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Early-stage phase separation in liquid-quenched Al-7 at % Zn

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The kinetics of GP zone formation in liquid-quenched Al–7 at % Zn was studied with small-angle X-ray scattering. It is found that liquid quenching yields a solid solution in the as-quenched condition which is significantly less clustered than for solid quenching. In addition, the ageing kinetics of the liquid-quenched specimens was observed to be significantly slower than that for solid-quenched specimens. The results indicate that slow ageing in liquid-quenched alloys results from the absence of a high concentration of quenched-in mobile vacancies. It is thus suggested that liquid quenching effectively enables studies of the earliest stages of phase separation in precipitation-hardenable alloys.

1. Introduction

Solid-quenched (SQ) dilute Al–Zn alloys have been extensively studied. On SQ from temperatures in the single-phase region, alloys containing 6 to 10% Zn (all compositions are given in at % unless specified otherwise) are known to decompose rapidly at temperatures near ambient and above. The first products of decomposition, for ageing below 150° C, are GP zones, which for this alloy are solute-rich spherical clusters ranging ~10 to 50 Å in diameter and coherent with the matrix [1]. Since the early stage is concomitant of rapid quenching, numerous efforts have been made to achieve higher quenching rates [2]. Faster quenches, however, also lead to an increased supersaturation of quenched-in vacancies, which in turn enhances the low-temperature ageing process. Thus, following quenching, phase separation is nearly complete in a matter of minutes, even at ambient temperature. The kinetics of the decomposition can be considerably decreased by using sub-zero ageing temperatures. Nevertheless, SQ invariably leads to significant quench-clustering, and thus the earliest stages of decomposition are most difficult to distinguish in SQ studies [2].

Liquid quenching (LQ) yields highly homogeneous supersaturated solid solutions by virtue of ultra-fast quenching rates. Furthermore, in other work from this laboratory, involving kinetic studies on LQ dilute Al–Si alloys [3] and Al–15% Ag [4], it is apparent that LQ specimens retain essentially no mobile vacancies. Consequently, this results in slower aging rates for LQ as opposed to SQ. Cantor and Cahn [5] have observed similar effects in vapour-quenched Al–Ni, Al–Cu and Al–Fe alloys. LQ thus presents us with the opportunity of studying early-stage phase separation, usually inaccessible with SQ. In the present work, the ageing behaviour of LQ Al–7% Zn was studied mainly by small-angle X-ray scattering (SAXS).

2. Experimental procedure

Because of the large difference between the atomic scattering factors of Al and Zn, this alloy system is ideally suited for SAXS studies. In addition, since the strain energy associated with the formation of GP zones for this alloy is relatively small, the zones are essentially spherical. The scattering from an array of spheres will be isotropic, and the use of fine-grained LQ specimens is possible for the SAXS study.

The Al–7% Zn alloy was prepared by melting high purity components (99.999%) in an inert-gas induction furnace. Repeated melting and quenching

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ensured the homogeneity of the alloy. Specimens of about 100 mg were LQ from ~750° C by a gun-technique to obtain thin foils for the X-ray diffraction experiments [4]. The foils were about 1.5 cm × 3 cm in size, with thickness varying from 50 to 70 μm. The central section of the LQ specimen was continuous and was appropriate for SAXS and diffractometer studies. The edges of the LQ foil provide specimens which were sufficiently thin for TEM work.

The SAXS measurements were performed with a Siemens Kratky camera. Slit dimensions were chosen so that the corresponding scattering profile would approximate the shape of a profile produced by a beam of infinite length under the same conditions. A Siemens special Kratky copper tube with a line focus was used. CuKα radiation was obtained by Ni-filtration together with pulse-height analysis. The measured SAXS intensities were corrected for background scattering. A Siemens diffractometer was used for wide-angle X-ray diffraction analysis. Ageing was carried out in liquid baths controlled to within 0.5° C.

3. Experimental results

From TEM and lattice parameter studies, it was concluded that the as-LQ Al–7% Zn consisted of a homogeneous solid solution. Details of the SAXS analyses are given in the Appendix and in the paper by Agarwal and Herman [6]. The evolution of the GP zones during isothermal ageing gives rise to an increase in scattered SAXS intensities with time and a maximum in the angular range of 1° to 2° 2θ. Fig. 1 shows the intensity scattered at 1° 2θ plotted versus ageing time at room temperature for LQ Al–7% Zn. The as-LQ intensity is low and no significant ageing occurs for the first several hours. However, when the same specimen was rehomogenized and SQ from 350° C, an appreciable increase in the as-quenched intensity was observed (above that obtained from LQ). It is also seen that the SQ specimen ages very rapidly during the first few minutes (Fig. 1).

