Phase decomposition of liquid-quenched Al–14 at. % Ag: small-angle X-ray scattering study

R. ROBERGE
IREQ, Institut de recherche de l'Hydro-Québec, Varennes, Québec, Canada

H. HERMAN
Department of Materials Sciences, State University of New York at Stony Brook, Stony Brook, New York, USA

Small-angle X-ray scattering was used to study phase decomposition of liquid-quenched Al–14 at. % Ag. Ageing was carried out at temperatures from 50 to 175°C. Though it is clear that ideal linear spinodal behaviour was not obtained, the general trend points to the early unmixing of this alloy as being characterized by spinodal decomposition. The activation energy for the process is that for equilibrium volume diffusion, and it is therefore concluded that quenched-in vacancies play no role in phase decomposition following liquid quenching.

1. Introduction

Spinodal decomposition is characterized by a diffusion-limited unmixing of an unstable super-saturated solution within a gap in miscibility. The main feature of the evolving microstructure is a predominate decomposition wavelength which is determined by optimizing the diffuse surface energy and kinetic limitations. The theory, as formulated principally by Cahn and Hilliard (see [1] and [2] for the appropriate references), is linearized to make the solutions amenable to both theoretical and experimental analysis. This, however, results in temporal restrictions and requires that the reactions be examined at extremely early times in the decomposition process. Furthermore, it is simplest to consider compositions at the centre of the miscibility gap, since this "symmetric" alloy will be more directly interpretable. For these reasons we have studied the phase decomposition of a liquid-quenched Al–14 at. % Ag alloy. The liquid quench results in an extremely fast quench (thus limiting quench-clustering) and the present alloy is at the centre of the metastable miscibility gap. The Al–Ag phase diagram, shown in Fig. 1, has a metastable miscibility gap within the equilibrium two-phase region [3].

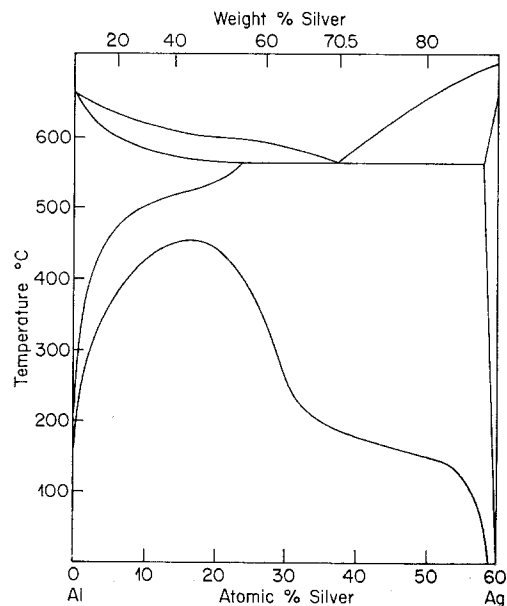Small-angle X-ray scattering (SAXS) is a

Figure 1 Aluminium-silver phase diagram with the metastable miscibility gap [3].

most direct technique for studying the evolution of compositional fluctuations and is ideally suited for analysing the spinodal process. Al–Ag is a good candidate alloy for SAXS since the

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TABLE II Summary of data extracted from experimentally measured $R(\beta)$ versus β plots

Temperature (°C)	Wavenumbers of the peaks in $R(\beta)$ versus β plots (cm⁻¹) × 10⁻⁷			Critical wavenumber β_c (cm⁻¹) × 10⁻⁷	Ratio of wavenumbers of the various peaks		Observed β_c/β_m ratio
	β_m	β_{m1}	β_{m2}		β_{m1}/β_m	β_{m2}/β_m	
50	0.90–1.10	1.75–2.00	2.9–3.2	3.9	1.9 ± 0.3	3.1 ± 0.5	*
100	0.80–1.20	1.90–2.10	3.0–3.2	3.5	2.1 ± 0.5	3.2 ± 0.8	*
150	1.40–1.60	—	—	2.65	—	—	1.65–1.89
175	1.40–1.60	—	—	2.60	—	—	1.62–1.86

