Effect of Pre-deformation on Precipitation Behavior of Automotive Al-Mg-Si-Cu Alloys (Postprint)

Authors: Cui Li, Guo Mingxing, Peng Xiangyang, Zhang Yan, Zhang Jishan, Zhuang Linzhong

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Abstract

The effects of pre-deformation on the precipitation behavior of Al-Mg-Si-Cu alloy were investigated by means of DSC, mechanical property testing, and TEM. The results indicate that during slow heating, the dissolution rate of GP zones in the pre-aged alloy decreases with increasing pre-deformation, and the activation energies for GP zone dissolution in alloys with 0%, 5%, and 15% pre-deformation were determined to be 137.1 kJ/mol, 189.5 kJ/mol, and 141.3 kJ/mol, respectively, using the Avrami-Johnson-Mehl method; when the alloy was subjected to paint baking hardening at 185°C/20 min directly after different pre-deformations, pre-deformation effectively promoted precipitate formation and increased the paint baking hardening increment, reaching a maximum of 160 MPa; however, the increase in paint baking hardening slowed down when the pre-deformation exceeded 10%; furthermore, the GP zone dissolution rate in paint-baked alloys after pre-deformation was lower at certain temperatures, but above a certain temperature, it became higher than that in the undeformed alloy, the resulting $\ln[(dY/dT)\phi/f(Y)]$-$1/T$ curves even exhibited a transformation from high to low activation energy; however, with increasing pre-deformation, the activation energy for β'' phase precipitation continuously decreased while the precipitation rate continuously increased, and the corresponding TEM microstructural observations were in good agreement with these results.

Full Text

Introduction

With growing awareness of energy conservation and environmental protection, automotive lightweighting has become a forefront and hot issue in automotive industry technology in the 21st century. One important approach to achieving lightweighting is the use of lightweight aluminum alloy materials, such as Al-Mg and Al-Mg-Si series alloys. The latter are widely used in manufacturing automotive body outer panels due to their excellent stamping formability and bake hardening properties. Currently, widely applied alloy grades in the Al-Mg-Si series include AA6016, AA6111, and AA6022, which generally exhibit good formability and bake hardening capability, attracting significant attention and application from numerous domestic and international automotive manufacturers.

However, with continuous development and in-depth research on aluminum alloys for automotive lightweighting, it is difficult for alloy sheets prepared with a single composition or process to comprehensively meet the different requirements for formability and strength of various automotive body components. For instance, some components undergo large deformation during stamping, imposing strict requirements on sheet formability, while also requiring the highest possible bake hardening increment during the paint-baking process to avoid denting during collision. Previous studies have shown that pre-aging treatment of solutionized Al-Mg-Si alloys can improve or stabilize sheet formability while ensuring good bake hardening increments during the paint-baking process. Nevertheless, pre-aged alloys subjected to different deformation amounts during subsequent stamping will inevitably exhibit differences in bake hardening increment. Therefore, understanding the influence of different pre-deformation amounts on subsequent aging precipitation behavior, precipitate size, morphology, and distribution, as well as bake hardening increment, is crucial for designing aluminum alloy materials for different automotive components and optimizing processing parameters.

This work focuses on pre-aged Al-0.6Mg-0.9Si-0.2Cu-0.07Mn (mass fraction, %) alloy sheets. The alloy was subjected to different degrees of pre-deformation after pre-aging treatment, followed by investigation of precipitation behavior, bake hardening response, and microstructural evolution to obtain the influence law of different pre-deformation amounts on bake hardening increment, precipitation behavior, and microstructure, thereby providing guidance for production and application of this alloy system.

Experimental

The alloy composition was Al-0.6Mg-0.9Si-0.2Cu-0.07Mn. Raw materials with mass fractions of 99.7% pure Al, Al-25.73%Mg, Al-12.7%Si, Al-50.29%Cu, and Al-9.56%Mn master alloys were melted in a resistance crucible furnace following a specific addition sequence. The alloy melt was then poured into a water-cooled steel mold (180 mm length × 110 mm width × 90 mm height). After casting, the ingot was trimmed and subjected to a two-stage homogenization treatment at 485°C for 3 h + 555°C for 16 h, followed by hot rolling on a Φ350 two-high hot rolling mill at 5.5 r/min. The initial rolling temperature was 550°C, the final rolling temperature was below 300°C, and the final thickness was 4 mm.