Because the LQ alloy does not age appreciably at room temperature, it was necessary to study ageing kinetics at higher temperatures. The SAXS profiles for various times of ageing at 50 and 75° C

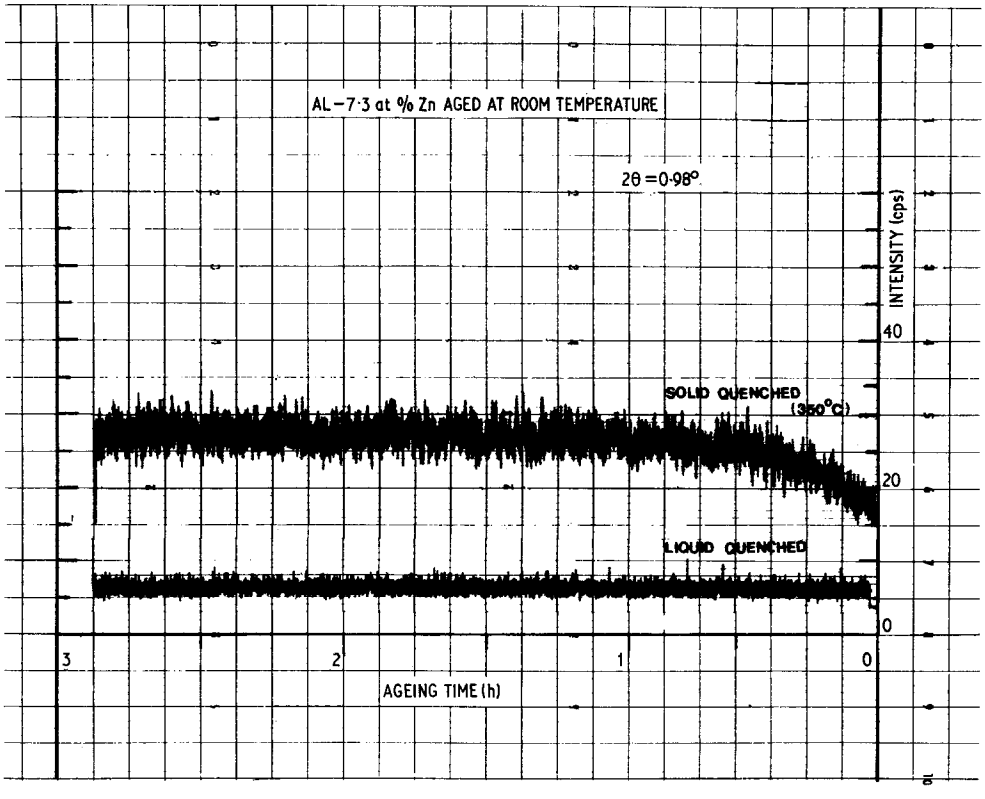

Figure 1 Intensity (counts sec^{-1}) versus time (msec) for LQ and SQ Al–7% Zn aged at room temperature. The scattering angle is 0.98° 2θ.

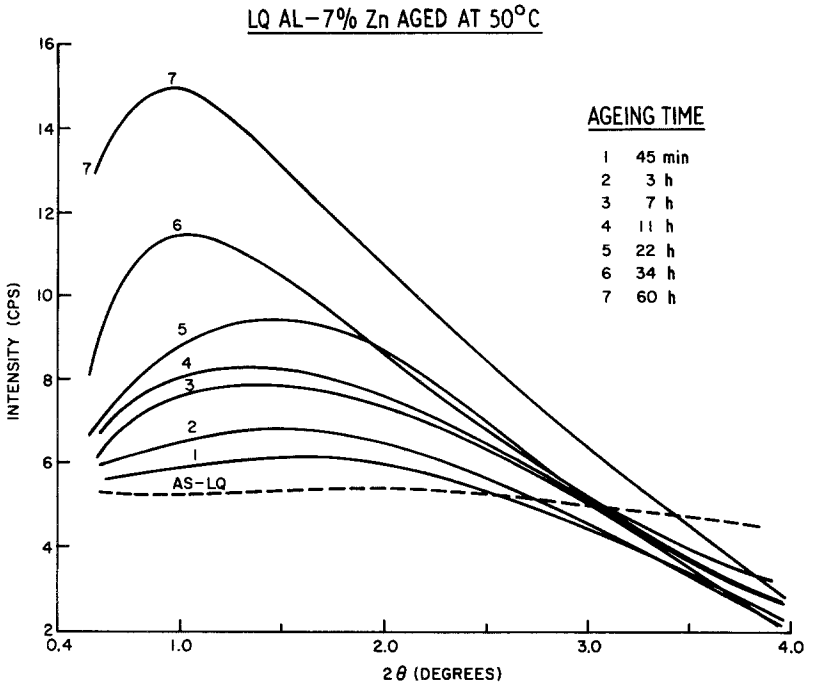

Figure 2 Intensity (counts sec^{-1}) versus 2θ profiles for LQ Al–7% Zn aged at 50° C.

