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Spinodal Decomposition in Al/Zn Alloys

Part 1 *Mechanical Properties*

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The effect of spinodal decomposition on the mechanical behaviour of Al/Zn alloys was studied over the range of 30 to 60 wt % zinc. Two solution treatment temperatures, 365 and 435° C, were used; extensive ageing studies were carried out at 22 and 100° C, and limited tests were made on samples aged at other temperatures, 0, 55, and 200° C. The yield and tensile strengths were significantly increased by spinodal transformation, but ductility was seriously impaired. The tensile fracture was intergranular, with one exception, and was related to grain-boundary precipitation and a narrow denuded zone.

Calculated yield strengths based on Cahn's analysis did not agree with those derived from the correct dislocation model. The wrong model did give fortuitous agreement. Spinodal hardening appears to offer a promising new hardening mechanism in aluminium alloys if the particular composition and treatment can be found to eliminate the serious lack of ductility.

1. Introduction

The development of ultra-high-strength aluminium alloys has not been as successful as the development of iron-base alloys. The highest strength aluminium alloys presently available derive their strength from age-hardening mechanisms, whereas iron-base alloys can achieve high strength by various mechanisms such as martensitic transformation, maraging, and ausforming. These mechanisms cannot be used for aluminium alloys for obvious reasons, but there is another strengthening mechanism available for face-centred cubic crystals that has not been exploited to date. This mechanism is spinodal decomposition, which is the basis for strengthening in gold/platinum alloys [1, 2].

The basis of spinodal decomposition is that any alloy lying in a two-phase field within the spinodal curve $\partial^2 F/\partial x^2 = 0$ will decompose spontaneously and nearly homogeneously. Because small fluctuations in composition can occur with a decrease in free energy, some regions are thermodynamically stable and tend to grow. Growth takes place in a coherent region, and, therefore, no surface energy is required to form nuclei as in the case of classical precipitation.

The compositional fluctuations in spinodal systems are periodic and thus give a three-dimensional array of precipitate nuclei. The spacing is of the order of tens of Ångströms. The close spacing and the regularity of the fluctuations suggest that considerable strengthening could be achieved in such alloys.

The Al/Zn system was selected for this study because spinodal decomposition is known to occur over a wide range of compositions in this system. Fig. 1 [3] shows a portion of the phase diagram, along with the calculated chemical and coherent spinodal curves. Alloy composition included in the study ranged from 30 to 60 wt % zinc.

This study was intended to explore the possibility that spinodal decomposition in Al/Zn alloys might be exploited for strengthening. The specific objectives were to discern whether such decomposition occurs, to determine whether strengthening resulted from the transformation, and to study the mechanism of the decomposition and its relation to any observed strengthening.

Supporting evidence for much of this paper is given in accompanying papers which summarise

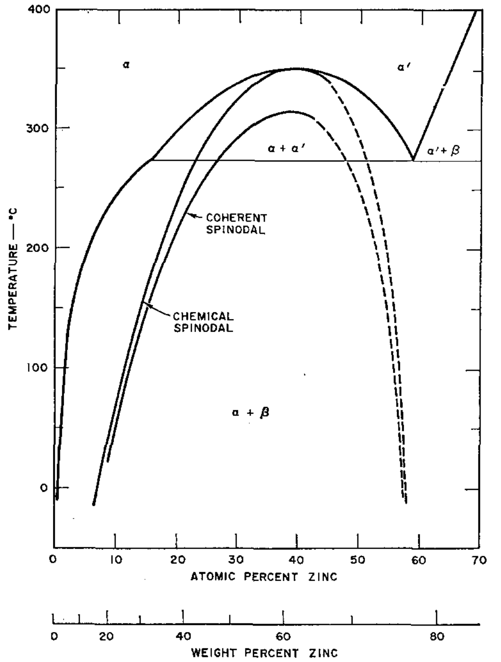

Figure 1 Part of the Al/Zn phase diagram (after Rundman and Hilliard [3]).

the results of X-ray diffraction studies [4] as well as microstructural studies [5].

2. Experimental Procedures

Three-pound ingots of alloys were prepared from 99.99% Al and 99.99% Zn by induction melting in magnesia crucibles in an argon atmosphere. The alloys were kept molten for about 10 min to ensure homogeneity and were then cast into a graphite mould 1.5 in.* square and 12 in. deep. The ingots were rolled at 420° C with intermediate reheating until a thickness of about 0.10 in. was obtained, and finally cold-rolled to sheet ranging from 0.020 in. to about 0.040 in. thick.

