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Spinodal Decomposition in Al/Zn Alloys

Part 3 *Metallography and Electron Microscopy*

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Decomposition of the quenched spinodal structure in Al/Zn alloys containing from 30 to 60 wt % zinc occurred by discontinuous zinc precipitation in the grain-boundaries followed by precipitation of zinc colonies within the grains. Precipitate morphology differed when solution-treated at 365 as compared to 435° C.

Fracture of tensile samples having the spinodal structure was intergranular with but one exception, cold-rolled spinodal structures.

Transmission electron microscopy showed significant variation in the size and density of dislocation loops depending upon solution-treatment and ageing conditions. Numerous helical dislocations were also observed. Individual dislocations generally were long and straight. The observed structures are analysed in terms of existing models for vacancy behaviour in alloys.

1. Introduction

It was pointed out in the first paper of this series [1] that spinodal decomposition offered a potential mode of strengthening that has not been exploited to date. Significant strengthening was observed in Al/Zn alloys over the range of 30 to 60 wt % zinc. The present paper summarises metallography and electron microscopy performed on the alloys for which mechanical property data were determined. In particular it was of interest to discern the dislocation structure of these alloys in order to apply Cahn's theoretical treatment of spinodal strengthening [2].

2. Experimental Procedures

Preparation of the alloys as well as the various ageing treatments were described in the first paper of the series [1].

Conventional metallographic techniques were employed. Samples were cold-mounted in order to prevent ageing. An etchant of 95% H_2O, 1% HF, 1.5% HCl, 2.5% HNO_3 was used throughout.

Thin foils for electron microscopy were prepared by electropolishing 0.0050 in. thick sheet in 90% acetic acid/10% perchloric acid at −30° C and 12 V. An aluminium cathode was used.

3. Results

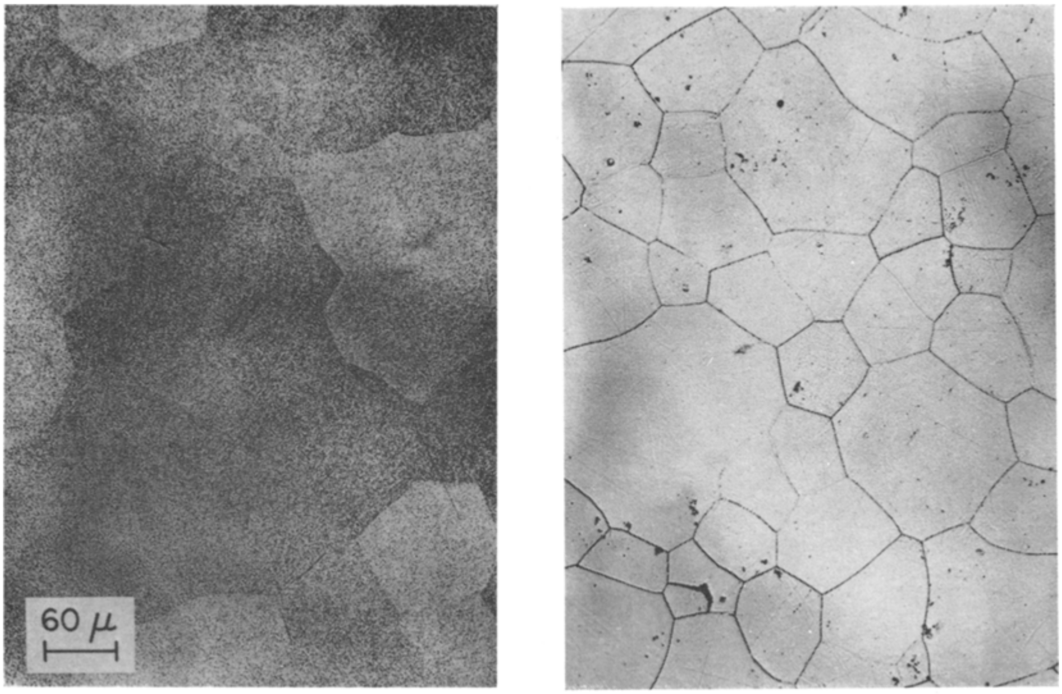
3.1. Metallography

3.1.1. Binary alloys

The microstructures of quenched alloys depended on the zinc content, because decomposition of the high-zinc alloys occurred quickly at room temperature. The low-zinc alloys, 30 and 38.5% Zn, appeared as single-phase, equiaxed structures, whereas the high-zinc alloys, 50 and 60% Zn, contained some discontinuous zinc precipitation by the time the samples could be prepared for metallography.

The structure of the quenched solid solution in 38.5% Zn is shown in fig. 1a. There is no zinc present, and the single-phase solid solution has a definite mottled appearance. Ageing of this alloy for 960 min at 100° C, (fig. 1b) resulted in the start of zinc precipitation at the grain-boundaries.

The 38.5% Zn alloy exhibited variable etching characteristics depending upon the ageing temperature (see fig. 1). The sample aged at 22° C was mottled; the X-ray pattern showed a



(a) (b)

Figure 1 Microstructure of Al/38.5% Zn quenched from 435° C. (a) Aged 1100 min, 22° C (bright field); (b) aged 960 min 100° C (bright field).

spinodal sideband [3]. The sample aged 960 min at 100° C was not mottled, and the sideband was not apparent in the diffraction pattern.

