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A test for diffusional coherency strain hypothesis in the discontinuous precipitation in Mg–Al alloy

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Abstract. Discontinuous precipitation (DP) occurs in many alloy systems under certain conditions. Although solute supersaturation is the chemical driving force for DP, this has to be coupled with another driving force for grain boundary migration. This was identified to be diffusional coherency strain ahead of the moving boundary in the case of diffusion induced grain boundary migration (DIGM) and liquid film migration (LFM). In the present work, the validity of diffusional coherency strain hypothesis is verified in Mg–Al alloy, which exhibits discontinuous precipitation. Samples were tested with an applied stress simultaneously with discontinuous precipitation and it was found that the velocity of the boundaries both parallel and transverse to the stress axis obeys the model for diffusional coherency strain. This work can be used as a conclusive evidence for diffusional coherency strain hypothesis for the occurrence of discontinuous precipitation in Mg–Al alloys.

Keywords. Discontinuous precipitation; diffusional coherency strain; Mg–Al alloy; DIGM; LFM; driving force.

1. Introduction

Diffusion induced grain boundary migration (DIGM) was first isolated by Hillert and Purdy (1978). They attributed the driving force for grain boundary migration to be that of free energy of mixing. Baluffi and Cahn (1981) pointed out that both alloying and dealloying can result during DIGM and also occur for positive or negative deviation from Raoult’s law (excursions from ideal solution behaviour). Baluffi and Cahn (1981) also pointed out that the chemical driving force (free energy of mixing) had to be coupled with another driving force for grain boundary migration. Yoon and Hupman (1981) first showed liquid phase sintering in W–Ni system where liquid films of nickel migrated (LFM) dissolving the W grains and depositing W–Ni solid solution behind the liquid film. When Fe was added to the melt, liquid films migrated and the migration behaviour could be predicted on the basis of coherency strain model proposed by Sulonen (1960, 1964) and Hillert (1983). Baik and Yoon (1986) showed LFM in Mo–Ni system with low Fe additions and found a parabolic dependence of migration velocity with coherency strain. Baik and Yoon (1987) studied the effect of curvature on the grain boundary migration in Mo–Ni alloy by adding Cu and Fe. The grain boundary did not migrate when 1 wt% Fe was added to the melt which they pointed out was due to coherency strain energy being zero.

Discontinuous precipitation (DP) or cellular precipitation occurs in many systems for certain compositions and temperatures. Fournelle and Clark (1972) studied the origin of cellular precipitation in Cu–In system where they found that nucleation of equilibrium precipitates takes place on grain boundaries and boundary bows out and alternate lamellae of the precipitate and the matrix are formed in the wake of the migrating boundary.

The same theoretical problem exists for DP as in DIGM, LFM. Although solute supersaturation is the chemical driving force, another driving force is needed to explain grain boundary migration. The coherency strain energy model has been previously identified qualitatively as controlling discontinuous precipitation in the experiments of Sulonen (1960, 1964) on Cu–Cd system. The velocities of moving grain boundaries giving discontinuous precipitation were modified by application of unidirectional tensile or compressive stresses. Boundaries parallel or normal to the stress axis had their velocities increased or decreased in predictable manner. Hillert (1972) has provided a clear analysis of the situation from which the velocities of boundaries parallel and transverse to the stress axis can be worked out. This result was used by Chung *et al* (1992) who carried out experiments on Al–21·8 at% Zn alloy and showed that diffusional coherency strain hypothesis works quantitatively for discontinuous precipitation.

In the present work, we have studied discontinuous precipitation (DP) in Mg–8·5Al system (alloy GA9) and the effect of applied tensile stress on DP is evaluated. This work is to further test the diffusional coherency strain hypothesis in Mg–Al system.

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2. Experimental

The chemical composition of the magnesium–aluminium alloy is shown in table 1. The samples were cast into Directorate of Technical Development (DTD) test bars. These test bars were homogenized at 430°C for 24 h and water quenched. The sectioned samples showed DP at 250°C for 1 h. Samples were machined with a gauge diameter of 6·25 mm and gauge length of 32 mm for application of stress during DP. The samples were tested in a satec creep testing machine with various loads to achieve stresses of 5, 10, 200 and 30 Mpa for 2 h at 250°C. The satec creep testing machine on loading applied a tensile stress to the sample. The sample was loaded with different loads to achieve different tensile stresses. Samples were sectioned parallel and perpendicular to tensile axis and polished using standard methods and etched in citric acid solution. The measurements were made on DP nodules in a Nikon Epiphot inverted metallurgical microscope. The velocity was determined by measuring the maximum nodule size divided by time at 250°C. Samples were also examined under the scanning electron microscope (LEO 440).