Several ternary and hybrid alloys were also similarly prepared. In general, they were fabricated according to the above technique. The hybrid alloys were made by using 7075 aluminium alloy (instead of pure aluminium) and zinc. Because of the hot shortness of the hybrid, it was necessary to fabricate these alloys at a lower temperature (about 350° C) than was used for the binary alloys.

Tensile samples cut from the cold-rolled sheet were then heat-treated in a salt bath at either 365 or 435° C. The samples were quenched into water at room temperature, although a few experiments were performed in which other quenching media were used, such as iced brine, oil, or air.

Ageing experiments were performed at various temperatures. The 200° C ageing was carried out in a low-temperature salt bath, and the 100° C ageing was done in boiling water in a flask with a reflux condenser.

Tensile testing was carried out at room temperature in an Instron tester at a strain rate of 0.02 in./min. A few tests were made at variable strain rates, but unless otherwise specified the 0.02 in./min rate was used.

3. Results

3.1. Hardness

Extensive hardness measurements were made on Al/60% Zn in order to determine the conditions under which decomposition occurs. Samples were solution-treated at two temperatures (365 and 435° C) and were quenched immediately to various temperatures between — 196 and 200° C and were then aged at those temperatures. Hardness was determined as a function of ageing time; the measurements were made at room temperature except for samples quenched to 0° C, for which measurements were made at 0° C. The hardness of Al/60% Zn samples aged at 55° C and higher decreased after several hours at room temperature, but the changes were sluggish enough to permit meaningful measurements to be made. Even samples that had undergone considerable softening at 100° C continued to soften at room temperature over a period of 2 weeks. For example, 60% Zn solution-treated 1 h at 365° C and aged 20 h at 55° C had a hardness of R_B36 (DPH 94), but softened to R_B2 (DPH 82) during 2 weeks at room temperature.

Hardness isotherms were not determined for the other alloys, because tensile data, which are more meaningful, were relatively easy to obtain. However, hardness readings were used as checks to determine whether a given tensile sample might have been changed by lengthy ageing at room temperature. No changes occurred in either the Al/30% Zn or the Al/38.5% Zn alloys after 220 000 min (5 months) and 400 000 min (9 months), the respective values being R_B68 and R_B83. The hardness values for Al/30% Zn samples solution-treated at 365 and at 435° C were the same.

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*1.0 in. = 2.5 cm.

3.2. Tensile Properties

The tensile properties as a function of ageing time at various temperatures are shown in figs. 2-6 for the four binary alloys, Al/30, 38.5, 50 and 60% Zn as well as for the hybrid alloy 62(7075 Al)/38% Zn. Generally two solution-treatment temperatures, 365 and 435° C, were used, although for some alloys only one temperature was used. The highest values of the yield and ultimate strength were usually found shortly after quenching, but sometimes further ageing increased the strength. Overageing occurred, being much more rapid in the high zinc alloys than in the low zinc alloys. The overageing was also more rapid for alloys solution-treated at 365 than at 435° C. The higher the ageing temperature the quicker overageing took place for a given alloy quenched from a given temperature.

The scatter in the yield strength data was much greater than in the ultimate strength data. The variation in load-elongation curves, from which yield strengths were calculated, was sometimes quite noteworthy for duplicate or triplicate samples of a particular heat-treatment. For example, some samples seemed to exhibit an initial linear relationship between load and elongation followed by a second linear region whose slope was less than the initial linear portion. On the other hand, some samples showed an extensive linear region followed directly by the plastic region and then fracture. Obviously, the second type of behaviour would give higher values of the yield strength. Loading-unloading experiments below the fracture load showed that the shape of the curve was markedly changed by plastic deformation. Moreover, the nature of the change depended on whether the samples were aged or overaged, which can be loosely termed "hard" versus "soft" conditions. The yield strengths were nearly comparable, but the ultimate strength and work-hardening characteristics were notably different. A few experiments were performed to assess the relative importance of work-hardening. The "hard" condition resulted in a high degree of work-hardening. Tensile samples of the 60% Zn alloy were solution-treated for 1 h at 435° C, quenched at 200° C, and aged for 2, 10, and 200 min. The samples were then loaded past the apparent yield point,