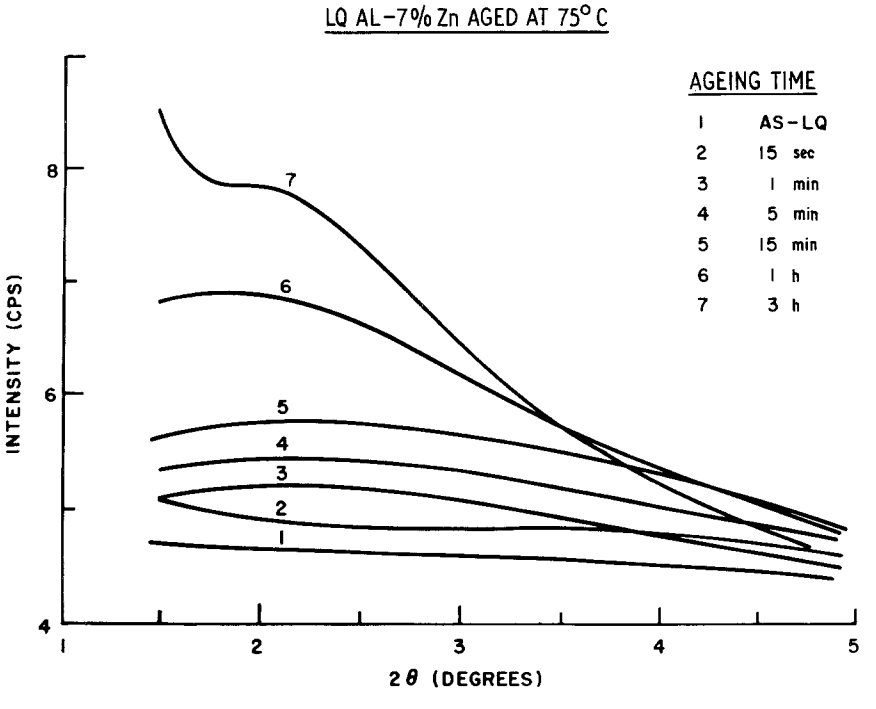

Figure 3 Intensity (counts sec^{-1}) versus 2θ profiles for LQ Al–7% Zn aged at 75° C.

are given in Figs. 2 and 3, respectively. Log I versus θ^2 plots of the above data were used for computing Guinier radii (see Appendix) as a function of time.

The integrated scattered intensity, Q_0, gives a measure of the total volume associated with the new phase. The quantity Q, which is an approximation for Q_0 (see the Appendix), is plotted in Fig. 4 versus time for ageing at 50° C. A monotonic change of Q with time is obtained.

4. Discussion

In a SAXS study of SQ Al–6.8% Zn, Gerold [7] observed that the X-ray intensity scattered to an angle of ~1° 2θ increased by an order of magni-

tude after only 20 min of ageing at ambient temperature. This observation obviously indicates a very rapid decomposition process. From further analysis of his SAXS data, Gerold concluded that the ageing was due mainly to coarsening rather than phase separation. In contrast, based on SAXS measurements, LQ Al–7% Zn undergoes no apparent ageing at room temperature (Fig. 1). However, the same specimen, when SQ, displays a significant increase in the SAXS integrated intensity for ageing at ambient temperature. This indicated very rapid early-stage decomposition. The absence of rapid ageing in LQ specimens, as compared with SQ, can be attributed to a lower concentration of quenched-in mobile vacancies which results on LQ.