3. Results and discussion

The magnesium–aluminium alloy (GA9) was selected because of its readiness to exhibit discontinuous precipitation. This behaviour of the alloy provides a basis for testing the diffusional coherency strain model for discontinuous precipitation in this system.

Figure 1 shows the microstructure of the alloy after 2 h at 250°C without application of any stress. Large DP nodules are seen on the grain boundaries. Figures 2 and 3 show the microstructure of the alloy after 2 h at 250°C with 5 MPa and 30 MPa stress oriented in such a way as to show parallel grain boundaries, which are parallel to the stress axis. Figures 4 and 5 show the microstructure of the alloy after 2 h at 250°C with 5 MPa and 30 MPa stress oriented in such a way as to show transverse grain boundaries i.e. transverse to the stress axis. In the above figures, DP nodules have grown to an extent determined by the applied stress and orientation of the boundary i.e. parallel to the stress axis or transverse to the stress axis. Figure 6 shows the DP nodule structure with lamellae structure as seen in the SEM where one can observe the alternate lamellae of the precipitate and the matrix respectively.

With the application of stress, DP nodule size was measured and the velocity determined with the maximum nodule size divided by time at temperature. Table 2 shows the maximum nodule size and the velocity of the parallel boundaries (parallel to the stress axis) and transverse boundaries (transverse to the stress axis). It is seen that the velocity of the parallel boundaries decreases with increasing applied stress. It is also seen that the velocity of the transverse boundaries increases with increasing applied stress. The results are plotted in figure 7 wherein velocity of the boundaries are plotted with applied stress.

Hillert (1972) suggested that part of the chemical free energy ΔG_m partitioned in such a way that frontal diffusion occurs in front of the grain boundaries and remainder ΔG_d will act as a driving force for grain boundary migration. The effect of applied stress on DP assuming coherency strain energy as the driving force was quantitatively analyzed by Hillert (1972). The theory assumes a thin

Table 1. Chemical composition (wt%) of the magnesium–aluminium alloy under study.

Aluminium	Zinc	Manganese	Magnesium
8·35	0·65	0·22	Balance

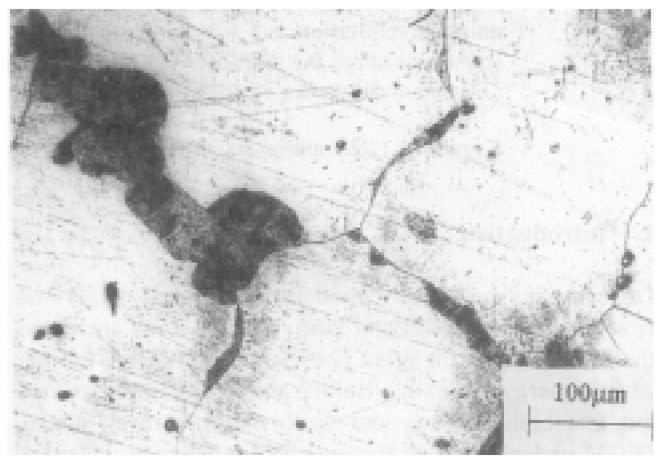

Figure 1. Microstructure of the alloy after 2 h at 250°C without application of any stress.

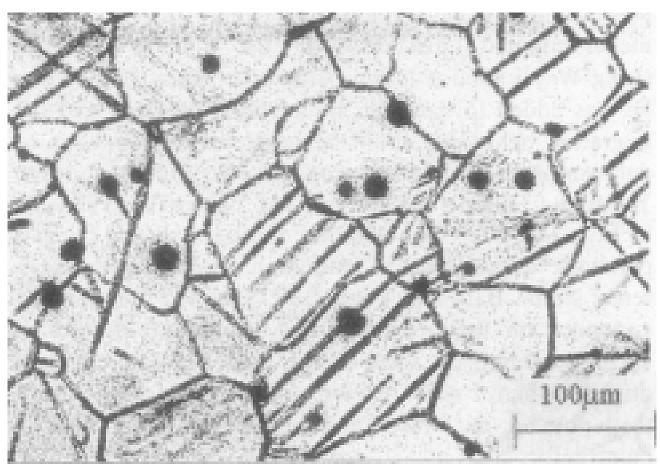

Figure 2. Microstructure of the alloy after 2 h at 250°C with 5 Mpa stress (parallel boundaries, i.e. parallel to the stress axis in the sample).