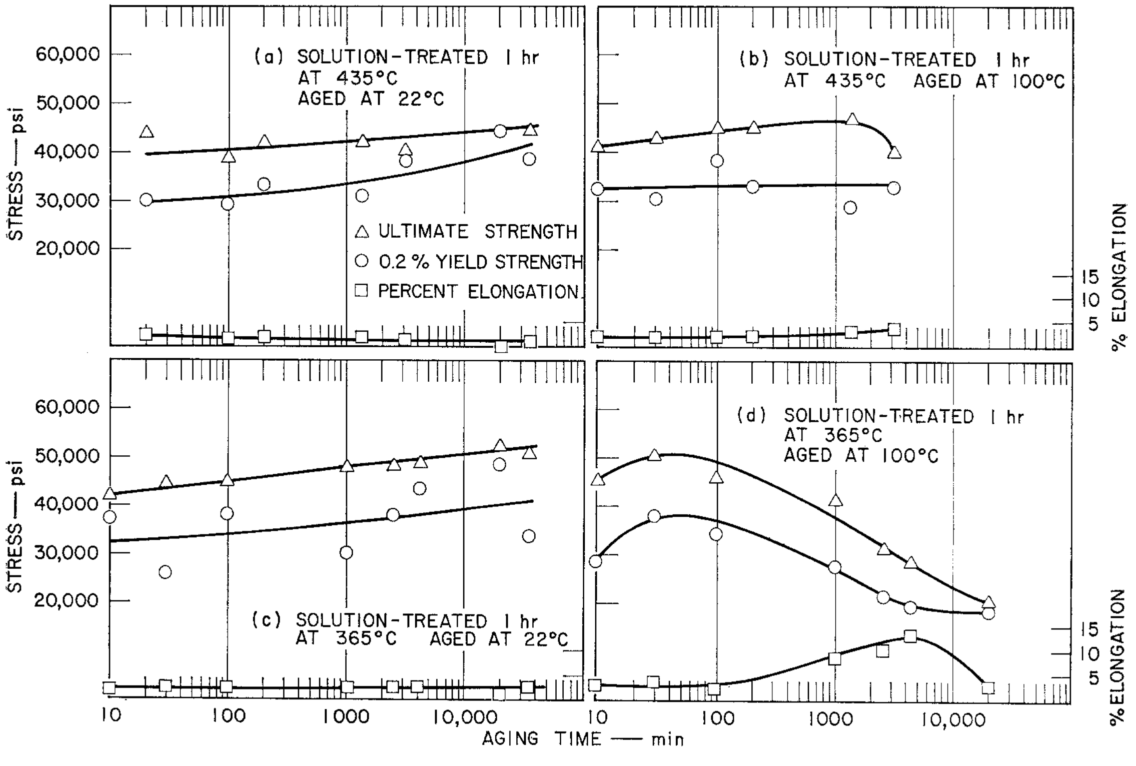

Figure 2 Effect of ageing on the tensile properties of Al/30% Zn.

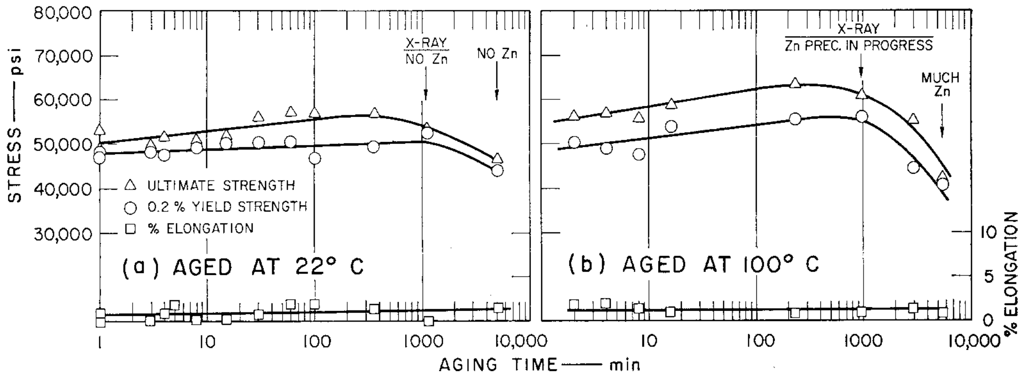

Figure 3 Effect of ageing on the tensile properties of Al/38.5% Zn (solution treated 1 h at 435° C).