After intermediate annealing at 400°C for 1 h, the sheet was cold-rolled to 1 mm thickness. The cold-rolled samples were solution-treated at 555°C for 2 min in a salt bath, pre-aged at 80°C for 12 h, and stored at room temperature for 14 days (T4P condition). Subsequently, the T4P samples were pre-deformed to 0, 5%, 10%, and 15% strain, followed by simulated bake hardening treatment at 185°C for 20 min to investigate changes in bake hardening increment and precipitation behavior.

The precipitation behavior of alloys in different states was analyzed using a Q2000 differential scanning calorimeter (DSC). Disc specimens of 3 mm diameter × 1 mm thickness (approximately 15 mg) were prepared, with high-purity Al as the reference standard, and heated from 20°C to 400°C at 10°C/min. Tensile tests were conducted on an MTS810 electro-hydraulic servo material testing machine at a strain rate of 3 mm/min, with specimens sampled along the rolling direction according to GB3076-1982 specifications. Microstructural observation was performed using a Tecnai G2 F30 field emission transmission electron microscope (TEM). Samples were prepared by mechanical thinning followed by twin-jet electropolishing in a solution of 25% HNO_3 + 75% CH_3OH (volume fraction) at -25 to -10°C and 20-30 V.

Theoretical Analysis

Numerous studies have reported on aluminum alloy precipitation behavior using various theoretical models. This work employs non-isothermal DSC analysis combined with the Avrami-Johnson-Mehl model to investigate precipitation kinetics. The relevant kinetic equations are as follows:

$$Y = 1 - \exp(-kt^n) \quad (1)$$

where Y is the volume fraction transformed within time t (in minutes), and k and n are constants related to nucleation type and growth mechanism.

$$k = k_0 \exp\left(-\frac{Q}{RT}\right) \quad (2)$$

where k_0 is a constant, Q is the activation energy (in kJ/mol), R is the universal gas constant (8.31 J/(mol · K)), and T is the thermodynamic temperature (in K).

Taking logarithms of both sides of Eq. (1) yields:

$$\ln[-\ln(1-Y)] = \ln k + n \ln t \quad (3)$$

The value of n can be easily obtained from the slope of the linear relationship between $\ln[-\ln(1-Y)]$ and $\ln t$.

Differentiating Eq. (1) gives the transformation rate during non-isothermal processes:

$$\frac{dY}{dt} = knt^{n-1}f(Y) \quad (4)$$

where f(Y) is an implicit function of Y. From Eqs. (1) and (4), the expression for Y as a function of T is:

$$Y = \frac{A(T)}{A_f} \quad (5)$$

where A(T) is the area between the baseline and the DSC peak from the peak onset to temperature T, and A_f is the total peak area.

The expression for $\frac{dY}{dT}$ can be derived as:

$$\frac{dY}{dT} = \frac{1}{A_f}\frac{dA(T)}{dT} \quad (6)$$

where ϕ is the heating rate (ϕ = 10°C/min in this experiment).

From Eqs. (2), (4), and (7), we obtain:

$$\ln\left[\frac{(dY/dT)\phi}{f(Y)}\right] = \ln(k_0 n) - \frac{Q}{RT} + (n-1)\ln t \quad (8)$$

Equation (8) shows that $\ln[(dY/dT)\phi/f(Y)]$ and $1/T$ satisfy a linear relationship. By plotting $\ln[(dY/dT)\phi/f(Y)]$ versus $1/T$, the activation energy can be determined from the slope $-Q/R$, thereby establishing the corresponding dissolution or precipitation kinetic equation.

Results and Discussion

3.1 Effect of Pre-deformation on Precipitation Behavior of Pre-aged Alloy

Figure 1 [Figure 1: see original paper] shows the DSC curves of T4P-treated Al-0.6Mg-0.9Si-0.2Cu-0.07Mn alloy after different pre-deformations. The DSC curves of the pre-aged alloy primarily include a dissolution peak a, and precipitation peaks b and c. Pre-aging can effectively promote the formation of nano-sized Mg-Si solute atom clusters, which are relatively stable and can directly serve as nucleation sites for precipitation strengthening phases during subsequent high-temperature bake hardening. Consequently, pre-aged alloys exhibit no other solute atom cluster precipitation peaks in the low-temperature region, and the dissolution peak a is smaller compared to alloys without pre-aging treatment.