At ageing temperatures above ambient, 50 and 75° C (Figs. 2 and 3), the ageing kinetics of the LQ specimens is still considerably slower than for SQ. Table I lists the Guinier radii of the GP zones computed from the LQ data for the 50° C ageing. Also given in Table I, for comparison, are results from other studies for SQ alloys in the same composition range (~7% Zn), and for ageing at temperatures near or below ambient. Guinier radii for the 75° C ageing of LQ Al–7% Zn are presented in Table II. Interesting differences between the results of LQ and SQ are to be noted from these tables: (i) LQ gives an as-quenched zone radius of ~2 to 3 Å as measured at room temperature. This is almost an order of magnitude smaller than that reported for as-SQ specimens by Harkness *et al.* [8] and Gerold [7]. (ii) The as-SQ zone radius of 5 Å reported by Bonfiglioli and Guinier [9] was obtained from specimens SQ from 400 to −54° C, their SAXS measurements being performed at −150° C.

It was pointed out by Bonfiglioli and Guinier [9] that in order to be able to examine early-stage kinetics in GP zone formation, sub-zero ageing and measuring temperatures must be employed. However, it is obvious from their results (Table I) that even sub-zero temperatures cannot eliminate the quench-clustering which will always accompany SQ. On the other hand, as demonstrated in this study, LQ is effective in both greatly limiting quench-clustering and in removing any possibility of early vacancy-enhanced room temperature ageing.

Another characteristic feature displayed by SAXS profiles during ageing of the LQ alloy is a broad intensity versus 2θ plot. Allain and Naudon [10, 11], who studied ageing of SQ Al–6.8% Zn

TABLE I Guinier radii for various ageing times obtained by SAXS (for dilute Al-base Zn)

Authors	Alloy composition	Quenching (T_Q) and aging (T_A) temperatures (° C)	Ageing time (min)	Guinier radius (Å)
Present work	7 at % Zn	LQ	as-LQ	~3.0
		$T_Q = \sim 750$	45	7.6
		$T_A = \sim 50$	180	8.9
			420	8.8
			660	8.7
			1320	10.2
			2040	10.0
			3600	9.8
Harkness *et al.* [8]	7 at % Zn	SQ	5	20.9
		$T_Q = 356$	10	23.0
		$T_A = 25$	20	28.9
			150	31.5
Bonfiglioli and Guinier [9]	20 wt % Zn (9.3 at % Zn)	SQ	0	5.0
		$T_Q = 400$	10	13.6
		$T_A = 45$	30	15.9
			90	15.0
			270	15.3
			810	15.4
			2430	16.4
Gerold [7]	9.0 at % Zn	SQ	36	22
		$T_Q = 350$	72	29
		$T_A = 25$	192	39
			420	51
			1320	60

TABLE II Guinier radii for vaious ageing times at 75° C for LQ Al–7% Zn

Ageing time (min)	Guinier radius (Å)
As-LQ	2.5
0.25	2.5
1.0	2.8
5.0	2.8
15.0	3.5
60.0	5.0
180.0	7.0

by SAXS, contend that such broad intensity profiles are observed when GP zones develop from the products of spinodal decomposition. The spinodal temperature for the 7% Zn alloy is 129° C. Therefore, if significant quench-clustering can be avoided during the quench, the first mode of decomposition during early ageing is likely to be the spinodal process. It is, of course, to be noted that there is no apparent direct evidence of the spinodal mode to be seen from the evolving intensity profiles of this study. In a LQ 22% Zn alloy, Agarwal and Herman [4] observed spinodal decomposition. Here it can only be concluded that GP zones are forming, and no more definite statement can be made based on the present data.

According to Porod [12], during the growth of particles with sharp interfaces, the "tail region" (i.e., the higher angle region) of the SAXS profiles will follow a $I \propto \theta^{-3}$ relationship. In the present study this is not found to be the case, the measured powers of θ for 50° C ageing ranging between −0.8 and −1.4. Therefore, it is believed that the present data do not correspond to the growth of sharp-interfaced particles. If the ageing observed in LQ Al–7% Zn is due to phase separation (as opposed to a coarsening reaction), then the integrated intensity, Q_0, should increase monotonically with ageing time. In the absence of Porod behaviour (see Appendix) simplification of the integral for Q_0 becomes impossible. Therefore, we have used an approximate method which is often employed in such a situation. As seen from Fig. 4 for 50° C ageing, the integral Q increases monotonically with time. It can only be concluded that since the effective integrated intensity is changing, the solution is decomposing, and coarsening is not the major process responsible for the observed evolution of the spectra.

The slow ageing kinetics which are noted here for LQ Al–7% Zn are consistent with previous results on Al–Si [3] and Al–Ag [4]. It is concluded that LQ gives fewer quenched-in mobile vacancies, with the result that vacancy-enhanced room temperature ageing is not observed.