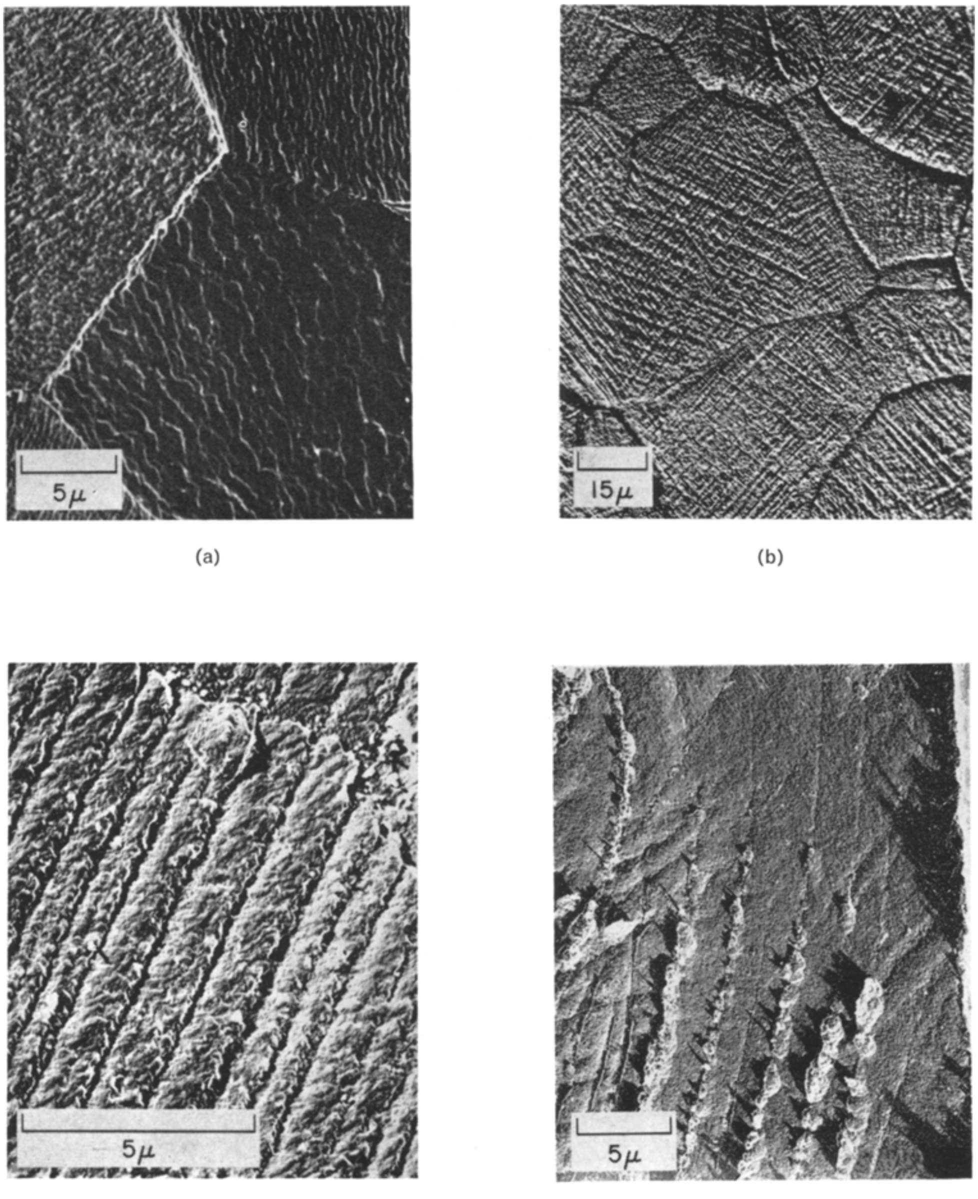
The structure of Al/38.5% Zn also was influenced by the extent of deformation. The sample shown in fig. 1a was examined both near the fracture surface and away from the fracture. A high density of slip bands existed in the deformed area. The slip bands were obviously decorated in some fashion, otherwise they would not have, been visible on the polished and etched surface. The structures in different regions are compared in fig. 2.

The precipitation of zinc during ageing can be seen in 50% Zn in fig. 3. The 10-min sample consisted of a mottled single-phase matrix of the quenched, metastable solid solution plus a trace of discontinuous zinc precipitation in the grain-boundaries. Increasing the ageing time caused more discontinuous precipitation in the boundaries, and after 25 min some zinc precipitation was observed in the grains in the form of rosettes or colonies. After ageing for 100 min, the sample was about 80 to 90% transformed with only small islands of matrix remaining.

Some typical microstructures of the 60% Zn alloy solution-treated at 435° C and aged at 100° C are shown in fig. 4. The short-time sample in the hardened condition (fig. 4a) consists of discontinuous precipitate at some of the grain-boundaries and a very fine continuous precipitate within the grain. The same sample after three weeks at room temperature was repolished and re-examined (fig. 4b). The general precipitate still existed within the grains, but a colony-type structure formed during the long-time ageing. The change in hardness of this sample was from DPH 168 to DPH 72.

A longer ageing (8 h) at 100° C resulted in the structure shown in fig. 4c. There was little discontinuous precipitate, and the continuous precipitate had coarsened markedly.

The nature of the deformation process was also studied in Al/60% Zn by compressing quenched samples that had been polished and etched. Fig. 5 shows an area that was photographed before deformation and after varying degrees of compression. Work-hardening was seen in the load-



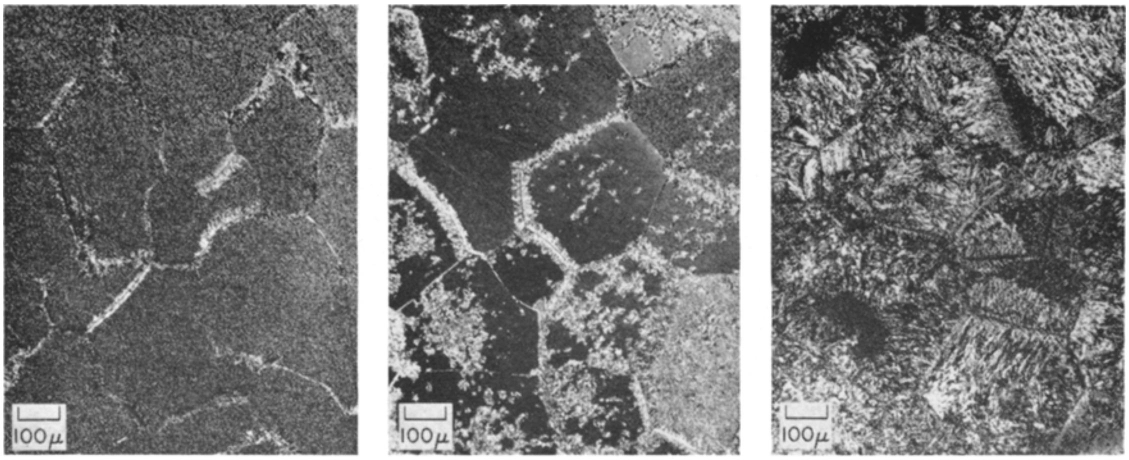
(a) (b) (c) (d)

Figure 2 Effect of deformation on the microstructure of Al/38.5% Zn quenched from 365° C. (a) Region away from fracture; (b) region near fracture; (c) region near fracture; (d) region near fracture.

elongation curves of samples that had not decomposed to the equilibrium products. This behaviour is indicative of inhibition of cross-slip, although some may be noticed in the large grain on the left side of fig. 5b. Heavy deformation, however, was sufficient to cause cross-slip (fig. 5c).

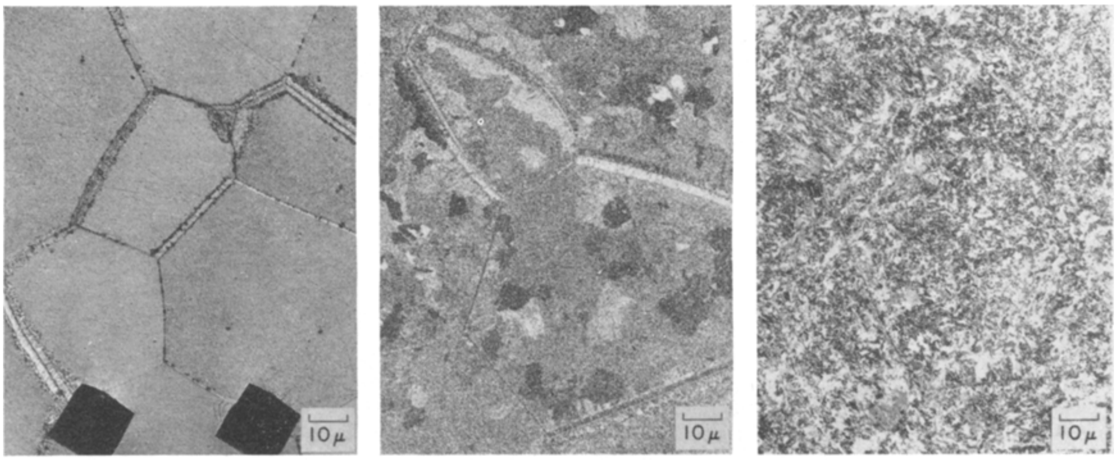
3.1.2. Ternary and Hybrid Alloys

Al/38.5% Zn/2%Cu was reported as having the highest ductility, about 6 to 8% elongation, for high strength levels [1]. The structure of this material after it was solution-treated at 435° C and quenched to 22° C is shown in fig. 6. The matrix was an equiaxed, metastable solid solu-