*The ratios are not included for the two lowest temperatures where multiple peaks are observed in the $R(\beta)$ versus β plots.

intensity scattered at small angles is proportional to the square of the difference between the component atomic factors. In the following, the change of the SAXS profiles with time are analysed after the method of Rundman and Hilliard [4]. In this method the scattered intensity is followed at a given scattering angle, 2θ (or wavenumber, $\beta = 2\pi/\lambda$, where λ is the decomposition wavelength), and the natural log of intensity, $\ln I(\beta, t)$, is plotted versus ageing time. If the process obeys linear spinodal theory, these plots should be linear with a slope equal to twice the amplification factor, $R(\beta)$. The data are then further analysed.

In the present study, liquid quenching was carried out using the torsion-catapult [5]. A quenching rate of 10^6°C sec⁻¹ was reported in a companion study, where this as well as other compositions of Al–Ag were studied with electrical resistivity and TEM [6]. For the SAXS studies, Kratky collimation was employed with monochromatized Cu$K\alpha$ radiation. The specimen was fixed permanently to a specimen holder and aged for various times at a given temperature (50 to 175°C). This ensured that the same area of the specimen was irradiated by the X-rays for the entire ageing process. The scattering intensities were corrected for both parasitic scattering and slit collimation errors.

TABLE I Isothermal ageing treatments of liquid-quenched Al–14 at. % Ag

Ageing temperature (°C)	Total ageing time investigated	Observed time of the linear portion of the variation of ln intensity versus time
50	900 min	500 min
100	25 min	20 min
150	75 sec	75 sec
175	20 sec	12 sec

Ageing was in a silicone oil bath controlled to ± 0.05°C.

2. Results and discussion

The isothermal ageing treatments are summarized in Table I: the logarithm of the corrected intensities versus time is linear for the ageing times indicated. The amplification factors, $R(\beta)$, were determined by least-squares analyses of the slopes of the linear portions of the logarithm of the corrected intensities as plotted against time. The spectra of $R(\beta)$ versus β for the temperature range investigated are given in Fig. 2a to d and summarized in Table II. The plots of $R(\beta)/\beta^2$ versus β^2 shown in Fig. 3a to d are also of interest to check the validity of the linear theory and they give the possibility of measuring the diffusivity coefficient.

At temperatures below approximately 200°C the alloy in question is no longer symmetric in the sense that equal volume fractions of conjugate phases are expected to form within the metastable gap. This effect alone should give rise to distorted decomposition waves and, hence, at least at temperatures well below the symmetric region (~ 200°C), ideal spinodal behaviour should not be expected, and deviations from linearity should be observed. For example, as seen from Table II, β_c/β_m deviates from ideal linear behaviour: the ideal ration is $\sqrt{2}$, whereas the observed ratio is at least 20% greater, i.e. the $R(\beta)$ versus β plots observed here are considerably broader than ideal. Furthermore, the $R(\beta)/\beta^2$ versus β^2 plots deviate from linearity. As pointed out by Hilliard these deviations from ideality seem to be common for Al–Ag [2]. In more recent work, however, using faster liquid quenching rates, behaviour closer to linear is noted [7].