However, if the alloy does not receive appropriate pre-aging treatment, solution-quenched alloys will rapidly form Mg-Mg and Si-Si solute atom clusters within 7 days of natural aging. The Mg-Mg clusters will dissolve within 7 days, while Si-Si clusters remain relatively stable at room temperature. With prolonged natural aging, Mg atoms continuously enter Si clusters to form Mg-Si clusters. This precipitation process fails to produce a large number of stable Mg-Si clusters or results in clusters that are too small, leading to a larger dissolution peak at lower onset temperatures in DSC analysis. Direct high-temperature bake hardening may cause bake softening, and various other solute atom clusters will continuously form during DSC heating. Therefore, recent research on Al-Mg-Si alloys for automotive lightweighting has emphasized appropriate pre-aging treatment to improve both formability and bake hardening performance.

Since alloy sheets require stamping forming after pre-aging, the deformation amount varies with component geometry. To better analyze the effect of different deformation amounts after pre-aging on precipitation behavior, T4P-state alloys were pre-deformed to 5%, 10%, and 15% strain. Figure 1 shows that after 5% pre-deformation, the GP zone dissolution peak is relatively small, while after 15% pre-deformation, the dissolution peak area significantly increases. However, the dissolution completion temperatures for both pre-deformed conditions are higher than that of the non-pre-deformed alloy. The higher dissolution completion temperature in pre-deformed alloys also shifts the β phase precipitation onset temperature to higher values compared to the non-pre-deformed alloy.

This phenomenon occurs because pre-deformation accelerates solute atom diffusion, promoting rapid growth of solute atom clusters formed during T4P treatment or precipitating new clusters. Since no new solute atom cluster precipitation peaks are observed in the low-temperature region of DSC curves, it can be concluded that pre-deformation does not promote the precipitation of new solute atom clusters during DSC heating but rather facilitates further growth of existing clusters formed during T4P treatment. However, the diffusion rates of Mg and Si solute atoms differ significantly, with Mg diffusion being much slower than Si (at 177-325°C: D_{Mg} = 0.06-0.0616 cm^2/s, D_{Si} = 2.42-2.45 cm^2/s). This leads to substantial Si atom segregation into existing Mg-Si clusters during DSC heating, reducing the Mg/Si ratio of the original clusters below that of the β phase (Mg/Si ratio of 0.9-1.2). These segregated clusters cannot serve as nucleation sites for β phase growth. When the temperature increases sufficiently, they must first partially dissolve until their Mg/Si ratio re-enters the β phase range, after which they can nucleate and grow rapidly. Moreover, as pre-deformation increases, solute atom diffusion accelerates further, causing more severe cluster growth during the low-temperature DSC heating stage and greater deviation of the Mg/Si ratio from the β phase range. This explains why the GP zone dissolution peak area increases and the β phase precipitation peak shifts to higher temperatures with increasing pre-deformation (the shift is attributed to the heat required for dissolution exceeding the heat released by β precipitation, resulting in an apparently higher precipitation onset temperature). Consequently, to avoid non-uniform diffusion of Mg and Si atoms into T4P-formed clusters after stamping deformation, alloy sheets should be heated as rapidly as possible; otherwise, this phenomenon will reduce the bake hardening increment.