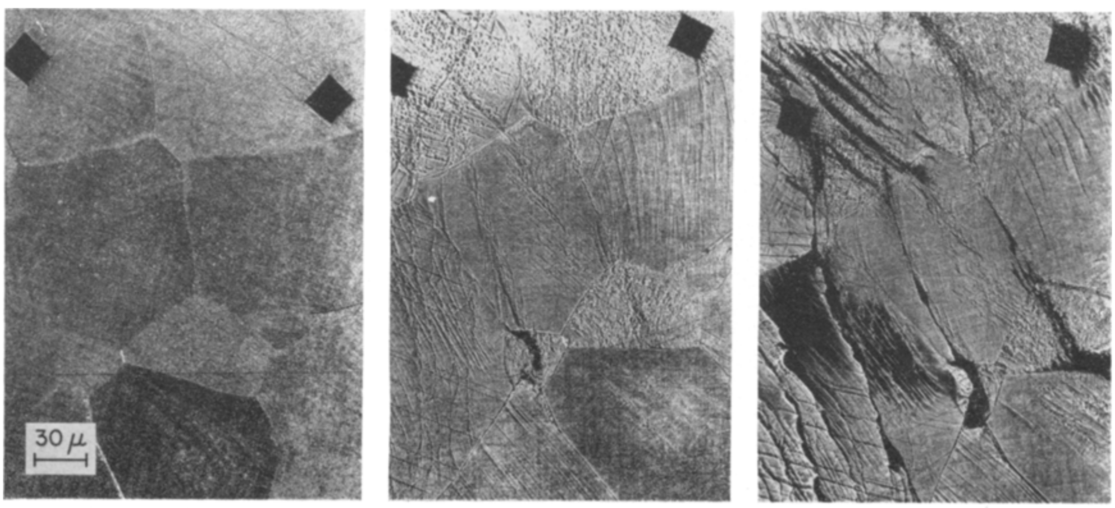
(a) (b) (c)

Figure 3 Decomposition of Al/50% Zn quenched from 435° C and aged at 100° C. (a) 10 min; (b) 25 min; (c) 100 min.



(a) (b) (c)

Figure 4 Microstructure of Al/60% Zn solution-treated 1 h at 435° C, aged at 100° C. (a) 2 min, 100° C; (b) 2 min 100° C, + 3 weeks, 22° C; (c) 8 h, 100° C.



(a) (b) (c)

Figure 5 Surface deformation markings in Al/60% Zn compressed at 22° C (sample quenched from 435° C) (a) Before deformation; (b) lightly compressed; (c) heavily compressed.

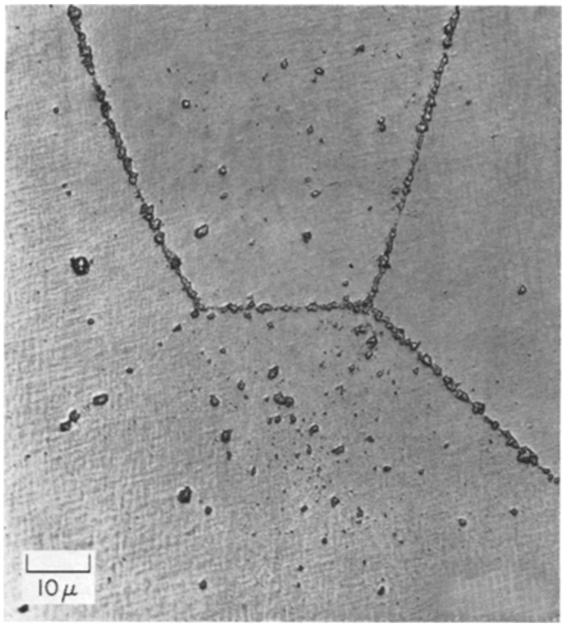
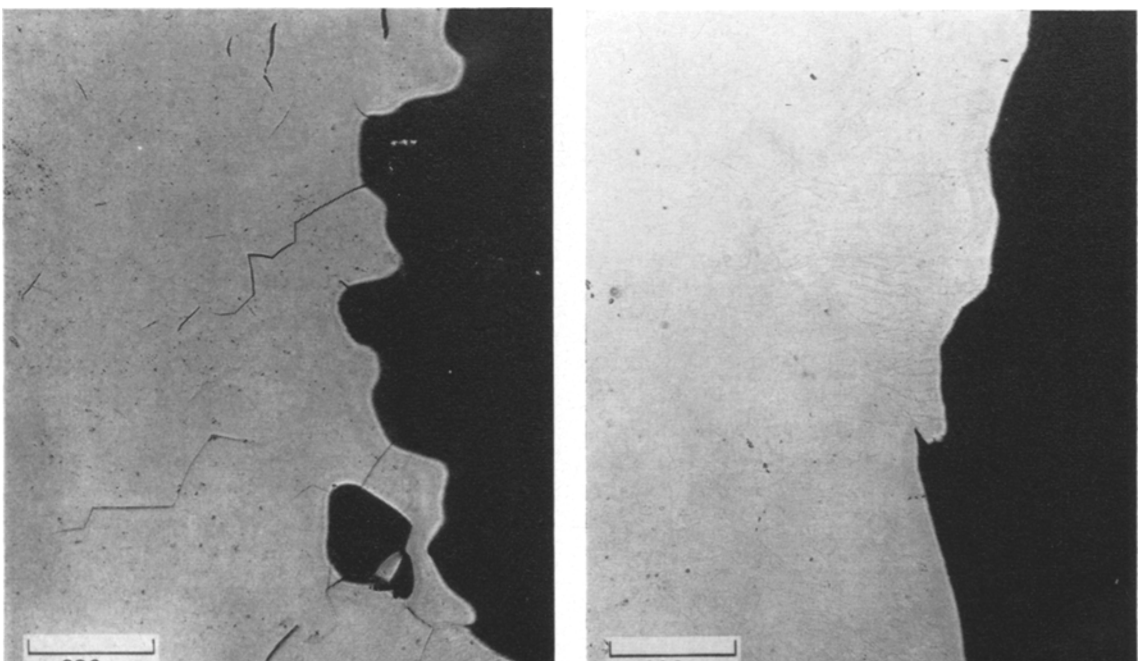


Figure 6 Structure of Al/38.5% Zn/2% Cu solution-treated 1 h at 435° C and quenched to 22° C.



(a) (b)

Figure 7 Fracture characteristics of Al/38.5% Zn/2% Cu solution-treated 1 h at 365° C and quenched to 22° C. (a) As-quenched; (b) cold-rolled 60%.