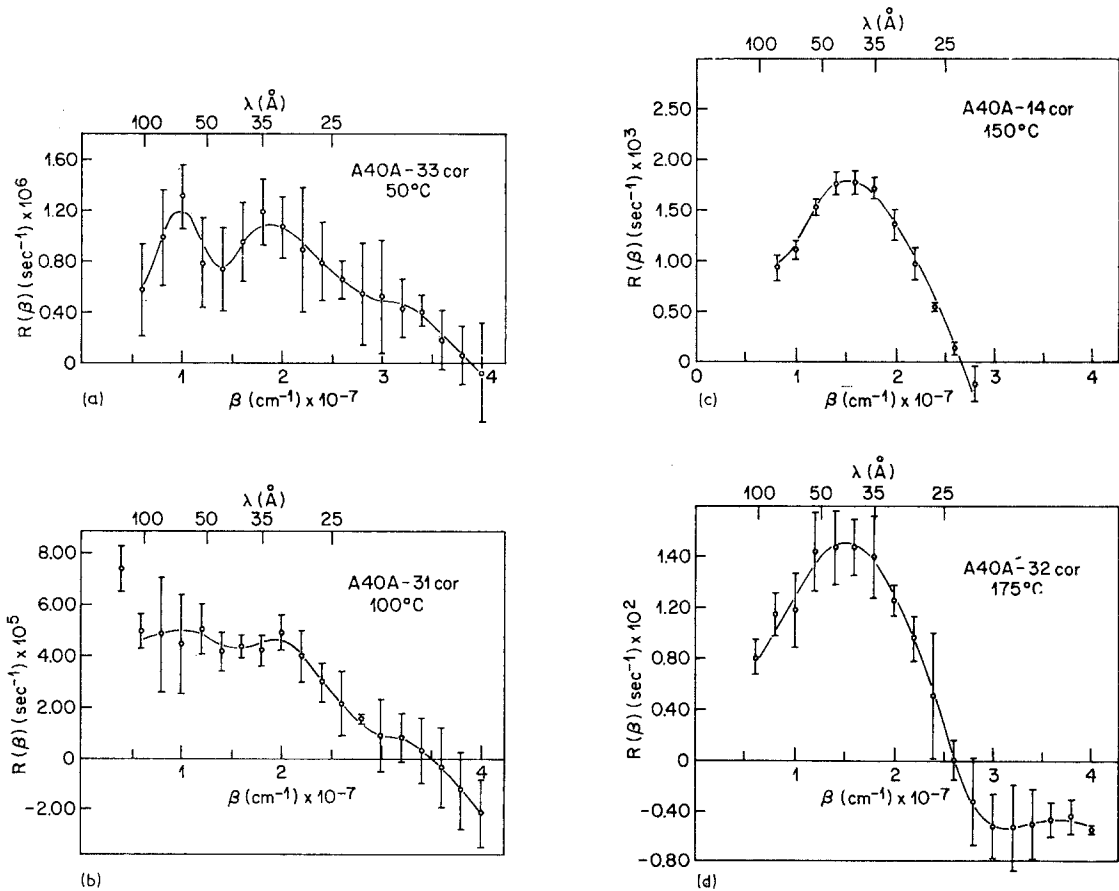It is of some interest to note from Fig. 2a to d as the temperature increases from 50 to 175°C,

Figure 2 Spectrum of the amplitude factors $R(\beta)$ versus β for liquid-quenched Al–14 at.% Ag alloys aged at various temperatures. (a) 50°C; (b) 100°C; (c) 150°C; (d) 175°C.

the $R(\beta)$ versus β plots become less complex, and exhibit only one maximum. This is to be expected since the alloy is being brought into a more symmetric region of the miscibility gap.

The observation that the amplification factor spectrum is broader than expected from linear theory appears to be the rule rather than the exception. Zarzycki and Naudin reported a β_c/β_m of about 1.9 for a B_2O_3–PbO–Al_2O_3 glass [8]. Similar deviations were seen by Nielsen [9] and Tomozawa *et al* [10] in studies of soda-silica glasses. Murakami *et al* [11] observed a ratio of 1.6 to 1.9 in Al–6.8 at.% Zn aged in the range 20 to 60°C.