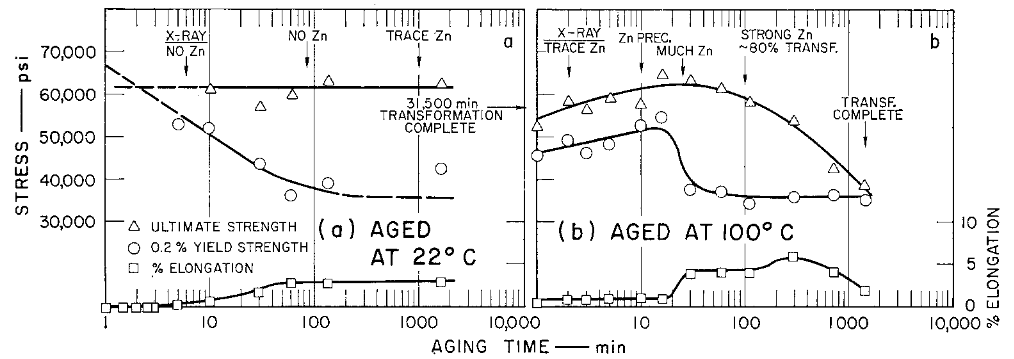

Figure 4 Effect of ageing on the tensile properties of Al/50% Zn (solution-treated at 435° C).

unloaded, and reloaded. The sample aged for 2 min had an initial strength of only 13 000 psi*, but after work-hardening in tension several times, the yield strength increased to 49 400 psi. Higher values of the yield could probably have been reached if the sequence had been repeated for additional cycles. On the other hand, the samples aged for 200 min increased in yield strength to 27 600 psi, which appeared to be saturation value. The 10 min sample exhibited a behaviour between these two extremes, the highest yield stress measured being 40 700 psi.

The ultimate strength of Al/30% Zn appeared to be independent of either solution-treatment temperature or ageing temperature, although the times at which the maximum values of the ultimate strength occurred varied with temperature. The results are marked by some scatter, as were the data for 38.5, 50, and 60 % Zn alloys. The scatter arises from the brittleness of the alloys and, in particular, the notch sensitivity. On numerous occasions, fracture was introduced at the notches by the knurling of the grips.

Ageing at 100° C of all alloys resulted in pronounced softening and a marked increase in ductility. However, prolonged ageing, e.g. 20 000 min for Al/30% Zn, caused the ductility to decrease significantly owing to copious precipitation of zinc. The acquired ductility remained until decomposition of the solid solution was nearly complete. This behaviour had been observed previously in both Al/50% Zn and Al/60% Zn samples.

Little change in strength of the 38.5% Zn alloys was noted for ageing times up to 1000 min regardless of whether the samples were quenched from 365 or 435° C or whether they were aged at 22 or 100° C. This was not the case for either the 50 or 60% Zn alloys. An apparent strength increase in 38.5% Zn, although very slight, is shown in fig. 3a for samples quenched from 435° C. This behaviour can probably be attributed to

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*1.0 psi = 1.0 lb/in^2. = 7.0 × 10^{-2} kg/mm^2.