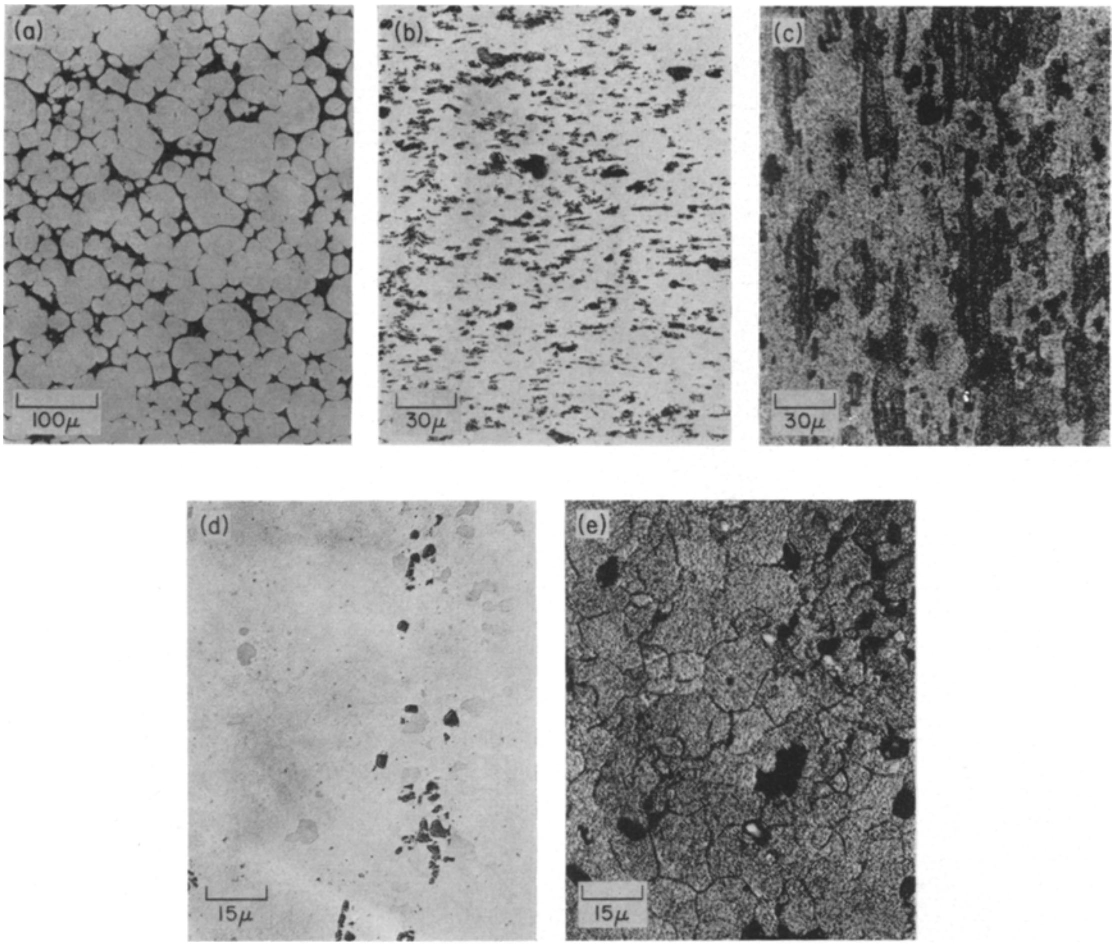


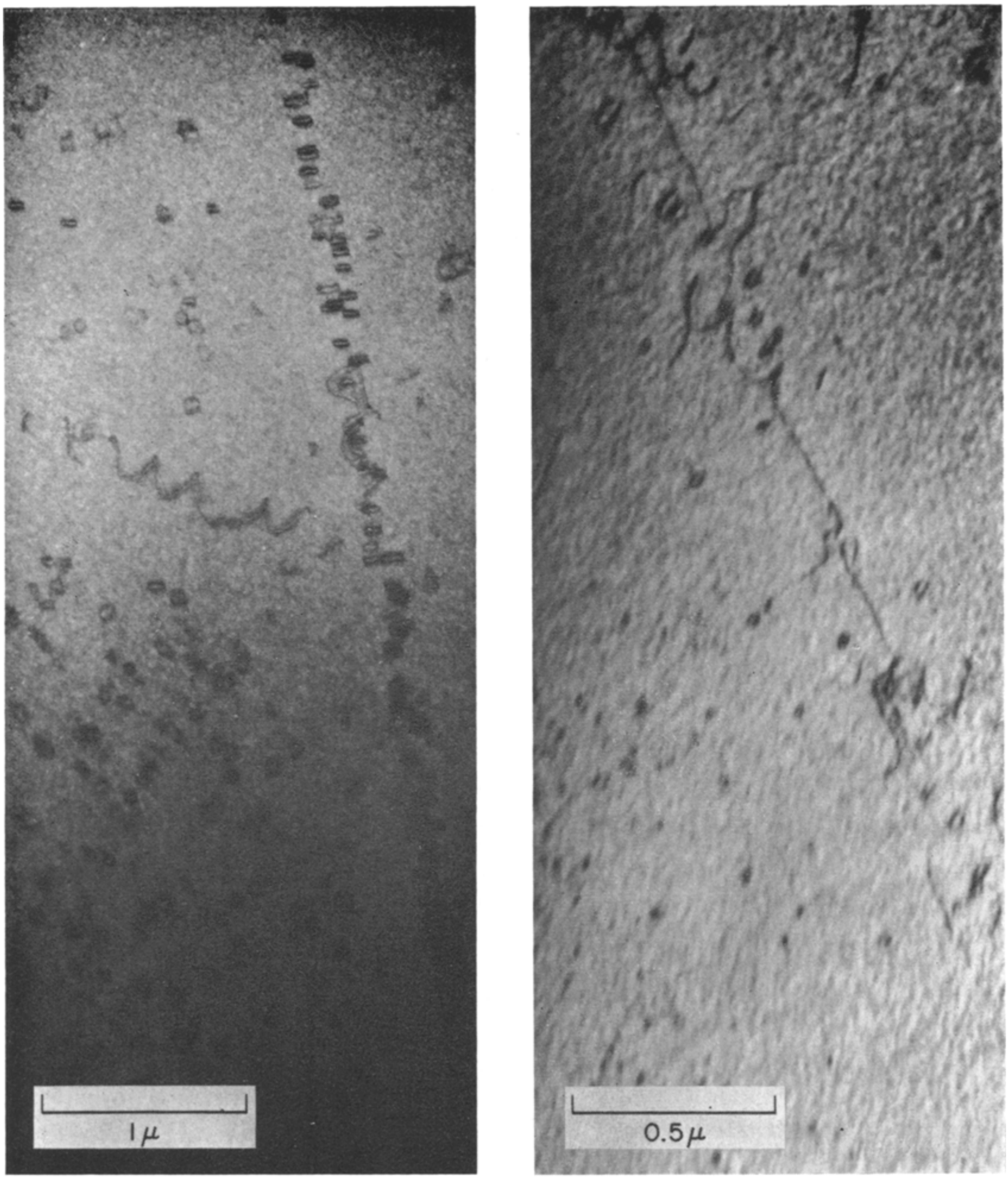
Figure 8 Structure of hybrid alloys (a) Solution-treated 1 h, 435° C; (b) solution-treated 1 h, 365° C, unetched; (c) solution-treated 1 h, 365° C, etched; (d) solution-treated 18 h, 365° C, unetched; (e) solution-treated 18 h, 365° C etched.

tion with grain-boundary as well as general precipitation of a second phase. The precipitation formed during solution-treatment because this alloy was still within the two-phase region at that temperature. A higher temperature would have dissolved all of the copper, but the ternary solvus for this system was probably between 450 and 475° C.