To quantitatively analyze the effect of different pre-deformation amounts on GP zone dissolution activation energy and kinetics, Figure 2 [Figure 2: see original paper] illustrates the detailed calculation process using the Avrami-Johnson-Mehl model. Figure 2(a) shows that both 5% and 15% pre-deformation increase the GP zone dissolution onset temperature and significantly reduce the dissolution rate compared to the non-pre-deformed alloy. From the ln[(dY/dT)ϕ/f(Y)]-1/T curves in Figure 2(c), the GP zone dissolution activation energies for pre-aged alloys with 0, 5%, and 15% pre-deformation are determined to be 137.1, 189.5, and 141.3 kJ/mol, respectively. The activation energies of pre-deformed alloys are higher than that of the non-pre-deformed alloy due to the non-uniform diffusion of excess Si into Mg-Si clusters during low-temperature DSC heating. However, the activation energy after 5% pre-deformation is significantly higher than after 15% pre-deformation. This is because the rapid DSC heating process is too short to completely eliminate the high density of dislocations introduced by 15% pre-deformation. Residual dislocations promote GP zone dissolution, resulting in lower activation energy for the 15% pre-deformed alloy compared to the 5% pre-deformed condition. The corresponding kinetic equations are: Y = 1 - exp[-2.892$\times10^{15}$ exp(-16534/T) × t], Y = 1 - exp[-1.0642$\times10^{21}$ exp(-22846/T) × t], and Y = 1 - exp[-2.577$\times10^{15}$ exp(-17011/T) × t]. The theoretically predicted GP zone dissolution Y-t kinetic curves are shown in Figure 2(d), clearly demonstrating that pre-straining increases dissolution difficulty due to reduced Mg/Si ratio and increased cluster size. The dissolution rates after 5% and 15% pre-strain are lower than in the non-pre-strained alloy, which requires only 6-7 min at 185°C for complete GP zone dissolution, whereas pre-deformed alloys need 20-30 min.

3.2 Effect of Pre-deformation on Bake Hardening Performance

Figure 3 [Figure 3: see original paper] shows the stress-strain curves of T4P-state alloys after pre-deformation to 0, 5%, 10%, and 15% strain followed by simulated bake hardening at 185°C for 20 min. With increasing pre-deformation, the elongation decreases while the yield strength increases, with a maximum increase of approximately 160 MPa compared to the T4P state. However, the strength increment for the 15% pre-deformed alloy is only slightly higher than that for the 10% pre-deformed alloy. The bake hardening increments after 185°C/20 min aging with 0, 5%, 10%, and 15% pre-deformation are 45.7, 132.4, 158.8, and 167.1 MPa, respectively, clearly demonstrating that pre-deformation promotes bake hardening increment.

The introduction of pre-deformation generates dislocations in the alloy matrix, which effectively promote the formation and growth of solute atom clusters during high-temperature bake hardening, resulting in numerous fine precipitates and increased strength. If the pre-deformation is too small, this promotion effect is insignificant; however, if the pre-deformation is excessive (e.g., 15%), the promotion effect also diminishes. Although dislocations provide effective diffusion channels for solute atoms, high dislocation densities lead to dislocation tangles in localized regions, causing non-uniform diffusion and consequently non-uniform precipitate size and distribution, which limits strength enhancement. Particularly, due to the difference in diffusion coefficients between Mg and Si elements, excessive strain energy causes rapid Si diffusion into solute clusters. Combined with the inherently high Si concentration, this further accelerates diffusion and ultimately limits the formation of the most strengthening-effective β phase. As predicted by DSC results, only rapid heating to high temperature (e.g., direct 185°C bake hardening) can accelerate β phase precipitation in pre-deformed alloy sheets.

3.3 Effect of Pre-deformation on Subsequent Precipitation Behavior of Bake-Hardened Alloy

Even after 185°C/20 min bake hardening, Al-Mg-Si alloys remain in a severely under-aged condition, making precipitates difficult to characterize clearly. To better analyze differences in solute atom clusters, GP zones, and β phases formed in bake-hardened alloys and understand the influence of pre-deformation on aging precipitation behavior, further DSC analysis was performed on several bake-hardened alloys, as shown in Figure 4 [Figure 4: see original paper]. No solute atom cluster precipitation or dissolution is observed in the low-temperature region for alloys pre-deformed to 5% or 15%, whereas the non-pre-deformed alloy shows some cluster re-dissolution. This indicates that 185°C/20 min aging transforms the originally distributed solute atom clusters into numerous fine GP zones or β phases, while also forming certain amounts of new fine clusters or GP zones. Due to fewer diffusion channels compared to pre-deformed alloys, solute atom diffusion is relatively slow, and the newly formed clusters or GP zones during 185°C/20 min aging are small (some may be smaller than the critical dissolution size r_c), resulting in slight re-dissolution during DSC heating. With further temperature increase, all alloys exhibit larger dissolution peaks, which can be preliminarily identified as GP zone dissolution based on the corresponding temperatures, confirming that 185°C/20 min aging does not produce large amounts of β phase but rather GP zones. Additionally, comparison of GP zone re-dissolution peaks and β /β phases reveals that increasing pre-deformation before bake hardening reduces the GP zone dissolution peak area, advances the β phase precipitation onset temperature (especially for the 15% pre-deformed alloy), and increases the area of the C peak corresponding to β phase precipitation compared to peak c in Figure 1. This further demonstrates that appropriate pre-deformation effectively promotes the transformation of solute atom clusters to GP zones and even β phases, significantly increasing precipitation kinetics during paint-baking. However, the promotion effect slows when pre-deformation exceeds a certain level, as evidenced by GP zone dissolution peak area and tensile properties.

