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Modelling of Precipitation Hardening of Al-Cu-Mg Alloys

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Abstract

A two-stage age hardening model has been developed to describe the microstructure evolution and the yield strength of Al-Cu-Mg alloys. It considers two types of strengthening precipitates, Cu/Mg clusters and S phase, with strength increments due to modulus hardening and precipitate by-passing, respectively. The model is applied to fit and predict the yield strength data from the literature; the predictions are in good agreement with experiments for both natural ageing and artificial ageing curves of 2024 Al alloys. The influence of Si content on plateau strength and softening rate is considered.

1. Introduction

Two-stage age hardening has been observed for Al-Cu-Mg alloys with composition in the (α+S) phase field at the ageing temperature. The first rapid rise in hardness is followed by a period of constant hardness until a second rise to peak [1]. There have been different interpretations in the literature about the precipitates responsible for the hardening, i.e. the first stage of hardening has been considered to be due to GPB zones [2], Cu/Mg clusters [1] or Cu/Mg clusters and S″ phase [3], and the second stage of hardening to be due to S'/S phase [2], GPB zones [1] or S″ [4]. Based on extensive microstructural studies of a solution treated, stretched and subsequently aged Al-Cu-Mg alloys [5], we have developed a two-stage age hardening model by considering two types of precipitates: Cu/Mg clusters and S phase. The predicted yield strengths agree well with experimental data [6, 7]. Due to the difference between Cu/Mg clusters (or vacancy-Cu-Mg complexes) and GPB zones not being clearly defined, here we will not distinguish between clusters and GPB zones, but prefer the nomenclature of clusters.

To apply the model to alloys with different composition, the composition dependency of precipitation rate, the amount of Cu and Mg present in undissolved intermetallic phases and the effect of Si on the precipitation process should be considered. It has been found that small additions of Si increased the response to age hardening of Al-Cu-Mg alloys, with an increased plateau hardness [8, 9]. It was suggested that much of the hardness increase resulted from the improved strength of the GPB zones, although the refinement of the S distribution also strengthened the alloy [8, 9]. Further studies [10] reported a modified structure of the Cu/Mg clusters, rich in Cu and Mg and containing a trace of Si.

In this paper, we will present a model that predicts the yield strength (YS) of Al-Cu-Mg alloys as a function of composition and heat treatments. The model was calibrated and validated by the yield strength and microstructural data on selected solution treated and stretched alloys, and tested against the experimental yield strength data in the literature.

2. The Model

The model describes the evolution of microstructure and the yield strength by considering S phase and its precursors in the form of clusters. The first stage of hardening is attributed to Cu/Mg clusters and the second stage of hardening is attributed to S phase.

2.1 Thermodynamic Model

The regular solution model [6,11] is applied to approximate the solvi of clusters and S phase. Based on three-dimensional atom probe analysis (3DAP) results [7], the Cu:Mg atomic ratio in the clusters is taken as 1:1, and the presence of substantial amounts of Al atoms in the clusters, approximately in the range of 70-90%, is considered. The formation of the largely insoluble Al_7Cu_2Fe and $Al_{20}Cu_2Mn_3$ particles and undissolved Al_2CuMg is accounted for in a treatment similar to that used in [11].

2.2 Kinetics Model

The transformed fraction of precipitates during ageing can be described by the Starink-Zahra (SZ) model for nucleation and growth [12, 13]:

$$\alpha(T,t) = 1 - \left(\left[k(T)t\right]^n / \eta_i + 1\right)^{-\eta_i} \tag{1}$$

where α is the transformed fraction, n is the reaction exponent, η_i is the impingement exponent and $k(T)$ is the rate constant which can be expressed by an Arrhenius relation with the activation energy E_{eff}. The amount of clusters is modelled by assuming S phase forms at the expense of the clusters:

$$x_{cl} = x_{cl}^{\max} \alpha_{cl} \left(1 - \alpha_S\right) \tag{2}$$

where x_{cl} is the amount of clusters formed and $x_{cl}^{\max}$ is the maximum amount of clusters that can form if no other precipitates were present. The evolution of the average size of the precipitate, $\bar{l}(t)$, is approximated by [6, 11]:

$$\bar{l}(t) = \bar{l}_g(t) + \bar{l}_c(t) - \bar{l}_0 = \bar{l}_0 \alpha^{1/3} + \bar{l}_c(t) - \bar{l}_0 \tag{3}$$

where $\bar{l}_g(t)$ is the average size of the precipitates in the nucleation and growth stages, $\bar{l}_c(t)$ is the average size during the coarsening stage [6, 11], which is taken to be in line with the classical coarsening theory, and $\bar{l}_0$ is the average size at the start of coarsening.