A very fine basket-weave structure is apparent in the matrix. The regularity of this structure suggests that it is related to the modulated structure of the spinodally transformed alloy.

The fracture characteristics changed from intergranular to transgranular after cold-rolling 60%. Fracture sections of quenched and of cold-rolled samples are shown unetched in fig. 7.

Cold-working induced a precipitation of a second phase which on the basis of only one X-ray diffraction peak could be identified as zinc. On the other hand, there were no peaks other than aluminium peaks in the quenched sample shown in fig. 6; the morphology of the precipitate was not that of zinc. Considering the solvus line of the Al/Cu system, one could conclude that the precipitate was most likely the tetragonal θ intermediate phase. The second phase also existed in samples quenched from 365° C, but it was much smaller in size. Although the second phase was readily observed micrographically, there was not enough present to give an X-ray pattern. The intensity of the (1 0 1) Zn peak in the cold-worked samples was sufficient for identifica-

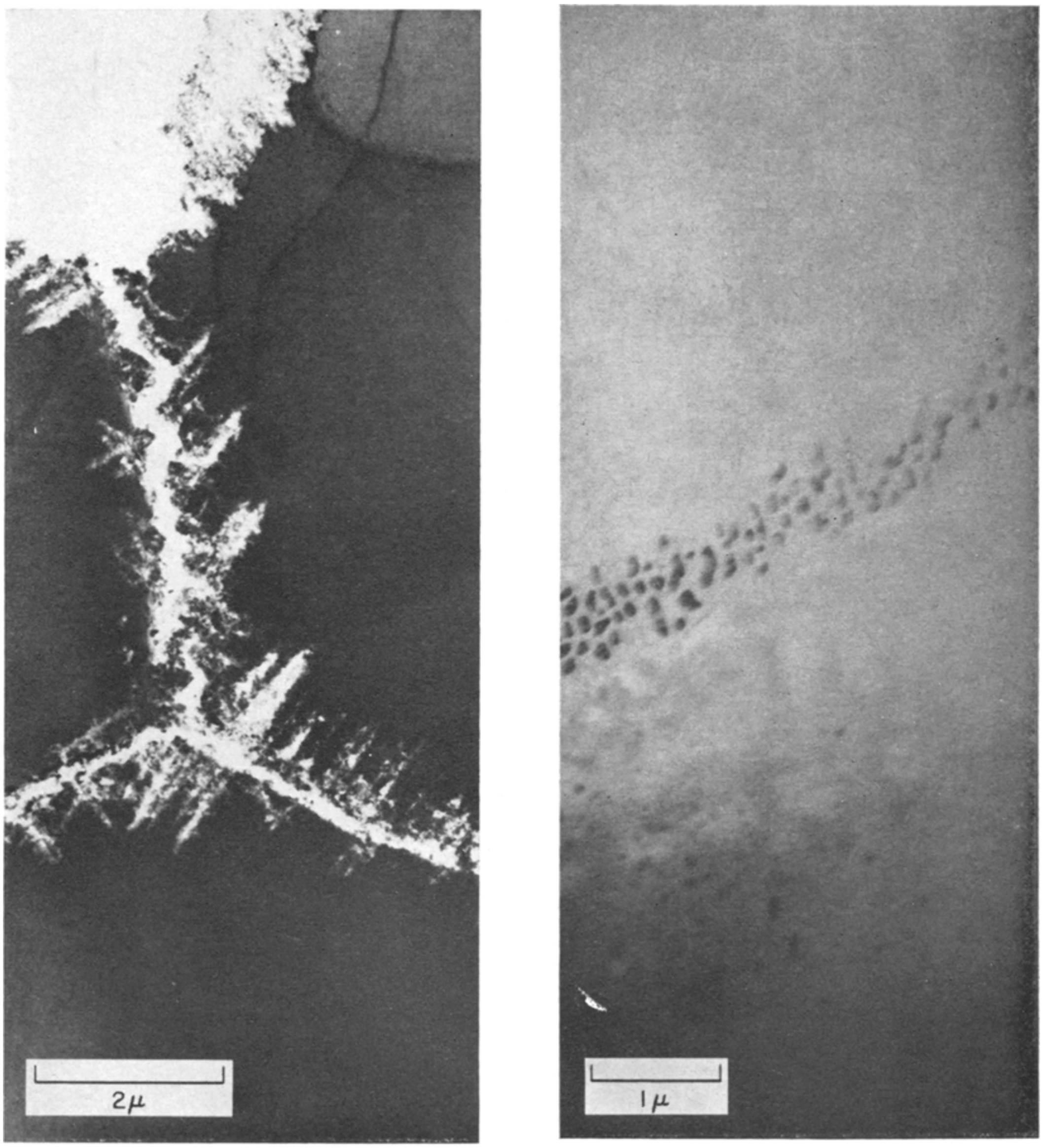


(a) (b)

Figure 9 Structure of Al/38.5% Zn aged at 22° C, showing dislocation loops and helices. (a) Solution-treated at 365° C; (b) solution-treated at 435° C.

tion; this peak was not present in the quenched samples.

The hybrid alloy, fabricated from 7075 Al with 38% Zn, could not be solution-treated at 435° C due to hot shortness (fig. 8a), and 365° C was insufficient to dissolve all of the alloying constituents (fig. 8b and c). The solution-treatment was insufficient to permit complete recrystallisation, as is shown by the elongated grains that resulted from the fabrication operation. Longer time at



(a) (b)

Figure 10 Effect of temperature on precipitate morphology in Al/38.5% Zn. (a) 365° C; (b) 435° C.

the solution temperature (18 h compared to 1 h enabled the matrix to recrystallise but did not dissolve the two types of intermetallic compounds (fig. 8d and e).

3.2. Transmission Electron Microscopy

Electron microscopy of Al/38.5% Zn aged at a given temperature showed little difference in the structure of samples solution-treated at 435° C and those treated at 365° C. The backgrounds were mottled and contained an extremely fine structure that could not be resolved. A high density of dislocation loops existed (fig. 9), and numerous helical dislocations were present. The collapsed loops were less dense in the vicinity of helices, as is to be expected.