diffusion layer formed in front of the grain boundary separating the DP nodule and the matrix. This thin layer coherent with the matrix and the strain energy associated with this thin diffusion layer is termed diffusional coherency strain which drives the grain boundary migration.

When DP occurs in an elastically isotropic solid under an external stress with a coherency strain δ in the diffusion layer ahead of the boundary, the elastic energy ΔG_e in the coherent zone at a grain boundary oriented transversely to stress axis as shown by Hillert is:

$$\Delta G_{\mathrm{e}} = \left[\frac{E}{(1-\nu)}\right]\delta^2 - \left[\frac{2\nu}{(1-\nu)}\delta\sigma\right] + \frac{\sigma^2}{2E}, \qquad (1)$$

where E is the Young's modulus and ν the poisson ratio.

Since the advancing grain will also be stressed with an elastic energy equal to $\sigma^2/2E$, the total elastic energy is given by

$$\Delta G_{\tau} = \left[\frac{E}{(1-\nu)}\right]\delta^2 - \left[\frac{2\nu}{(1-\nu)}\right]\delta\sigma. \qquad (2)$$

The total driving force for a grain boundary aligned parallel to the stress axis is

$$\Delta G_{\mathrm{p}} = \left[\frac{E}{(1-\nu)}\right]\delta^2 + \delta\sigma. \qquad (3)$$

These equations predict that DP will either be enhanced or suppressed depending on the relative orientation of the

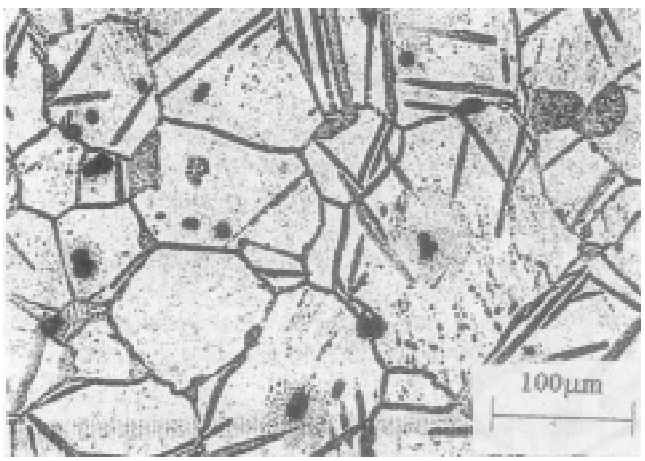

Figure 3. Microstructure of the alloy at 250°C with 30 Mpa stress (parallel boundaries).

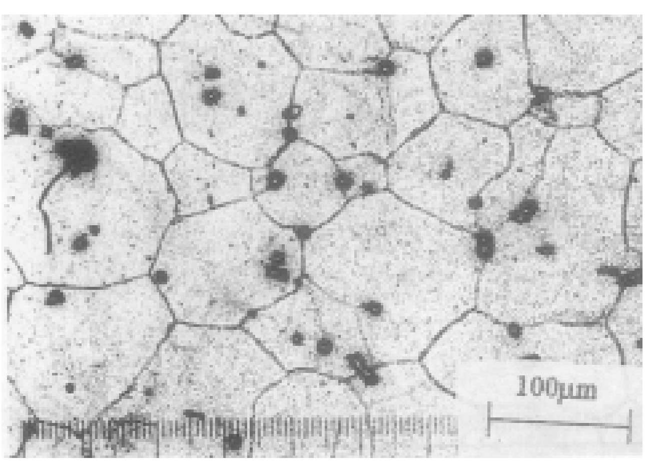

Figure 4. Microstructure of the alloy after 2 h at 250°C with 5 Mpa stress (transverse boundaries, i.e. transverse to the stress axis in the sample).

