

A STUDY OF PHASE DECOMPOSITION  
IN LIQUID-QUENCHED ALUMINUM-SILVER ALLOYS

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The aluminum-silver phase diagram is shown in Fig. 1. Gerold (1) has established that the concentration of silver in the zones is controlled by a metastable miscibility gap which is totally submerged within the equilibrium phase diagram. Of interest is the fact that the gap is inaccessible by bulk solid quench for a considerable composition range. Since the gap reaches the relatively high temperature of 450°C, quenching speed is of primordial importance for the preservation of a high temperature state. Quenching from the liquid has then great appeal for this system.

A study of the as liquid-quenched (LQ) condition and its decomposition is presented. The specimens were quenched using either the Duwez-gun technique or the torsion-catapult. The retention of a single phase was initially examined with X-ray-Debye-Scherrer and transmission electron microscopy. The Debye-Scherrer results are shown in Fig. 2. The lattice parameters were obtained using the Nelson-Riley extrapolation. The lattice parameter composition relation is not linear but increases fairly rapidly up to 14 at.% after which the lattice parameter is nearly constant. Compared with the literature values, our results of lattice parameters are the highest with the exception of those of Simerska (2) and Guljaev and Trusova (3) which show a positive deviation from Vegard's relation. The experiments of Guljaev and Trusova are subject to serious doubt according to Pearson (4) who remarks that similar measurements by the same authors also disagree with other recent work. On the other hand, the values of Simerska were determined at high temperatures and extrapolated to room temperature. Two interesting observations can be made: 1) there appears to be a pattern, i.e. the higher the quenching

rate, the higher the value of the parameters. Clustering would be reflected in a change of lattice parameter corresponding to a loss of solute. Since the lattice parameter increases with solute, the difference in lattice parameter between fast quench and slow quench should be positive for a clustering reaction. Our results are then indicative of the superiority of the IQ technique over bulk quenching in minimizing clustering; 2) a considerable extension of solid solubility is observed, result also confirmed by Dixmier and Guinier (5).

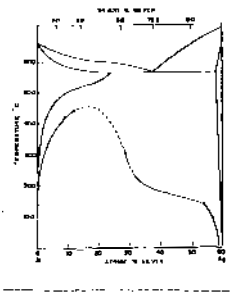


FIG. 1

Al-Ag phase diagram

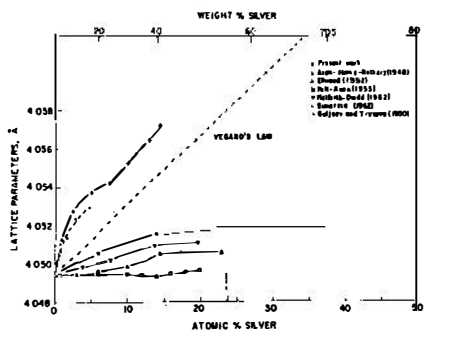


FIG. 2

Lattice parameters versus composition

Typical microstructures for the Al 20 wt % Ag are shown in Fig. 3. In all cases a single FCC phase was observed. The grains are elongated and the grain boundaries apparently free of precipitates. The examination of IQ Al 40 wt % Ag, Fig. 4, gave similar results - apparently only a single FCC phase. Examples of micrographs for the eutectic, Al 70.5 wt % Ag, are seen in Fig. 5. Even in the thinnest sections the grain boundaries contain some form of precipitate. In the highly concentrated Al 80 wt % Ag alloy a dendritic-type structure is observed, Fig. 6. The tree-like pattern has a spacing of approximately 1200 to 1600 Å. The edges of the torsion-catapult foils were also sufficiently thin and the results were similar to those using the gun technique. Electron microscope observations not only confirm the X-ray results but also give information on the structure; i.e., grain size, shape, orientation and defect distribution.



FIG. 3

Electron micrographs  
from Al 20 wt.% Ag



FIG. 4

Electron micrographs  
from Al 40 wt.% Ag



FIG. 5

Electron micrographs  
from Al 70.5 wt.% Ag



FIG. 6

Electron micrographs  
from Al 80 wt.% Ag

The preliminary observations using Debye-Scherrer and electron microscopy indicate that we are apparently successful in preserving a single phase by quenching from the liquid. However, these techniques are insensitive to small scale decomposition. SAXS studies were undertaken to qualify the observations of single phase material. If the logarithm of the intensity is plotted versus  $\epsilon^2$  (the Guinier's plot), Fig. 7, the slope of the line can be used to determine the radius of the scattering regions or particles. It is observed that the plots are not linear, an indication that the system contains a distribution of particle sizes. Jelinek et al (6) have suggested a graphical method for analyzing the data. The approach is simple but sufficient for the present use. The distribution is approximated by a set of discrete fractions. A tangent is drawn to the experimental curve at the largest measured angle; a new curve not containing the contribution of this fraction is obtained by subtracting from the original curve the values of the tangent. The SAXS results are summarized in Table 1. The particle size distribution is considerably narrower in specimens quenched from the liquid than from the solid.