An attempt has been made to correlate the precipitation rate to the solute contents within the framework of the SZ model [12, 13] by using the expressions given by the classical precipitation kinetic theories. The rate constant $k(T)$ in Eq.(1) is expressed as:

$$k(T,c) = k_0(c - c_e)\exp(-\frac{E_{eff}}{RT}) \quad (4)$$

where E_{eff} is determined by [7] the activation energy for diffusion of solute atoms Q_d and the energy barrier for homogeneous nucleation ΔG^* which is given by :

$$\Delta G^* = \frac{16\pi\sigma^3}{3} / \left[\frac{RT}{V_m}\ln\left(\frac{c}{c_e}\right)\right]^2 \quad (5)$$

where σ is the interfacial energy, V_m is the molar volume, c_e is the equilibrium solute concentration in the matrix and c is the current solute concentration in the matrix. Here c is taken as the initial solute concentration. Thus ΔG^* is related to the solubility limit via the supersaturation c/c_e.

2.3 Strengthening Model

Four contributions to the critical resolved shear stress (CRSS) of grains are considered: precipitation strengthening by clusters and S phase, solution strengthening by Cu and Mg atoms and dislocation strengthening introduced by the stretching. The clusters strengthen the alloy via the modulus strengthening mechanism [6, 14]:

$$\Delta\tau_{cl} = \frac{\Delta\mu}{4\pi\sqrt{2}} f_{cl}^{1/2} \quad (6)$$

where $\Delta\mu$ is the difference between the shear modulus of the matrix and the clusters, f_{cl} is the volume fraction of the clusters. S rods are considered to be non-shearable and bypassed by an Orowan looping mechanism in both underaged and overaged conditions:

$$\Delta\tau_S = \frac{0.81\mu_m b}{2\pi(1-\upsilon)^{1/2}} \ln\left(d/b\right)\left(0.615d\sqrt{\frac{2\pi}{3f_S}} - d\right)^{-1} \quad (7)$$

where μ_m is the shear modulus of the matrix, b is the Burgers vector, ν is the Poisson's ratio for Al, d is the diameter of the cross-section of S phase and f_S is the volume fraction of S phase. The contribution of dislocation strengthening $\Delta\tau_d$ is described by Ashby model [15]. The solid solution strengthening is taken as:

$$\Delta\tau_{SS} = \sum k_j c_j^{2/3} \quad (8)$$

where c_j is the concentration of Cu or Mg and k_j are constants. The superposition of various strengthening contributions to the total CRSS of the grains is calculated as [6, 11]:

$$\Delta\tau_{\Sigma}^2 = \Delta\tau_d^2 + \Delta\tau_S^2 \quad (9)$$

$$\Delta\tau_{tot} = \tau_{ss} + (\Delta\tau_{\Sigma}^q + \Delta\tau_{cl}^q)^{1/q} \quad (10)$$

where the superposition exponent q is an adjustable parameter between 1.0 and 2.0. The yield strength of the alloys is related to the total CRSS by Taylor factor M: $\sigma_y = \sigma_i + M\Delta\tau_{tot}$, where the intrinsic strength of the matrix σ_i is assumed to be constant throughout the model. σ_i consists of the yield strength for (commercially) pure aluminium and the contribution of the grain boundary strengthening.

3. Experimental Data

The compositions of the Al-Cu-Mg alloys used in this paper are given in Table 1. Alloys A and B were solution treated and stretched by about 2.5% to T351 specifications before undergoing artificial ageing or re-solution treatment followed by natural ageing. To test the prediction capability of the model, published experimental hardness and yield strength data from [8, 9, 16, 17] are used. For artificial ageing, alloy C from [17] was solution treated, deformed by 2% immediately after quenching, room temperature aged for an unknown time and then aged at temperatures from 150 to 225°C.

Table 1: Compositions of the alloys in this work (wt.%)

Alloy	Cu	Mg	Mn	Si	Fe	References
Alloy A	4.20	1.36	0.58	0.06	0.08	This work
Alloy B	4.34	1.37	0.42	<0.05*	<0.08*	[5]
Alloy C	4.25	1.68	0.71	0.14	0.24	[17]

*Estimated.

4. Model Predictions

Parameters associated with the solvi of clusters and S phase, the coefficient k_j for solution strengthening and the Taylor factor M (2.6) were set by using data from the literature and fixed throughout the model. Calibration parameters were found by minimising the root mean squared error (RMSE) to give the best agreement with experiments.