One final point relative to the evolution of the X-ray scattering profiles observed here. As indicated above, it is our belief that the alloy studied here is not within the coherent spinodal region. Thus, linear behaviour would not be expected to occur. Under the circumstances there is little definitive that can be said about the peak end cross-over positions of Figs. 2 and 3.

5. Conclusions

LQ yields an extremely homogeneous solid solution in Al–7% Zn. Also, the LQ alloy, as observed previously in aluminium alloys, retains lower concentrations of quenched-in mobile vacancies; consequently, the kinetics on subsequent ageing is much

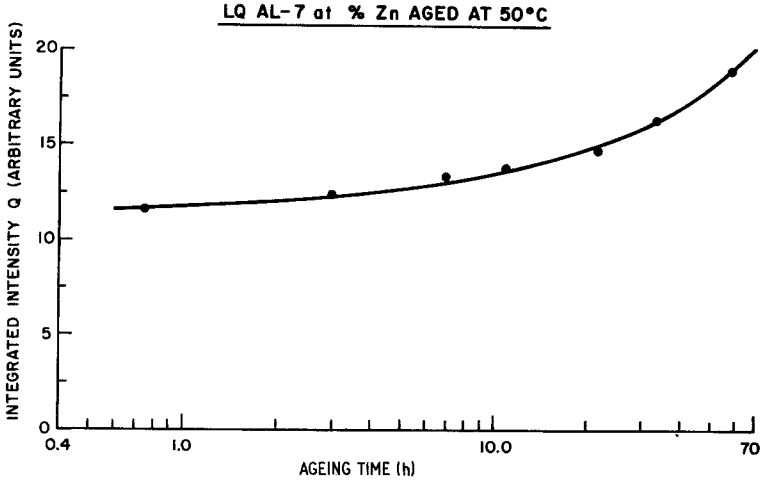

Figure 4 Integrated intensity (Q) versus time (h) for LQ Al–7% Zn aged at 50° C. See Appendix.

slower for the LQ specimens as opposed to SQ. The present results demonstrate the utility of LQ for studying the early-stage phase separation.

Appendix

From analyses of the SAXS spectrum, one can frequently extract information about size, shape, size distribution of the particles, extent of decomposition, atomic concentrations inside and outside the particles and limits of the metastable miscibility gap [13]. The last two quantities require absolute intensity measurements. The SAXS method has been very useful in studies of GP zones. A size parameter, which can be derived from experimental SAXS profiles and frequently used in the study of GP zones, is the "Guinier radius". The Guinier approximation assumes that the scattering curve for spherical particles has a Gaussian shape. The Guinier radius, R_s, is given by:

$$I(\bar{h}) \propto \exp \frac{(-4r^2 h^2 R_s^2)}{5} \qquad (1)$$

where $I(\bar{h})$ is the scattering function or X-ray intensity for line collimation and $\bar{h}$ is the reciprocal lattice vector, $|\bar{h}| = \frac{2 \sin \theta}{\lambda}$. 2θ is the scattering angle and λ is the wavelength of the X-rays. In Equation 1 R_s is the radius of a homogeneous sphere and it is related to the radius of gyration, R_g, by

$$R_g^2 = \tfrac{3}{5} R_s^2 \qquad (2)$$

A useful parameter obtained from the SAXS profiles is the integrated intensity, Q_0, which can be used to monitor the extent of decomposition (or changes in volume fraction);

$$Q_0 = 4\pi t_0 \int_0^\infty hI(h)\mathrm{d}h \qquad (3)$$

where $2t_0$ is the length of the primary beam.

In the beginning of the phase separation process, Q_0 increases with time, but when the coarsening process starts to predominate, Q_0 approaches a constant value. At this stage, according to Porod [12], the tail-end of the scattering curve should follow $I(\bar{h}) \propto h^{-3}$ or θ^{-3} relationship. This relationship at higher scattering angles [yet still within the SAXS region (e.g., $<15^\circ$ 2θ)] is referred to as "Porod behaviour".

For our Al–7% Zn SAXS data, measured powers of θ for the 50° C ageing vary between −0.8 and −1.4, instead of −3.0. This departure from Porod behaviour makes it impossible to simplify the integrated intensity integral in Equation 2. Therefore, an approximate method for evaluating this integral is employed. The cut-off limits for the integral in Equation 2 were chosen at the value of the scattering angle where measured SAXS intensities (after correction) dropped off to the background level. The approximate integrated intensity, Q, thus obtained, by measuring the area under $I \times 2\theta$ versus 2θ curves, was used in predicting the extent of decomposition in the Al–7% Zn alloy.

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