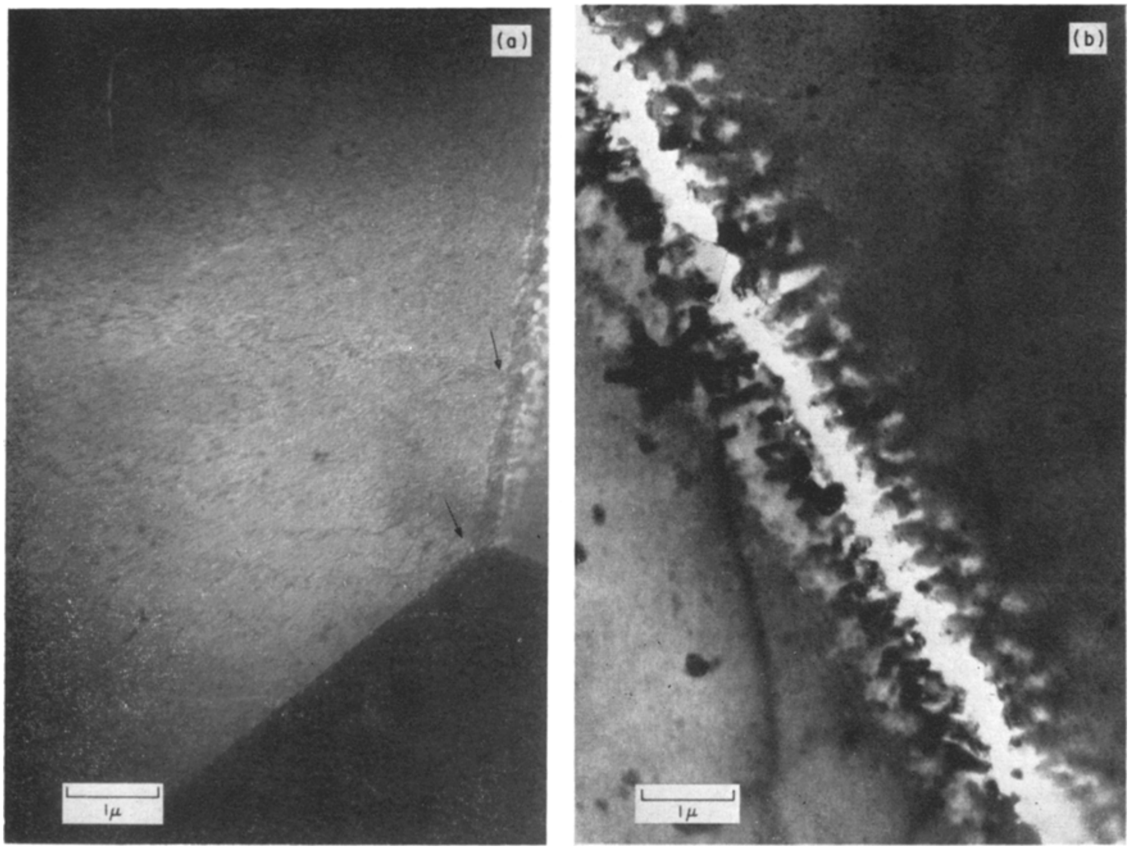


Figure 11 Various grain-boundary areas in Al/38.5% Zn quenched from 435° C and aged for 2000 min at 22° C. (a) Dislocation sources emanating from the grain-boundary precipitates; (b) selectively attacked grain-boundary.

Grain-boundaries were generally clean, although occasional precipitates were observed. The nature of the precipitate did depend upon the solution-treatment temperature, e.g. samples treated at 435° C contained small precipitate particles scattered along some of the boundaries. On the other hand, samples treated at 365° C exhibited the discontinuous type of precipitate that nucleated at grain-boundaries and grew laterally into the grains. These two types of precipitate can be seen in fig. 10. A relatively clean boundary and a selectively attacked boundary containing much precipitate are shown in fig. 11. Numerous dislocation sources were also found in the boundaries, as is indicated by the arrows. It was thought that the sources were active during the quench because of thermal stresses generated upon cooling.

The structure shown in fig. 10a is shown in more detail in fig. 12. Selected-area diffraction shows that the fan-like, discontinuous structure was zinc, and the matrix was an Al/Zn solid solution.

Ageing at 100° C after solution-treatment at either 365 or 435° C caused some precipitation within the matrix (fig. 13), as well as in the grain-boundaries. A dark field image is also shown. The precipitates were strongly diffracting for the spot circled in the selected-area diffraction pattern. Grain-boundary precipitation generally resulted in a narrow denuded zone adjacent to the boundary.

Cold-working by rolling 10%, resulted in grain matrices that contained very high dislocation densities which were not resolvable (fig. 14a). The grain-boundaries were much different from those in any of the other samples (fig. 14b) and may have contained some discontinuous zinc precipitate caused by rolling. The polishing characteristics of the cold-rolled foils were very

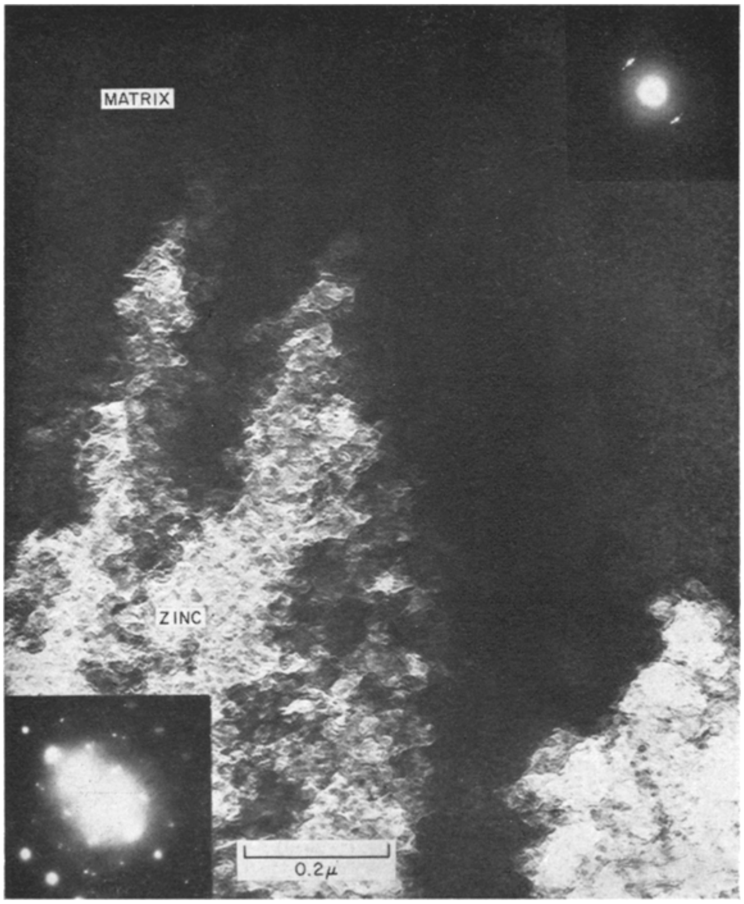


Figure 12 Structure of discontinuous zinc precipitate present in Al/38.5% Zn solution-treated at 365° C.