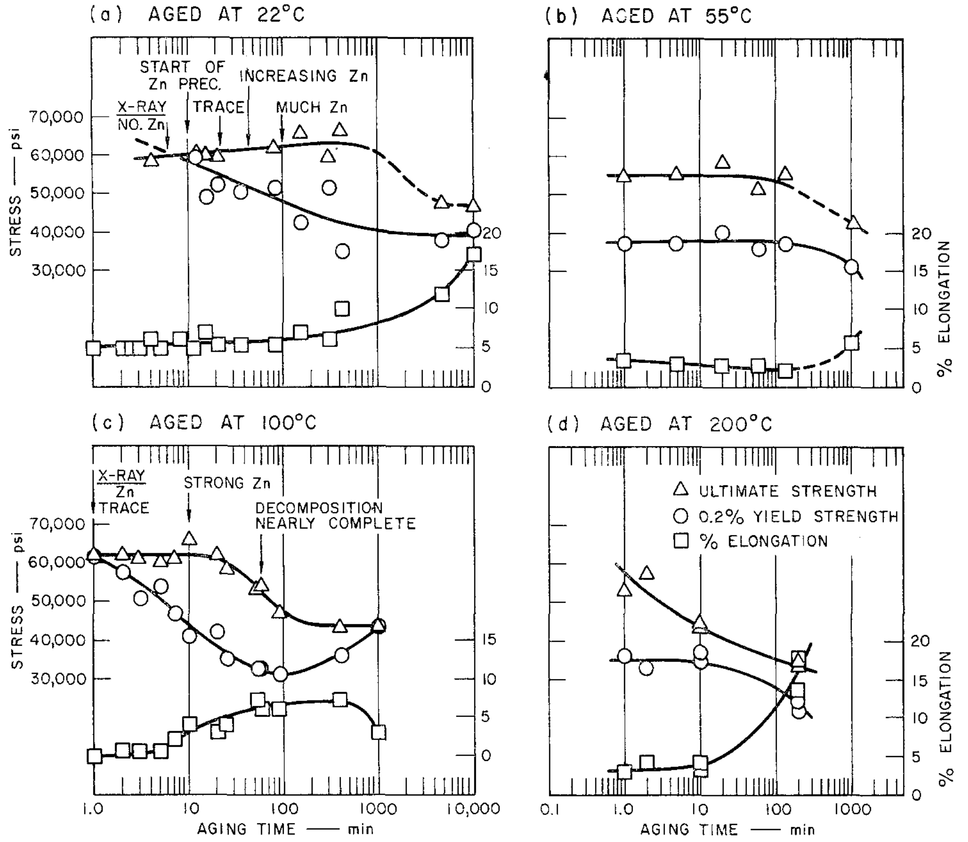

Figure 5 Effect of ageing on the tensile properties of Al/60% Zn (solution-treated 1 h at 435° C).

the high degree of brittleness in samples aged for short periods. Many samples failed in the grips and are therefore not shown on the plot. There was no measurable ductility in these samples. Failure took place at the sites where the knurled grips indented the surface. In these cases, ultimate strengths were less than 50 000 psi, and the load-extension curve was typical of completely brittle materials.

Ageing of the 50 and 60% Zn alloys caused a decrease in the 0.2% yield strength before a decrease in the ultimate strength was observed. The decrease in yield strength in the 50% Zn alloy occurred sooner at room temperature than at 100° C; on the other hand, the 60% Zn alloy behaved normally in that the decrease occurred sooner at the higher temperature. The loss of yield strength was associated with an increase in ductility as measured by the per cent elongation.

Ageing of both these alloys at 100° C for about 1000 min resulted in decreased ultimate strengths but little additional loss of yield strength. The values of ultimate strength and yield strength approached each other at these ageing times, and an associated loss of ductility was found. This behaviour is due to the nearly complete decomposition of the metastable solid solution into the two equilibrium phases, zinc and aluminium containing zinc.

The highest yield strengths of all alloys studied in this programme were attained in a hybrid alloy made from a mixture of 62% 7075-Al and 38% zinc. It was thought that the alloying additions in 7075-Al might result in precipitation-hardening in a high zinc matrix which was spinodally transformed. The high concentration of alloying additions resulted in a marked lowering of the solidus, and thus it was necessary to fabricate at lower temperatures than in the case of the Al/Zn binary alloys. It was found that 400° C was the maximum temperature which prevented hot shortness, hence all solution-treating was performed at 365° C. This temperature was insufficient to dissolve the precipitates, even if a 24 h anneal was used. The structure of the quenched samples was therefore one of rather

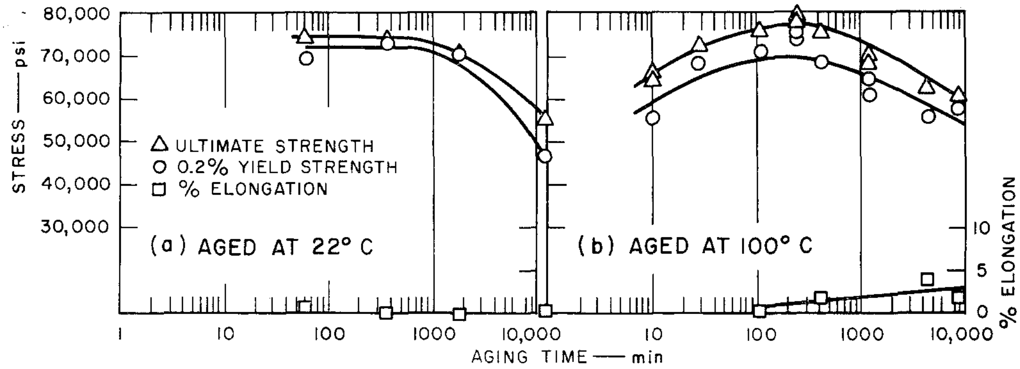

Figure 6 Effect of ageing on the tensile properties of 62% (7075-Al)/38% Zn hybrid alloy (solution treated 1 h at 365° C).