4.1 Natural Ageing (NA)

In this case, the contributions due to cluster hardening and solution hardening are added linearly. The activation energy E_{eff} has been obtained from DSC studies of alloy A at three heating rates (5, 10 and 20°C/min) as 75kJ/mol, other parameters related to the rate of cluster formation (k_0, n, η_l and σ) have been calibrated using isothermal calorimetry curve of alloy A and a commercial purity alloy Al-2.81Cu-1.05Mg-0.41Mn at 25°C [7] and were fixed. The only parameter to be tuned is the shear modulus of clusters, μ_{cl}. This was achieved by considering that the clusters contain about 90% Al atoms, and the Cu:Mg atomic ratio in clusters is 1 [7], σ_l estimated as 30MPa. Optimizing μ_{cl} for best fit to NA curves of these two alloys, and to the plateau strengths of alloy A at 120°C and 170°C then provides μ_{cl} =29.3GPa [7]. These fixed parameters can then be used to make predictions for data in the literature. As shown in Figure 1, a good agreement is observed with RMSE=9MPa, which indicates that the model is sound. (The alloys in Figure 1 are very high purity, and hence σ_l is taken as 10MPa).

4.2 Artificial Ageing (AA)

Two data sets, one for low Si content alloys (see Figure 2) and one for a high Si content alloy (see Figure 3) were used. In the modelling, parameters associated with the clusters have been fixed at their values for NA modelling. For modelling of S precipitation, n was chosen as 2.5, η_l had little effect on model prediction and was taken as 1. E_{eff} for S

precipitation in alloy A was determined by calorimetry studies as 146kJ/mol [18], and for alloy C, E_{eff} was obtained from the times to peak in the ageing curves as 158kJ/mol [17]. After verifying that small variations of E_{eff} between 145-160kJ/mol do not appreciably influence the quality of the fit, an average value of 152 kJ/mol was used for both alloys. To limit model complexity, the activation energy for S coarsening was taken as the activation energy for S precipitation. The average size at the start of coarsening was chosen as 4.7nm on the basis of TEM data [6], three parameters were fitted: the pre-exponential factor for precipitation k_0, the pre-exponential factor for coarsening $k_{0,c}$ and q. A best fit for both data sets was obtained with q=1.5 and average modelling accuracy RMSE=11MPa (excluding data points of ageing time <1h) (see Figure 2 and 3). Different values of $k_{0,c}$ had to be taken and $\Delta\mu$ had to be slightly increased by about 1GPa to obtain a good fit for the high Si content alloy. The latter indicates that the high Si content alloy has higher $\Delta\mu$ and smaller $k_{0,c}$.

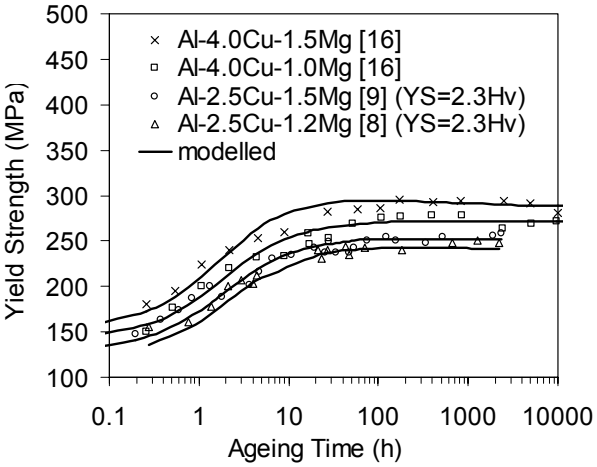

Figure 1: Predicted and measured strength evolution for four alloys aged at room temperature. Data are taken from [8,9,16].

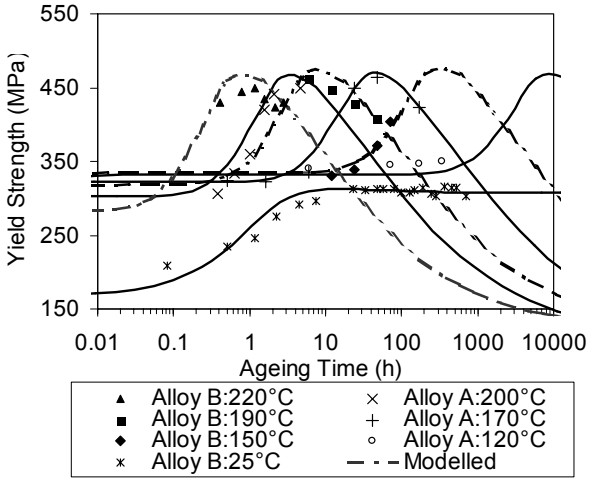

Figure 2: Predicted and measured strength evolution for alloy A and B. YS=3Hv for 220°C curve and YS=2.3Hv for 25°C curve [7].