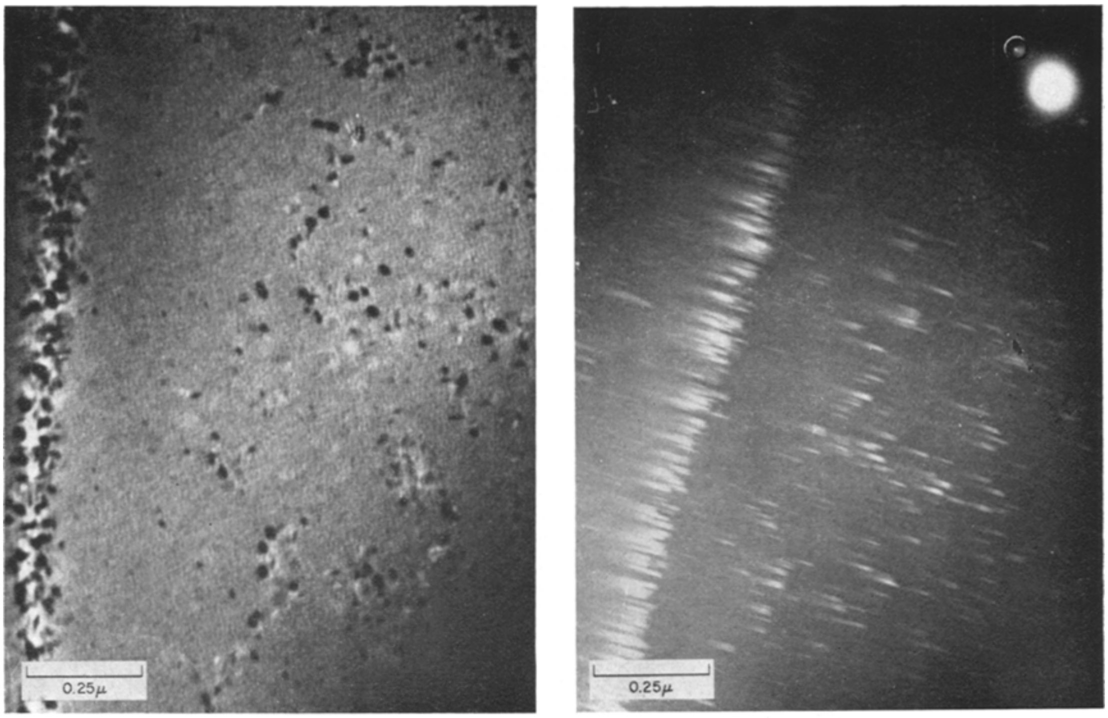
different from those of the quenched and aged foils, and the foils were generally difficult to prepare.

In many respects the structure of Al/30% Zn was similar to that of Al/38.5% Zn, although certain differences were apparent. A comparison of dislocation loop size in Al/30% Zn resulting from different solution-treatment temperatures is shown in fig. 15. The loops in samples quenched from 435° C were resolved (fig. 15a) and were of the order of 200 to 300 Å, whereas the loops formed in samples quenched from 365° C could not be resolved (fig. 15b).

Ageing for 200 min at 100° C after quenching from 365° C resulted in some fine grain-boundary precipitates which were preferentially etched out during electropolishing (fig. 16a). The grain-boundaries acted as dislocation sources, as is shown in fig. 16b. The grain-boundary precipitates were not selectively attacked in this foil. Dislocations were generally fairly straight and long, as fig. 16c shows. They were probably formed from the grain-boundary sources during quenching. There was no matrix precipitation in Al/30% Zn in contradistinction to Al/38.5% Zn subjected to the same treatment (fig. 13). Zinc precipitation took longer in Al/30% Zn and was not readily apparent until after 1000 min of ageing.

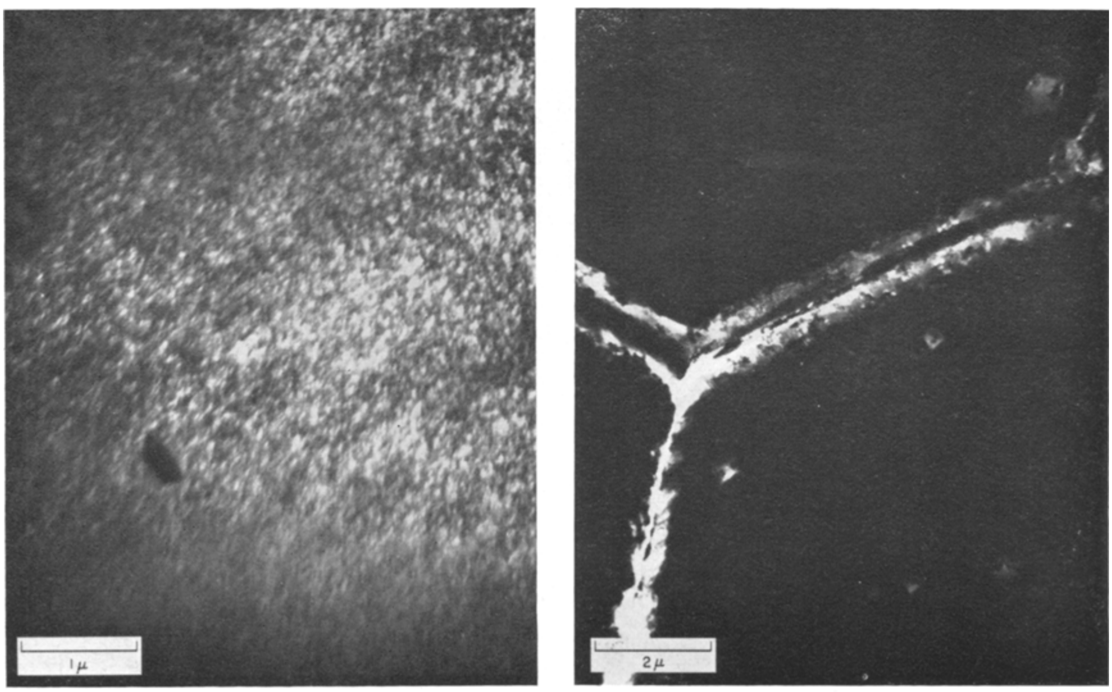
4. Discussion

The more rapid overageing of samples aged at 100° C when quenched from 365° C compared to those quenched from 435° C [1] seems unusual upon superficial examination. The vacancy concentration should be much higher in samples quenched from the higher temperature, perhaps by a factor of 1000, since the concentration is



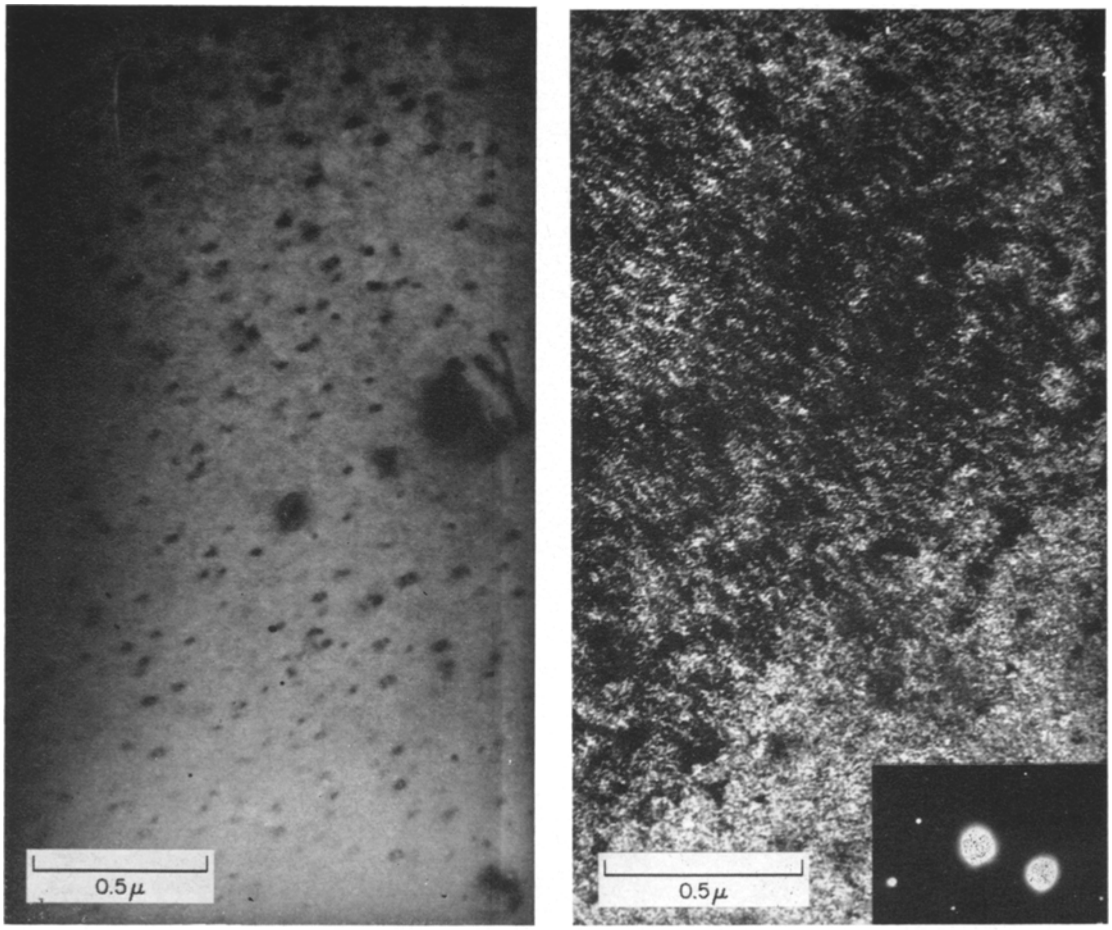
(a) (b)