large second-phase particles in a matrix that exhibited spinodal sidebands. Even though the structure was far from ideal and presumably much too coarse for precipitation-hardening, yield strengths of over 70 000 psi were attained, as is shown by the ageing curves in fig. 6. Ductility was very low, of the order of 1 to 2% elongation until overageing occurred, in which case the maximum ductility observed was about 4% elongation. No ageing effect was found at 22° C, but there did appear to be a slight effect at 100° C. All short-time treatments at 22° C (less than about 1h) resulted in completely brittle failure and fracture in the grips originating at the knurling marks.

An additional alloy was fabricated of Al/38.5% Zn/2% Cu. The addition of copper (without the presence of Si, Fe, Mn, Mg, and Cr associated with 7075) was found to be very beneficial with respect to ductility and work-hardening behaviour. This alloy, solution-treated 1 h at 365° C and either quenched or air-cooled to room temperature, had a yield strength of about 30 000 psi, an ultimate strength of about 64 000 psi, and about 8% elongation. Cold-rolling 60% raised the yield strength to 50 000 psi and the ultimate strength to 90 000 psi, but the ductility was still about 6.5%. The same alloy cold-rolled 40% and subsequently aged 5 min at 100° C had a yield strength of 42 000 psi, an ultimate strength of 78 000, and 6% elongation. Spinodal sidebands were prevalent before cold-rolling, but, because of the severely broadened X-ray peaks, it was not possible to identify a spinodal structure after rolling.

The strength of spinodally decomposed alloys increased with increasing zinc content. The maximum observed strengths for various combinations of solution-treatment and ageing temperatures are shown as a function of alloy content in fig. 7. Generally there was not much difference between the properties obtained by various treatments, except that the yield strength of the highest zinc-content alloys, 60%, was lower than that of the 50% Zn alloy when solution-treated at 365° C and aged at 100° C. This is consistent with the hardness changes that were found to occur more rapidly in samples quenched from the lower solution temperature. The 60% Zn alloy was by far the least stable structurally, and apparently some decomposition occurred even after the shortest ageing times at 100° C [4].

4. Discussion

4.1. Contributions to Strengthening

There is no doubt that the strength of quenched Al/Zn alloys containing 30 to 60% Zn is greater than that of equilibrium, two-phase alloys. It is also apparent from the X-ray identification of sidebands on the (200) Al peak that a spinodal structure exists [4], but it is not unequivocally possible to assume that the strengthening was derived solely from the spinodal structure. It would be desirable to know the strength of the equilibrium solid solution and then to ascribe any strengthening above such a base value to the spinodal structure. However, Al/Zn alloys of the compositions studied do not exist at room temperature as a solid solution, and it is not possible to retain a metastable solid solution that does not show X-ray sidebands.

Although theories of solution-hardening exist from which one might calculate the strength of the solid solution, the theories are valid only for dilute solutions. Fleischer [6, 7] has considered

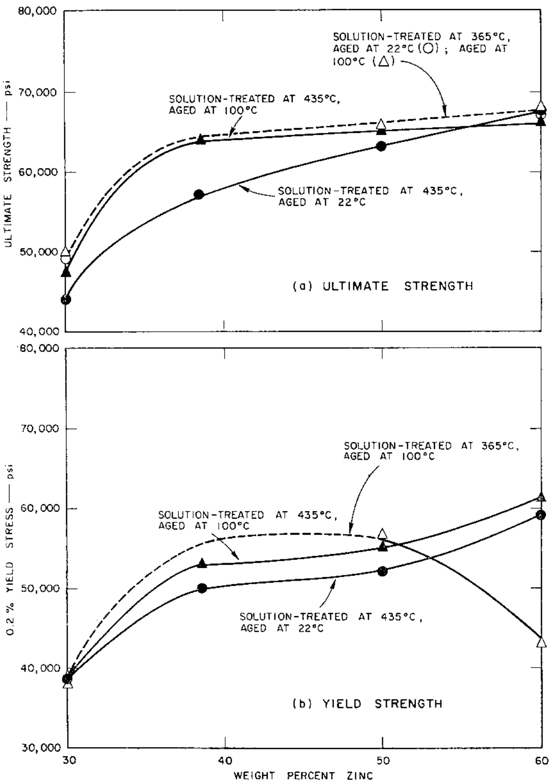

Figure 7 Effect of composition on maximum strength obtained by spinodal decomposition.