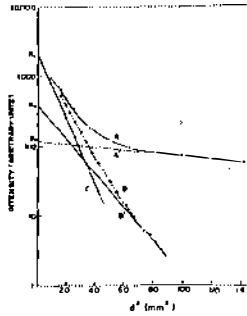


FIG. 7  
Illustration of the  
graphical decomposition

TABLE 1  
Summary of Calculations

Condition	Radius ( $\text{\AA}$ )	Weight Fraction	Number Fraction
<u>SOLID-QUENCHED</u>	7.4	0.15	0.98
550°C → Brine (-22°C)	20.9	.60	.015
	26.8	.25	.005
<u>LIQUID-QUENCHED</u>			
1) substrate 320 grits	8.1	0.56	0.97
temperature 40°C	18.7	.15	.02
	26.6	.29	.01
2) substrate sand blasted	6.4	0.96	0.996
temperature 40°C	15.2	.04	.004
3) substrate sand blasted	5.6	0.95	0.99
temperature 12°C	13.7	.05	.01

Following the analysis of the as-quenched condition, the decomposition of the torsion-catapult specimens was investigated using electrical resistance, high-angle X-ray and SAXS.

The empirical analysis of the electrical resistance and high-angle X-ray work will not be reported here but the results briefly summarized. The estimate of the activation energy from the resistance data in the temperature range 110 to 175°C,  $20.0 \pm 2.0$  K cal/mole is in fair agreement with the literature results. The apparent activation energy obtained from X-ray study at 150 and 175°C,  $27.0 \pm 2.0$  K cal/mole is also near the values of similar studies previously reported.

Finally the Al 40 wt % Ag was investigated for the presence of a spinodal mode of decomposition. The Rindman-Hilliard analysis (7) of the

SAXS spectra, the only available reliable test for spinodal was applied. The analysis will not be reproduced here but the necessary plots are shown schematically in Fig. 8. The natural logarithm of the measured intensity plotted against time should be linear with a slope of  $2R(\beta)$ . Then when the amplification factor,  $R(\beta)$ , is plotted against  $\beta$ , a maximum and a critical value of  $\beta$  are obtained. The plot of  $R(\beta)/\beta^2$  versus  $\beta^2$  should be linear.

The temperature range 50 to 175°C was investigated. The spectrum of  $R(\beta)$  versus  $\beta$  is shown for only one temperature, 150°C, in Fig. 9. The more stringent test of the theory is in the linearity of the plot  $R(\beta)/\beta^2$  versus  $\beta^2$  shown in Fig. 10. The observed relationship is definitely not linear. Our proposal to explain the deviation from "ideality" is that two paths of decomposition are occurring simultaneously. The apparent curvature is then due to the sum of two linear sections. The two modes of decomposition were not observed during aging of the SQ specimen.

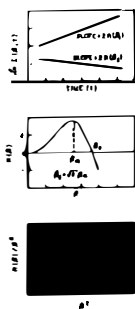


FIG. 8

Schematic representation of Rindman-Hilliard analysis

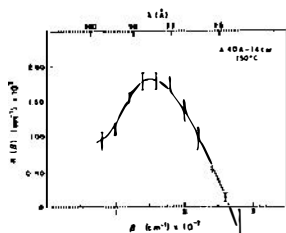


FIG. 9

$R(\beta)$  versus  $\beta$ ,  
LQ Al 40 wt. % Ag  
aged at 150°C.

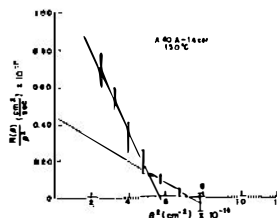


FIG. 10

$R(\beta)/\beta^2$  versus  $\beta^2$ ,  
LQ Al 40 wt. % Ag  
aged at 150°C.

#### References:

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2. M. Simerska, *Czech. J. Phys.* **12**, 54 (1962).
3. A. P. Guljaev and E. F. Trusova, *Structure Reports*, **13**, 6 (1950).
4. W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 1, Pergamon Press (1958).
5. J. Dixmier and A. Guinier, *Mem. Scient. Rev. Metal.* **64**, 53 (1967).
6. M. H. Jellinek et al. *Ind. Eng. Chem. Anal. Ed.* **18**, 172 (1946).
7. K. B. Rindman and J. E. Hilliard, *Acta Met.* **15**, 1025 (1967).

## DISCUSSION

- R.W. Cahn : What is the "Torsion - catapult" ?
- R. Roberge : The torsion-catapult, details of which will be found in the literature (*Materials Science and Engineering* 3, 62 (1968)), is a technique in which the liquid is propelled by a catapult out of a curved furnace and into a copper ski-slide substrate.
- A. Guinier : 1. The verification of Cahn's theory relies on approximations valid for the very first stages of precipitation. Unfortunately in that stage, measurements of diffracted X-ray intensity are difficult because they are very small.
2. It is not correct to use the  $(\log I - \xi^2)$  plot in a quantitative way outside of the initial linear regions.
- R. Roberge : 1. The comment of Prof. Guinier on the verification of Cahn's theory is well appreciated. The intensities were small and the linearity of the logarithm of the intensity versus time was only of the order of 75 sec at 150°C for example. The point to keep in mind is that we do have strong evidence for spinodal decomposition even if the small deviations from "ideality" are not fully explained.
2. The simple graphic method for the analysis of the  $(\log I - \xi^2)$  plot was only for qualitative comparison of the size distribution in liquid and solid quenched specimen.