Figure 13 Precipitation within matrix of Al/38.5% Zn formed during ageing for 200 min at 100° C. Sample solution-treated at 365° C. (a) Bright field; (b) dark field.



(a) (b)

Figure 14 Structure of Al/38.5% Zn solution-treated at 435° C, quenched and cold-rolled 10%. (a) Matrix; (b) grain-boundaries.



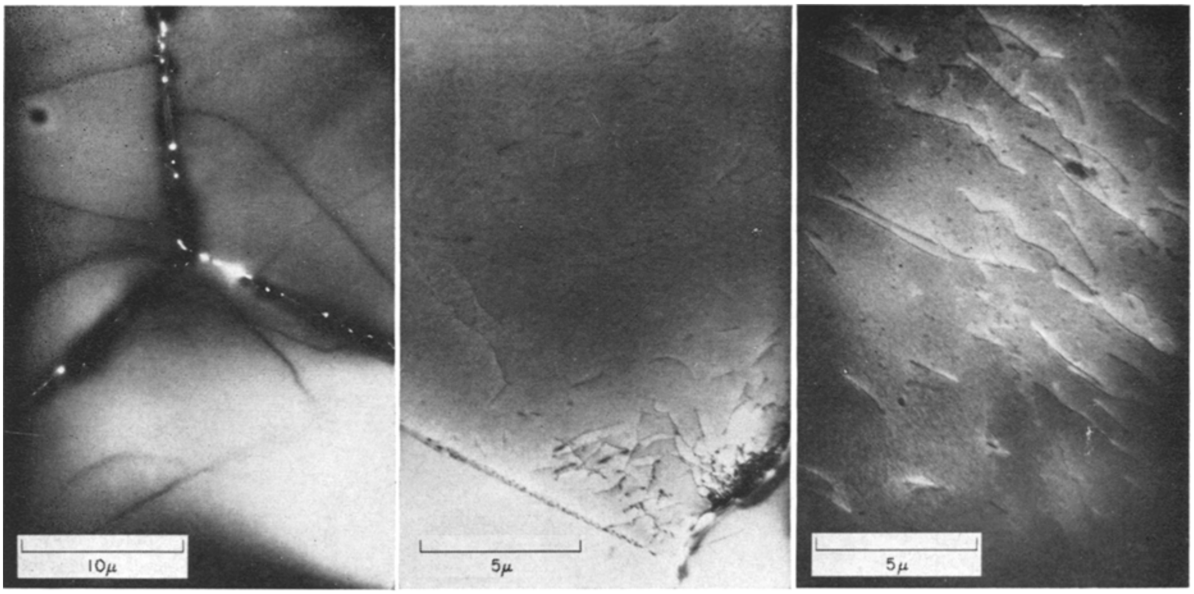
(a) (b)

Figure 15 Effect of solution temperature on dislocation loop size in Al/30% Zn aged at 22° C. (a) 435° C; (b) 365° C.

an exponential function of temperature. If most of the vacancies were retained by quenching, diffusion should be more rapid in the material containing the higher concentration, and thus diffusion and overageing should be more rapid. However, the presence of dislocation loops indicates that the vacancies coalesced and collapsed into loops. Ageing at 100° C anneals out the loops by dislocation climb, but the rate increases with decreasing loop radius [4]. If the loops formed in material quenched from 435° C are larger than loops formed in the samples quenched from 365° C, these loops will be more stable. This behaviour was observed by Panseri and Federighi [5] in pure aluminium quenched from various temperatures and subsequently annealed. The resistivity recovery was slower after quenching from 470° C and above than after quenching from 400° C and below.

As loops anneal out by climb, they act as vacancy sources, thus the effective vacancy concentration in the samples quenched from 365° C and aged at 100° C may actually be greater than that in samples quenched from 435° C, even though the total initial vacancy concentration was greater in the latter sample. Thus, the diffusion rate would be higher in the former, and overaging by zinc diffusion away from the modulated zones would tend to destroy these regions and any associated hardening.

Measurement of loop sizes would support the above hypothesis, but because of the very fine size of the loops it is difficult to make meaningful measurements. A comparison of loop sizes in Al/30% Zn solution-treated at the two temperatures does indicate that the loops formed in



(a) (b) (c)

Figure 16 Structure of Al/30% Zn solution-treated at 365° C and aged 200 min at 100° C. (a) Selectively etched grain-boundaries; (b) dislocation sources at boundaries; (c) dislocation structure.

material treated at 435° C are larger than loops formed in samples treated at 365° C. The former can be seen in fig. 15a, and the latter are not resolvable (fig. 15b). Thomas [6] studied the formation of loops in Al/10% Zn quenched from both 540 and 580° C. The size of the loops was about the same, 100 to 200 Å, but the density of loops was greater in the 580° C samples, $10^{16}/cm^3$ compared to $2.5 \times 10^{15}/cm^3$ in the 540° C samples. Thomas suggests that samples quenched from the lower solution temperature act similarly to those having higher solute content. If this is true, in the present study the faster ageing in Al/30% Zn quenched from 365° C can be attributed to the "higher solute content effect", which was shown to result in much more rapid breakdown of the spinodal structure.

Rao *et al* [7] found that overageing in Al/50% Zn occurred more rapidly in samples quenched from 375°C than in those quenched from 450°C. Their explanation was that the second stage of ageing was more prominent in the 375° C samples due to solute clustering. The explanation appears vague and may be questionable, but the agreement of their findings with those of the present study is significant.

Garwood and Davies [8] studied the hardening kinetics in Al/25% Zn solution-treated at 500° C and then step-quenched to lower temperature before the final quench. It was found that the ageing occurred much more rapidly the higher the temperature of the step quench. It was suggested that the vacancy concentration was higher in the samples quenched from the higher temperatures and that the effective diffusion rate was therefore greater in those samples.

Acknowledgements

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