hardening by "high symmetry" additions such as substitutional solute-atoms and found their effect to be significantly less than that associated with "low symmetry" defects. For example, the rate of hardening per unit concentration can be expressed in terms of the shear modulus. Substitutional atoms in aluminium increase the yield strength by the factor $G/10$, whereas vacancy discs (giving rise to large tetragonal distortions) increase the yield strength by the factor $2G$ per unit concentration. If we therefore consider that the asymmetrical defects such as vacancy discs are much more potent strengtheners than substitutional atoms such as zinc, we can assume that the solution hardening from the zinc is negligible compared to either vacancy discs or spinodal effects.

The question to which we must address ourselves is simply, is the observed strength of quenched Al/Zn alloys due to the presence of the modulated spinodal structure or to the vacancy loops, or to both?

Electron microscopy [5], showed a very high loop density in Al/38.5% Zn solution-treated at 435° C and aged at 22° C. On the other hand, the same material solution-treated at the same temperature but aged 200 min at 100° C showed a decided lack of dislocation loops. The tensile properties of these samples, shown in fig. 3, revealed virtually no difference for the two ageing temperatures. It thus appears that the loops *per se* are not the chief contribution to the observed strengthening.

4.2. Calculated Spinodal Strengthening

Cahn's [8] theoretical consideration of spinodal hardening showed that for small periodicities of the modulated structure the yield strength should increase linearly with the wavelength. This result was derived from a consideration of the forces on dislocations caused by the internal stress field that arises from the fluctuations. The force required for a dislocation to cut through the regions of compositional variation is less than the force required for a dislocation to bow out between the pseudo-particles. In other words, the regions of compositional fluctuation are not hard particles in the sense of dispersion hardening. On the other hand, at larger wavelengths the yield stress is dependent upon the reciprocal 2/3 power of the wavelength. This results from the fact that the more widely-spaced pseudo-particles are not readily sheared because the force to bow out dislocations between the pseudo-particles is quite small.

Cahn considers two extremes in his analysis. When the parameter $A\eta b Y/\gamma\beta$ is less than unity, the dislocation line is nearly straight because the wavelength or amplitude of the internal stresses is too small to cause bending. On the other hand, if the parameter is greater than unity, the dislocation can curve around all obstacles. In this parameter A is the amplitude in the Fourier component of the composition fluctuation whose wave vector β is in the [001] direction (z direction);

$c - c_0 = A(\beta) \cos \beta z$, c is composition of the solute-rich zone, c_0 is alloy composition, η is $\partial \ln a/\partial c$, a is lattice parameter; $\mathbf{Y} = (C_{11}+2C_{12})(C_{11} - C_{12})/C_{11} \approx G$, $\mathbf{b}$ is Burger's vector; $\gamma \cong G\mathbf{b}^2 \approx \mathbf{Y}b^2$.

The parameter in this study was evaluated using $A = 0.4$; $\eta = 1.76 \times 10^{-2}$, $\mathbf{Y} = 3.5 \times 10^6$ psi, $\mathbf{b} = 0.57 \times 10^{-8}$ in., $\gamma = 1.25 \times 10^{-10}$, $\beta = 1.58 \times 10^6$ in.$^{-1}$ for a value of $\lambda = 100$ Å. A value of 0.8 was obtained. Two equations for the yield stress were derived, depending upon the extremes of the parameter. In the first case,

$$\sigma = \frac{A^2 \eta^2 \mathbf{Y}^2 \mathbf{b}}{3\sqrt{6}\beta\gamma} \text{ for screw dislocations} \quad (1)$$

and for the second case,

$$\sigma = 0.57\,(A\,\eta\mathbf{Y})^{\frac{1}{3}} \left(\frac{\gamma\beta}{6}\right)^{\frac{2}{3}} \text{ for edge dislocations.} \quad (2)$$

Equation 1 shows a linear dependence of yield strength on the wavelength, whereas equation 2 gives a reciprocal 2/3 dependence. Although the parameter for Al/38.5 % Zn in this study was 0.8 and is more or less between the two extremes discussed by Cahn, values of yield strength of 46 000 psi for $A = 0.4$ and 37 000 psi for $A = 0.2$ were calculated from equation 2. These values would correspond to the proportional limit in an engineering type of stress-strain curve and are very close to values found experimentally 35 000 to 43 000 psi. Equation 1 was not valid, giving values of the order of 100 psi.