Figure 5 [Figure 5: see original paper] and Figure 6 [Figure 6: see original paper] illustrate the calculation processes for GP zone dissolution and β phase precipitation activation energies in bake-hardened alloys. The Y-T and dY/dT-T curves for GP zone dissolution (Figure 5) reveal that at certain temperatures, the dissolution rates of 5% and 15% pre-deformed alloys are lower than that of the non-pre-deformed alloy. However, above a specific temperature, the GP zone dissolution rates become higher than in the non-pre-deformed alloy. Notably, the ln[(dY/dT)ϕ/f(Y)]-1/T curve for the 15% pre-deformed alloy consists of two segments: the first with high activation energy and the second with low activation energy (only 97.7 kJ/mol), even lower than the non-pre-deformed alloy. In contrast, the GP zone dissolution activation energy for the 5% pre-deformed alloy remains higher than that of the non-pre-deformed alloy throughout. This again demonstrates that increasing pre-deformation promotes not only the growth of clusters formed during T4P treatment but also the formation of new clusters during 185°C/20 min aging. Due to limited time, these new clusters are small and dominate the later dissolution process, requiring lower activation energy and resulting in the two-stage dissolution behavior. For β phase precipitation in bake-hardened alloys, Figure 6 [Figure 6: see original paper] shows that increasing pre-deformation continuously increases the precipitation rate and decreases the activation energy. This is because dislocation defects generated by pre-deformation serve as short-circuit diffusion channels, accelerating atom migration. The new solute atom clusters or GP zones formed during 185°C/20 min aging can also serve as nucleation sites for β phase growth during subsequent heat treatment, leading to gradually decreasing β phase precipitation activation energy. This result is consistent with findings by Hirata and Matsue.

Based on the Q and k_0 values calculated from Figures 5 and 6, the kinetic equations for GP zone dissolution and β phase precipitation are summarized in Table 1 . The corresponding Y-t curves at 185°C are plotted in Figure 7 [Figure 7: see original paper]. Figure 7(a) shows that with increasing pre-deformation, the GP zone dissolution rate eventually exceeds that of the non-pre-deformed alloy with prolonged aging time. For β phase precipitation (Figure 7(b)), the precipitation rate continuously increases with pre-deformation, with the 15% pre-deformed alloy essentially completing precipitation in approximately 2 h.

3.4 TEM Microstructural Analysis

To better compare the effect of pre-deformation on precipitate size and distribution, alloys with different pre-deformation amounts were bake-hardened at 185°C for 20 min, then heated from 20°C to 250°C at 10°C/min (identical to the DSC heating process in Figure 4), water-quenched, and examined by TEM, as shown in Figure 8 [Figure 8: see original paper]. Statistical analysis software calculated the area fractions of precipitates in the three alloys as 40.1%, 47.2%, and 49.7%, respectively. Figure 8 reveals that increasing pre-deformation not only reduces precipitate size but also significantly increases precipitate number density compared to the non-pre-deformed alloy. The alloy with 15% pre-deformation contains substantially more fine dot-shaped or short needle-shaped β precipitates than the other two conditions. However, precipitate distribution uniformity begins to decrease due to significant increases in dislocation density with pre-deformation, leading to some non-uniformity in precipitation. This explains why the bake hardening increment for the 15% pre-deformed alloy is only slightly higher than that for the 10% pre-deformed alloy. The Y-T curves in Figure 6(b) also show that the transformed fraction Y increases with pre-deformation when heating from 20°C to 250°C, consistent with the TEM observations.