The curvature of the plot of $R(\beta)/\beta^2$ versus β^2 is also a common observation. If we assume that the linear relationship is valid for small β, the interdiffusion coefficient, neglecting strain, can be obtained [4] using

$$\tilde{D} = -4R(\beta_m)/\beta_c^2 . \tag{1}$$

The results are plotted in Fig. 4 versus reciprocal absolute temperature and compared with the equilibrium measurements of Heumann and Bohmer [12]. The activation energy obtained, 35.9 ± 1.0 kcal mol^{-1}, is a reasonable value for equilibrium diffusion. Of interest here is the fact that decomposition is occurring with an activation energy indicative of an equilibrium vacancy concentration. Normally, in bulk quenching of Al-base Ag alloys, a smaller activation energy is observed, pointing to quenched-in vacancy enhanced solute motion [13]. That this is not generally the case in liquid-quenched alloys has been previously noted [14, 15].

In order to explain the observed deviations from linear behaviour it could be assumed that the reaction is simply beyond the region where linear approximations are justified. In fact, it has been shown by de Fontaine [16] and Tomozawa *et al* [10] that the observed β_c/β_m ratio, the
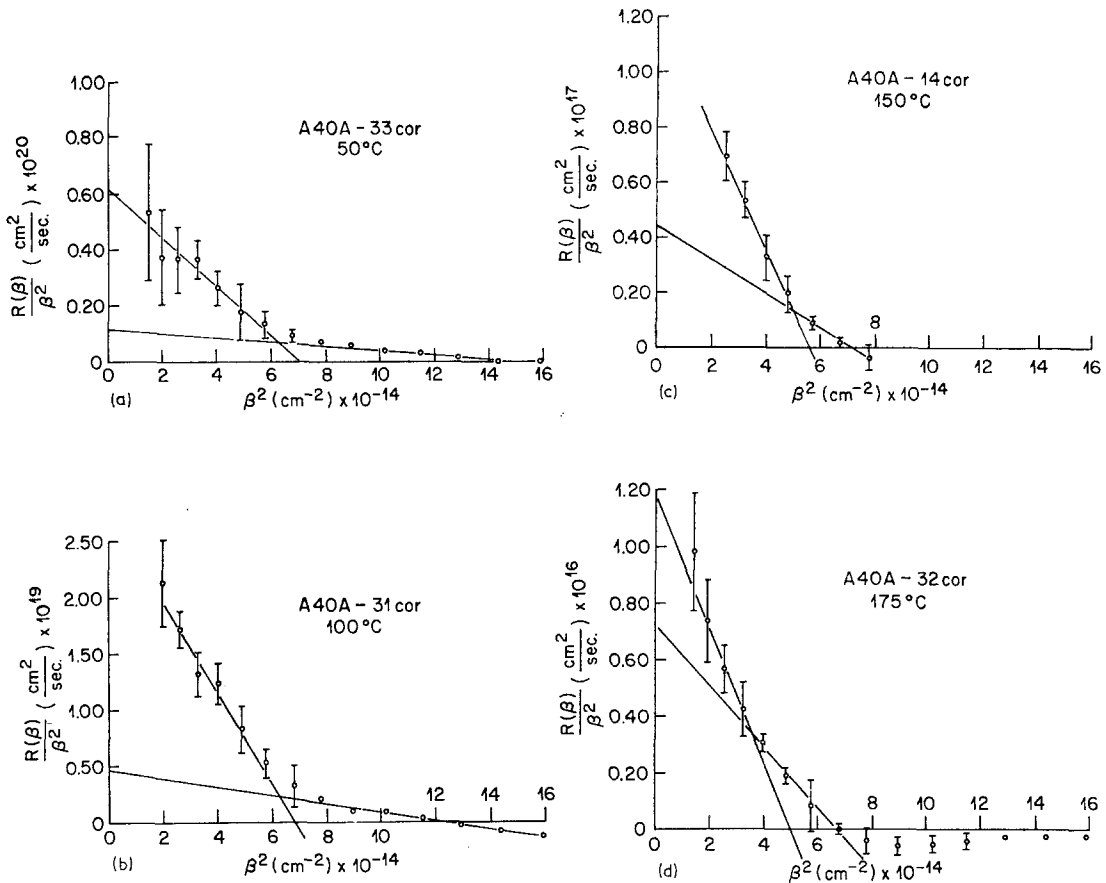
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Figure 3 Observed relationships of the $R(\beta)/\beta^2$ versus β^2 for liquid-quenched Al–14 at. % Ag alloys aged at various temperatures. (a) 50°C; (b) 100°C; (c) 150°C; (d) 175°C.