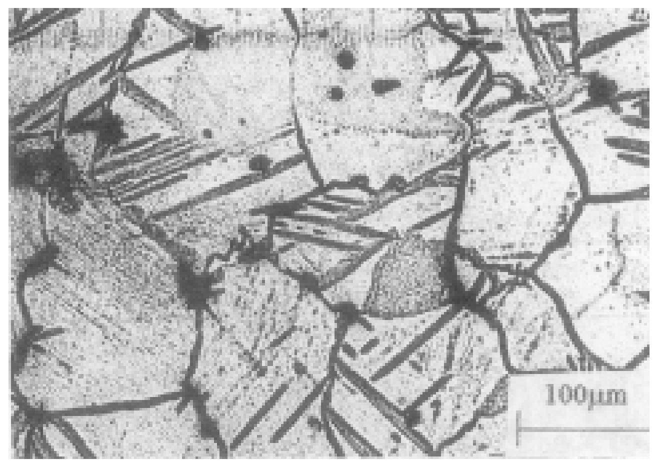

Figure 5. Microstructure of the alloy after 2 h at 250°C with 30 Mpa stress (transverse boundaries).

Figure 6. DP nodule as seen in the SEM.

grain boundaries to the stress axis and also on the signs of δ and σ.

The velocity is the product of mobility times driving force:

$$v = M\Delta G_{\mathrm{f}}, \tag{4}$$

where v is the velocity, M the mobility and ΔG_{f} the driving force.

Therefore for parallel boundaries,

$$V_{\mathrm{p}} = M\left\{\left[\frac{E}{1-v}\right]\delta^2 + \delta\sigma\right\}. \tag{5}$$

For transverse boundaries,

$$V_{\mathrm{t}} = M\left\{\left[\frac{E}{1-v}\right]\delta^2 - \left[\frac{2v}{1-v}\right]\delta\sigma\right\}. \tag{6}$$

Figure 7 shows the plot of velocity of parallel and transverse boundaries with applied stress. This shows that the velocity of the parallel boundaries decreases with applied stress whereas the linear regression was carried out for the data points of parallel boundaries and transverse boundaries; velocity of the transverse boundaries increases with stress.

Table 2. Velocity of the boundaries as a function of applied stress.

Sl no.	Applied stress	Parallel boundaries (Å/sec)	Transverse boundaries (Å/sec)
1.	5	90·3	60·4
2.	10	60·4	69·4
3.	15	50·7	39·6
4.	20	53·5	71·5
5.	30	50·7	76·4

Using (5) and (6) and from the slopes and intercepts of figure 7, δ_{exp} for parallel boundaries was 0·001 and for transverse boundaries it was 0·00111.

3.1 *Analysis of results*

The above results of δ_{exp} for parallel boundaries and transverse boundaries have to be compared with the theoretically estimated δ. This exercise will provide the clue as to whether diffusional coherency strain theory is valid for DP in the Mg–Al alloy system.

3.2 *Calculation of theoretical coherency strain parameter, δ_{th}*

$$\delta_{\mathrm{th}} = n_{\mathrm{Al}}(C_{\mathrm{s}} - C_{\mathrm{o}})_{\mathrm{Al}}, \tag{7}$$

where δ_{th} is the theoretical coherency strain parameter, n_{Al} fractional change of lattice parameter of magnesium with aluminium = $(1/3)(1/V_{\mathrm{unit\ cell}})(\mathrm{d}v/\mathrm{d}x)_{\mathrm{Al}}$, where $V_{\mathrm{unit\ cell}}$ is the volume of the unit cell (Mg is hcp), = $0{\cdot}8662a^2c$ for Mg and C_{s}, C_{o} are concentrations in the frontal layer and bulk matrix compositions.

Since a and c are functions of compositions (x), by Vegard's law, differentiating with respect to x (composition)

$$\frac{\mathrm{d}V}{\mathrm{d}x} = [0{\cdot}866]a\left[2c\left(\frac{\mathrm{d}a}{\mathrm{d}x}\right) + a\left(\frac{\mathrm{d}c}{\mathrm{d}x}\right)\right],$$