Conclusions

(1) Pre-aged Al-0.6Mg-0.9Si-0.2Cu-0.07Mn alloy subjected to pre-deformation exhibits reduced Mg/Si ratio in solute atom clusters formed during pre-aging due to the higher diffusion rate of Si during slow heating. This not only fails to promote β phase precipitation at high temperatures but also increases the GP zone dissolution peak area. Using the Avrami-Johnson-Mehl method, the GP zone dissolution activation energies for alloys with 0, 5%, and 15% pre-deformation are determined to be 137.1, 189.5, and 141.3 kJ/mol, respectively, and corresponding GP zone dissolution kinetic equations are established.

(2) When pre-aged alloys with different pre-deformation amounts are directly subjected to high-temperature simulated bake hardening at 185°C for 20 min, pre-deformation effectively promotes precipitate formation. The bake hardening increment increases with pre-deformation, reaching a maximum of approximately 160 MPa, but the increment rate slows when pre-deformation exceeds 10%.

(3) Avrami-Johnson-Mehl analysis of bake-hardened alloys reveals that GP zone dissolution rates for 5% and 15% pre-deformed alloys are lower than that of the non-pre-deformed alloy below certain temperatures, but become higher above specific temperatures. The resulting $\ln[(dY/dT)\phi/f(Y)]$-$1/T$ curves even exhibit a transition from high to low activation energy. However, with increasing pre-deformation, the β phase precipitation activation energy continuously decreases while the precipitation rate continuously increases.

References

[1] Birol Y. Mater Sci Eng A, 2005; 391:175 [2] Roven H J, Liu M P, Werenskiold J C. Mater Sci Eng A, 2008;483:54 [3] Esmaeili S, Wang X, Lloyd D J, Poole W J. Metall Mater Trans A, 2003;34:751 [4] Shen C H. J Mater Sci Technol, 2011; 27(3): 205 [5] Esmaeili S, Lloyd D J, Poole W J. Mater Lett, 2005; 59(5): 575 [6] Shen C H, Ou B L. J Chin Inst Eng, 2008; 31(1): 181 [7] Staab T E M, Krause-rehberg R. J Mater Sci, 2006;41:1059 [8] Gupta A K, Lloyd D J, Court

S A. Mater Sci Eng A, 2001;(301)2:140 [9] He L Z, Zhang H T, Cui J Z. J Mater Sci Technol, 2010;26(2):141 [10] Han Y, Ma K, Li L, Chen W, Nagaumi H. Mater Des, 2012;39:418 [11] Cai M, Field D P, Lorimer G W. Mater Sci Eng A, 2004;373:65 [12] Gupta A K, Jena A K, Chaturvedi M C. Scri Metall, 1988; 22(3): 369 [13] Jena A K, Gupta A K, Chaturvedi M C. Acta Metall, 1989; 37(3): 885 [14] Ghosh K S, Gao N. Trans Nonferrous Met Soc China, 2011; 21(6): 1199 [15] Ghosh K S, Das K, Chatterjee U K. Mater Sci Technol, 2004;20:825 [16] Oguocha I N A, Yannacopoulos S. Mater Sci Eng A, 1997; 231(1): 25 [17] Gupta A K, Marois P H, Lloyd D J. Mater Sci Forum, 1996; 217: 801 [18] Gupta A K, Lloyd D J. Metall Mater Trans A, 1999; 30(13):879 [19] Luo A, Lloyd D J, Gupta A, Youdelis W V. Acta Metall Mater, 1993; 41(3): 769 [20] Zhang Q X, Guo M X, Hu X Q, Cao L Y, Zhuang L Z, Zhang J S, Acta Metall Sin, 2013; 49(12):1604 [21] Edwards G A, Stiller K, Dunlop G L, Couper M J. Acta Mater, 1998;46(11):3893 [22] De Geuser F, Lefebvre W, Blavette D. Philos Mag Lett, 2006;86(4):227 [23] Bryant J D. Metall Mater Trans A, 1999, 30(8): 1999 [24] Brandes E A, Brook G B. Smithells Metals Reference Book, 7th ed. Bath: Reed Educational and Professional Publishing Ltd, 1992:73 [25] Sha G, Möller H, Stumpf W E, Xia J H, Govender G, Ringer S P. Acta Mater. 2012;60:692 [26] Hirata T, Matsuo S. Trans Nat Res Inst Met, 1973, 15(6): 271

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