curvature of $R(\beta)/\beta^2$ versus β^2 plot and the shift of the critical wavelength, should be attributed to non-linear terms in the diffusion equation. Let us recall the approximations leading to the linear early-stage theory. The basis of this theory is the solution of a diffusion equation

$$\frac{\partial C}{\partial t} = D_1\nabla^2C - D_2\nabla^4C + D_1'\,(\nabla C)^2 \qquad (2)$$

$$+ \ldots \text{non-linear terms of order} \geqslant 4.$$

The coefficients D_1 and D_2 are dependent on atomic mobility and free energy. D_1 is dependent also on the elastic energy term while D_2 is dependent on gradient energy. D_1' is the derivative with respect to compositions C. In the early-stage approximation, the coefficients D_1 and D_2 are assumed to be composition independent, and the general solution of the diffusion equation is thus obtained. If the coefficients D_1 and D_2 are composition dependent, they can be expanded

by a Taylor's series around the initial composition C_0,

$$D_1(C) = D_1(C_0) + (C - C_0)D_1'(C_0) \qquad (3)$$
$$+ \tfrac{1}{2}(C - C_0)^2\,D_1''(C_0) + \ldots$$

and similarly for D_2. The initial wave representation is deformed and for a symmetric composition the effect is to flatten out the maxima and minima of the sinusoidal wave. For asymmetric compositions the effect is to increase the maxima and decrease the minima, thus sharpening the interfaces. Thus, the influence of other than $R(\beta_m)$ becomes non-negligible and must be taken into account. The result is the appearance of other maxima. Tomozawa *et al* [10], using this view, have qualitatively explained similar results in glass.

It is additionally important to note that significant decomposition might have occurred
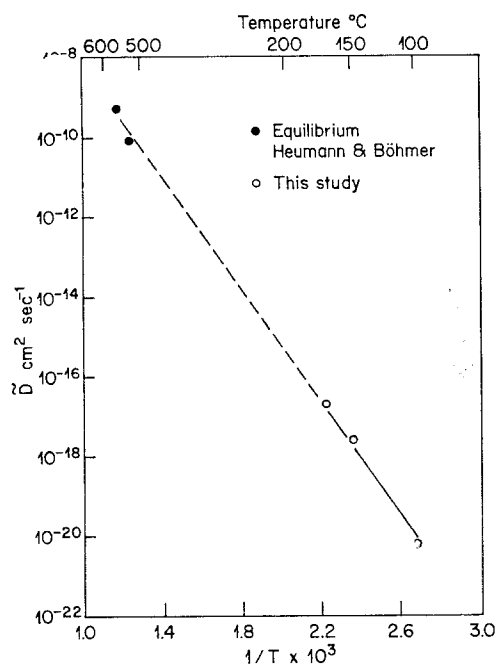
Figure 4 Extension of measured interdiffusion coefficient to the range where equilibrium data on diffusion is available.

during the quench, since the metastable miscibility gap in Al–Ag reaches a relatively high temperature, (450°C). The diffusion distance, x, for a given time, t, can be calculated from $(2 \mid D \mid t)^{1/2}$. Substituting typical values for $x^2 = 2 \times 10^{-13}$ cm^2 (wavelength $\lambda = 50$ Å) and since $D \simeq 10^{-10}$ cm^2 sec^{-1} (as calculated for 450°C from the presently determined activation energy), the time required for diffusion would be one millisecond. There is then a possibility of obtaining decomposition at high temperatures,

even in our rapidly quenched specimens. In this regard, it should again be noted that in the more recent work, where faster liquid quenching rates were obtained, the results more nearly approximate linear spinodal behaviour [7].

Acknowledgement

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