It should be noted that there are really two independent variables, amplitude and wavelength. The wavelength was measured [4] although not controlled, but the amplitude was not known. Various values could be assumed from the known spinodal region shown in fig. 1. However, since the amplitude enters into the calculation as a 1/3 power, there is not a strong dependence of yield strength upon amplitude. Nevertheless, the fact that amplitude and wavelength vary independently can lead to numerous values of yield strength.

It is significant to note that the two variables in spinodal hardening, wavelength and amplitude, correspond to particle spacing and particle hardness, respectively, in precipitation-hardening. Wavelength in spinodal structures is determined by the temperature and is relatively insensitive to time at temperature. On the other hand, the amplitude is a function of time at temperature and is nearly independent of temperature [9]. It was shown [4] that there was about a two-fold difference in wavelength of Al/38.5 % Zn solution-treated at 365 when aged at 22° C compared to ageing at 100° C. Al/30 % Zn had a wavelength of 159 Å when aged at 22° C. The wavelength was independent of solution temperature. The yield strength of Al/30 % Zn was identical within experimental scatter for samples aged at 22° C and at 100° C. If Cahn's theory is correct and equation 1 is valid, the samples aged at 100° C should have had yield strengths 50 % higher than samples aged at 22° C. If equation 2 is valid, the sample aged at 22° C ($\lambda = 100$ Å) should have a yield strength 30 % greater than samples aged at 100° C ($\lambda = 150$ Å). Once again, there was no discernible difference.

The calculated strengths suggest that equation 2 is valid, whereas equation 1 does not apply. Equation 2 represents the situation for which dislocations bow out between the zones of composition fluctuation because the bowing force is considerably less than the force to cut the zones. Straining of Al/30 % Zn foils in the electron microscope introduced dislocations that were long and straight [5]. Movement of the dislocations upon heating was slight but did not indicate any tendency for bowing out between two zones of the matrix. Since the expected dislocation structure for the model that predicted yield strengths in nearly perfect agreement with observed values was not observed, it can be concluded that Cahn's model does not apply in this case, and that the agreement obtained is fortuitous. Carpenter [2] has also found bad agreement between observed yield strengths of spinodal Au/Pt alloys (100 000 psi) and values calculated using Cahn's model of only 600 psi.

4.3. Brittleness of Spinodal Structure

It appears that the lack of ductility in spinodally transformed samples would limit any attempts to utilise such a structure for engineering applications. However, the fracture of all samples, except those that were cold-rolled, was intergranular. Microhardness indentations made within individual grains of the spinodally transformed samples did not indicate that there is an inherent brittleness. The indentations were clearly delineated, and no cracks were ever observed to emanate from these indentations as they do in oxides [10] or other inherently brittle structures. Transmission electron microscopy revealed narrow denuded zones at the grain-boundaries and fine grain-boundary precipitates. This type of structure is known to promote brittle behaviour [11]. Thus it should be possible to promote ductility if the denuded zones and grain-boundary precipitates could be eliminated, possibly by changes in composition or heat-treatment. The addition of copper, for example, appeared very beneficial, although massive precipitates existed in the structure. The reason for the improved ductility in copper-bearing samples is not known, but this behaviour certainly warrants further study.

4.4. Work-Hardening Behaviour

The existence of the modulated spinodal structure markedly increases the work-hardening capacity of Al/Zn alloys. There was a noticeable lack of cross-slip, as evidenced by the decorated slip lines which were straight and parallel [5]. Cross-slip occurred at higher deformation, e.g. 70% deformation. Some cross-slip occurred at about 20% deformation, but the tensile samples that fractured at strains considerably less than 20% showed virtually no cross-slip. The load-elongation curves of overaged samples indicated that cross-slip took place. The lack of cross-slip is in agreement with Cahn's theory [8], which states that cross-slip for the (1 1 1) $[1 1 \bar{0}]$ slip system would be of no help in avoiding the resistance imposed by internal stresses in the modulated structure. It thus appears that the spinodal strengthening is associated to some extent with the inhibition of cross-slip in these alloys.

Acknowledgements

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