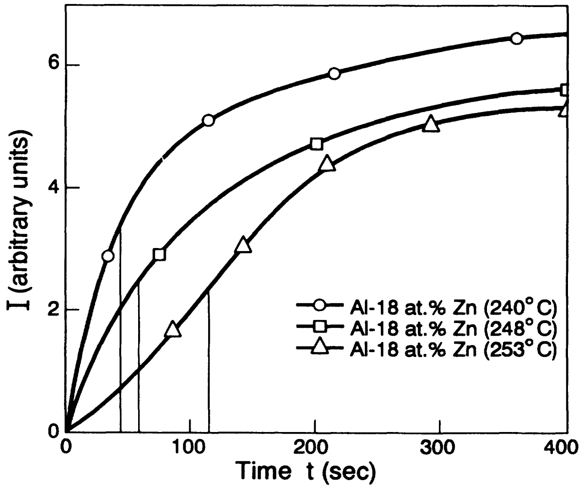

FIG. 2. Integrated intensity vs time for three experiments. Vertical lines show the half completion times.

coefficient is the most imprecise. However, errors in D appear only in the conversion to the scaled time, which is then plotted on a logarithmic scale in Fig. 1. In terms of the uncertainty of the data points plotted on the semilogarithmic representation of Fig. 1, the surface energy estimation is by far the most important and in fact renders any experimental imprecision in all other parameters insignificant. The surface energy was estimated by using an empirical free-energy model,[24] the known gradient energy coefficient for Al-Zn,[23] and an expression for σ originally derived by Cahn and Hilliard.[25] The free-energy model is clearly suspect but, as possible justification for its use, the resulting value of the surface energy (4.7 ergs/cm^2) is close to that for the coherent δ' nuclei in Al-Li.[26] The value of x_0 [Eq. (3)] with the above surface energy was found to be $\simeq 1.75$, however, the uncertainty in σ represents the largest uncertainty in the data and x_0 was thus taken to be in the range 1.5–2.0.

The experimentally measured half completion times are plotted as open circles in Fig. 1, where the error bars result from the uncertainty in σ discussed above. The upward arrow on the data point at the lowest y_1, indicates that the plotted τ_c is a lower bound; the actual half completion time for this value of y_1 may very well be infinite. The data seem to confirm an important aspect of the LS model, namely that the onset of nucleation occurs at higher values of the initial supersaturation than predicted by classical theory. However, the results also indicate that the LS model underestimates the half completion time at high y_1.

Elastic strain energy increases the work of formation of a critical nucleus and therefore lowers the nucleation rate. Thus lattice mismatch between particle and matrix may be a plausible explanation for the discrepancy noted in Fig. 1, but in Al-Zn the elastic strain is small and LeGoues, Aaronson, and Lee[27] have shown that such an effect is most prominent at low supersaturations. In Al-Zn alloys the Zn-rich precipitates nucleate as spheres and, after growing to a certain size, become plates along $\{111\}$.[28] The platelike morphology suggests that the growth mechanism for spheres used in the LS treatment is not strictly valid. This complication does not drastically effect the results of Fig. 1 since the half completion times occurred when nearly isotropic (i.e., spheres) SAXS spectra were observed.

Alternatively, one could attempt to explain the underestimation of the LS result by invoking a more sophisticated model[29] which avoids some of the assumptions used by LS. However, we feel the most plausible explanation for the discrepancy of Fig. 1 is due to the use of a steady state, rather than a time-dependent, nucleation rate in the LS computation. That is, an incubation time has been neglected.

Shi and co-workers[30] have recently solved the time-dependent nucleation problem using a singular perturbation approach. However, to simply illustrate that the incubation time is important in interpreting the present results, we have found it most convenient to use an approximate form of the time-dependent nucleation rate developed many years ago in the metallurgical literature.[31] Here the nucleation rate is given by

$$J(\tau)=\exp(-\tau'/\tau)J_{ss} , \qquad (5)$$

where J_{ss} is the steady-state nucleation rate and τ' is a time constant. Based on previous work[32] τ' has been estimated to be $1290/y^2$ for the Al-Zn data of Fig. 1. It should be noted that Kampmann and Wagner[33] also discussed the inclusion of a time-dependent nucleation rate into the LS theory.

Modifying the LS model to include the nucleation rate of Eq. (5), one obtains the τ_c vs y_1 behavior given by the dashed line in Fig. 1. Clearly the time dependence of J explains much of the difference between model and experiment. In summary then, the LS treatment of nucleation and growth appears to be accurate provided a time-dependent nucleation rate is included.