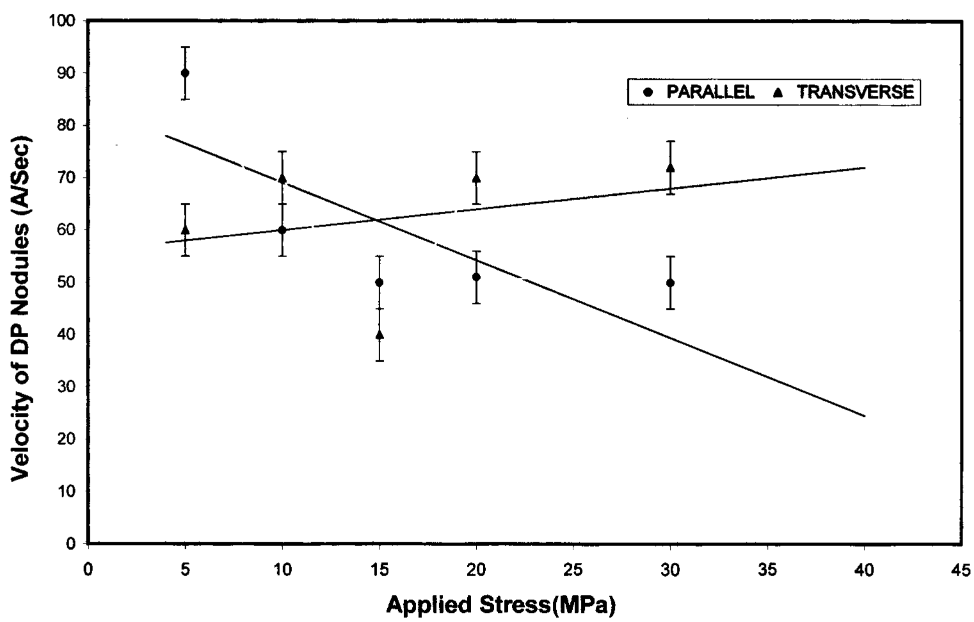

Figure 7. Plot of velocity of parallel and transverse boundaries with applied stress.

$$\left(\frac{\mathrm{d}a}{\mathrm{d}x}\right)_{\mathrm{Mg/Al}} = -0{\cdot}03934 \text{ Å/at\%},$$

$$\left(\frac{\mathrm{d}a}{\mathrm{d}x}\right)_{\mathrm{Mg/Al}} = -0{\cdot}00533 \text{ Å/at\%}.$$

Taking $a = 3{\cdot}2025$ Å, $c = 5{\cdot}20$ Å for magnesium (since it is hcp),

$$V_{\text{unit cell}} = 46{\cdot}185 \text{ Å}^3\text{/at\%},$$

and

$$\mathrm{d}V/\mathrm{d}x = -\,0{\cdot}1598 \text{ Å}^3\text{/at\%}.$$

Hence,

$$n_{\mathrm{Al}} = (1/3)(1/46{\cdot}185)(-0{\cdot}1598),$$

$$= -\,0{\cdot}0011533\text{/at\%}.$$

From careful EDX on the DP nodule,

$$C_s = 7{\cdot}62 \text{ at\%},$$

$$C_o = 10{\cdot}01 \text{ at\%},$$

$$\delta_{th} = -\,0{\cdot}0011533(7{\cdot}62 - 10{\cdot}01),$$

$$= 0{\cdot}0027563.$$

From the above analysis, δ_{th} (0·00276) is close to δ_{exp} of 0·001 for parallel boundaries and δ_{exp} of 0·00111 for transverse boundaries. The mobility $M = 1{\cdot}3 \times 10^3$ for parallel boundaries and $M = 0{\cdot}691 \times 10^3$ for transverse boundaries, are calculated using (5) and (6).

Now since δ_{exp} for parallel boundaries and δ_{exp} for transverse boundaries are close to theoretical coherency strain parameter δ_{th}, it can be argued that diffusional coherency strain ahead of the moving boundary during DP is responsible for grain boundary migration during discontinuous precipitation. This result is in concurrence with the work of Chung *et al* (1982) where in Al–21·8 at%Zn alloy, they conclusively showed that diffusional coherency strain was responsible for grain boundary migration during discontinuous precipitation. It is also consistent with the work of Kashyap *et al* (2000) where in the novel experiment in Mg–Al system, they showed retardation of DP by the addition of 1% Pb to the alloy which was a direct evidence for the diffusional coherency strain theory in explaining grain boundary migration during DP.

4. Conclusions

Diffusional coherency strain is the coupling driving force for grain boundary migration during DP apart from solute supersaturation which is the chemical driving force for precipitation.

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