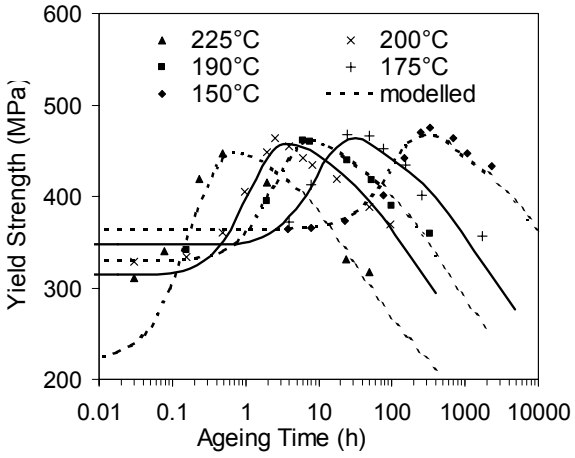

Figure 3: Predicted and measured strength evolution for alloy C. Data are taken from [17].

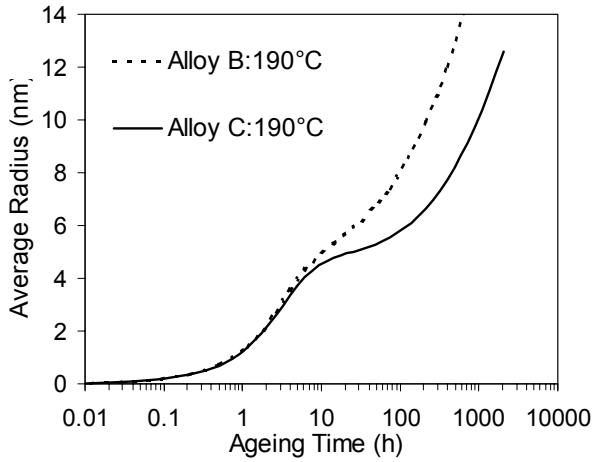

Figure 4: Predicted evolution of S particle size in alloy B (low Si content) and alloy C (high Si content).

Within the present model, this implies that the shear modulus of the clusters is changed due to Si modification of the clusters; and the rate of S coarsening is reduced by the Si addition. As seen in Figure 4, the model predicts that Si content does not influence the rate of nucleation and growth, whereas Si addition would slow down the rate of coarsening.

5. Discussion

As much remains unknown about the chemistry and structure of clusters, and about the mechanism by which Si modified clusters enhances hardening, a simple treatment by adjusting $\Delta\mu$ was adopted in the present work. Some support for our treatment may be derived from Wilson et al.'s [8] suggestion that the observed change in selected area diffraction in the TEM with addition of Si is due to the strain associated with the formation of the clusters and increased perfection of cluster structure. Except for the change in shear modulus, two other effects may explain the difference. It is likely that the Si modified clusters have a higher solvus temperature [19], which will similarly lead to an increase in plateau strength. And, since Si is known to have strong interaction with Mg atoms, it is possible that the clustering of Mg-Si might change the Cu:Mg ratio in the clusters.

The modelling indicates that coarsening of S phase is reduced by Si addition. This is in line with TEM observations by Weatherly and Nicholson [20] which show that cross sections of S phase precipitates are reduced by addition of Si. Another possible explanation is that the reduced softening rate might associate with σ phase ($Al_5Cu_6Mg_2$) formation. This phase was observed to form in Al-Cu-Mg alloys with 0.5wt%Si especially on overaging [9, 21], and is known to exhibit a low rate of coarsening [22] and contributes to strengthening. However it has been shown that stretching after quenching will tend to reduce the propensity for σ phase formation [21].

6. Conclusions

A model has been developed for two-stage age hardening of Al-Cu-Mg alloys. The first stage of hardening is attributed to Cu/Mg clusters and the second stage of hardening is attributed to S phase. The model takes account of the effect of alloying contents on precipitation rate and strength increase due to Si modified clusters. The predictions are in good agreement with literature data for both naturally aged and artificial aged 2024 alloys with two different Si contents. The model can be adapted to take account of the reduced softening rate in the higher Si content alloy by reducing the coarsening rate of S phase. The modelling accuracy on unseen yield strength data is about 11MPa.

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