This work was supported by the National Science Foundation under Contract No. DMR 8919193. The Oak Ridge National Laboratory is operated by Martin Marietta Energy Systems Inc. under Contract No. DE-AC05-84OR21400 for the U.S. Department of Energy.

---

[1] J. W. Gibbs, *Collected Works* (Yale University Press, New Haven, CT, 1948), p. 1.

[2] R. Becker and W. Doring, Ann. Phys. (N.Y.) **24**, 719 (1935).

[3] B. E. Sundquist and R. A. Oriani, J. Chem. Phys. **36**, 2604 (1962).

[4] R. B. Heady and J. W. Cahn, J. Chem. Phys. **58**, 896 (1973).

[5] J. Huang, S. Vernon, and N.-C. Wong, Phys. Rev. Lett. **33**, 140 (1974).

[6] J. S. Huang, W. I. Goldburg, and M. R. Muldover, Phys. Rev. Lett. **34**, 639 (1975).

[7] K. Binder and D. Stauffer, Adv. Phys. **25**, 343 (1976).

[8] J. S. Langer and A. J. Schwartz, Phys. Rev. A **21**, 948 (1980).

[9] A. J. Schwartz, S. Krishnamurthy, and W. I. Goldburg, Phys. Rev. A **21**, 1332 (1980).

[10] R. G. Holand, N.-C. Wong, and C. M. Knobler, J. Chem. Phys. **73**, 522 (1980).

[11] E. D. Siebert and C. M. Knobler, Phys. Rev. Lett. **52**, 1133 (1984).

[12] E. D. Siebert and C. M. Knobler, Phys. Rev. Lett. **54**, 819 (1985).

[13] H. Wendt and P. Haasen, Acta Metall. **31**, 1649 (1983).

[14] J. P. Simon, P. Guyot, and A. Ghilarducci de Salva, Philos. Mag. A **49**, 151 (1984).

[15] G. Sundar and J. J. Hoyt, J. Phys. Condens. Matter **4**, 4359 (1992).

[16] R. W. Hendricks, J. Appl. Crystallogr. **11**, 15 (1978).

[17] J. Lasek, Czech. J. Phys. **15**, 848 (1965).

[18] G. B. Stephenson, K. F. Ludwig, J. L. Jordan-Sweet, S. Brauer, J. Mainville, Y. S. Yang, and M. Sutton, Rev. Sci. Instrum. **60**, 1537 (1989).

[19] F. K. LeGoues and H. I. Aaronson, Acta Metall. **32**, 1855 (1984).

[20] V. Gerold, in *Small Angle Scattering of X-rays*, edited by H. Brumberger (Gordon and Breach, New York, 1967).

[21] P. A. Naudon and J. Caisso, J. Appl. Crystallogr. **7**, 25 (1974).
[22] D. Schwann and W. Schmatz, Acta Metall. **26**, 1571 (1978).
[23] K. B. Rundman and J. E. Hilliard, Acta Metall. **15**, 1025 (1967).
[24] J. J. Hoyt, M. Sluiter, M. Kraitchmann, and D. de Fontaine, Acta Metall. **35**, 2315 (1987).
[25] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **28**, 258 (1958).
[26] J. J. Hoyt and S. Spooner, Acta Metall. Mater. **89**, 689 (1991).
[27] F. K. LeGoues, H. I. Aaronson, and Y. W. Lee, Acta Metall. **32**, 1845 (1984).
[28] A. R. Forouhi and D. de Fontaine, Acta. Metall. **35**, 1863 (1987).
[29] M. P. Marder, Ph.D. thesis, University of California, Santa Barbara, 1986.
[30] G. Shi, J. H. Seinfeld, and K. Okuyama, Phys. Rev. A **41**, 2101 (1990); G. Shi and J. H. Seinfeld, J. Chem. Phys. **93**, 9033 (1990); J. Mater. Res. **6**, 2091 (1991).
[31] J. W. Christian, *The Theory of Transformation in Metals and Alloys* (Pergamon, New York, 1975).
[32] K. C. Russell, in *Phase Transformations,* edited by H. I. Aaronson (American Society of Metals, Metal Park, OH, 1970), p. 219.
[33] D. Kampmann and R. Wagner, *Decomposition of Alloys: The Early Stages* (Pergamon, New York, 1984).