Available online at www.sciencedirect.com
ScienceDirect

Trans. Nonferrous Met. Soc. China 24(2014) 2289−2294

Transactions of
Nonferrous Metals
Society of China

www.tnmsc.cn

Effect of copper on precipitation and baking hardening behavior of Al−Mg−Si alloys

Cong-hui LIU, Xin-ming ZHANG, Jian-guo TANG, Xing-xing LIU, Liang CHEN

School of Materials Science and Engineering, Central South University, Changsha 410083

Received 17 October 2013; accepted 22 May 2014

Abstract: The effects of copper on the ageing precipitation behavior of as-quenched and pre-aged AA6016 aluminum alloy were studied by differential scanning calorimetry (DSC), Vickers hardness measurement and transmission electronic microscopy (TEM). The results indicate that the addition of copper facilitates the growth of clusters (GP I) to the critical size during pre-ageing. Therefore, the addition of copper accelerates the transition from GP I (pre-β'') to GP II (β'') during final artificial ageing, and finally results in the favorable paint-bake response. However, the one with the copper level of 0.3% does not show significant baking hardening response as expected. Pre-aging can also reduce the detrimental effect due to natural aging of copper-containing alloys.

Key words: Al−Mg−Si−Cu alloy; baking hardening behavior; Cu contained precipitates

---

1 Introduction

Heat treatable Al−Mg−Si aluminum alloys are extensively used for auto body sheet applications recently. Special Al−Mg−Si alloys with improved formability and baked strength are in demand by the automotive industry. The strength and paint bake response of auto body sheet are important and these are not only influenced by the alloy compositions but also by the processing cycles. In Europe, AA6016 sheets are particularly applied successfully in gauge of 1−1.2 mm [1]. The material is delivered in the T4 temper to ensure low yield strength and high elongation for good formability. Pre-aging treatment is employed shortly after quenching (often denoted as T4P) for the purpose of reversing GP I zones formation and providing GP II zones (β'') nuclei, which lead to a large number of β'' precipitates during final artificial aging (i.e., the paint bake cycle). These high density β'' precipitates contribute to the higher final strength for dent resistance after forming operation [2].

The summary of information from the latest investigations on precipitation sequence [3−8] of Al−Mg−Si alloy shows inconsistency about the initial stages of decomposition of the solid solution. And natural ageing occurs during processing, which has a significant negative effect on artificial ageing of Al−Mg−Si alloys. The Mg/Si co-clusters were found in the 6061 alloy aged at room temperature [3], while GP I zones were also found by TAMIZIFAR and LORIMER [5]. But there is a common sense that such kind of microstructure formed during low-temperature ageing influences the final aged strength [8−12]. Though the natural ageing between quenching and artificial ageing is generally detrimental, there are a number of variables, determining the beneficial or detrimental effects, such as Mg_2Si in the alloy, duration of delay. As the distribution of hardening GP I zones and GP II zones (β'') strongly depends upon the distribution of co-clusters, EDWARDS et al [3] proposed that for any low-temperature pre-ageing to be beneficial, sufficient time must be allowed to develop a large number of co-clusters. In these cases, copper is general accepted to enhance the ageing kinetics and increase stability of GP I zones during paint-baking and the final strength. It is believed that addition of copper to Al−Mg−Si aluminum alloys are needed to enhance post paint-bake strength [2,5,13], but leads to decrease in formability [13,14] and deleterious effect on the corrosion resistance properties of the natural-aged alloys. This complexity is why an effort has been launched to do such analyses on the

---

Foundation item: Project (51105139) supported by the National Natural Science Foundation of China; Project (2010CB731706) supported by the National Basic Research Program of China

Corresponding author: Jian-guo TANG; Tel: +86-731-88830265; E-mail: jgtang@csu.edu.cn

DOI: 10.1016/S1003-6326(14)63346-X

effect of copper addition on the ageing behavior of Al−Mg−Si alloys. And there are numerous reports on the effect of the quaternary element addition on ageing precipitation of Al−Mg−Si alloys [4,7−9,13,15].

In order to understand the effect of copper on age hardening due to natural aging and the following artificial aging of 6016 aluminum alloy, it is worthy of detailed study of the effect of copper addition on pre-ageing and final artificial ageing precipitation behavior of the investigated alloys. For this purpose, it is attempted to clarify the precipitation products which form after pre-ageing, natural ageing and artificial ageing in AA6016 based alloys with different amounts of copper addition by Vickers hardness measurement, differential scanning calorimetry (DSC) and transmission electron microscope (TEM).

2 Experimental

The chemical composition of the investigated are given in Table 1, i.e., three alloys based on 6016 with 0, 0.1% and 0.3% Cu. The materials were cast in an induction furnace. The as-cast alloys were homogenized at 550 °C for 12 h in an air furnace, and then were hot- and cold- rolled to 1.0 mm-thick sheets.

Table 1 Chemical composition of experimental AA6016 based alloys (mass fraction, %)

Alloy	Mg	Si	Cu	Fe	Mn	Al
A4	0.42	1.25	0	0.08	0.13	Bal.
A21	0.41	1.30	0.10	0.07	0.08	Bal.
A10	0.37	1.26	0.32	0.09	0.13	Bal.

The cold-rolled sheets were solution heat treated at 550 °C for 30 min and quenched in cold water. The as-quenched sheets were pre-aged at 100 °C for 2 h and at 200 °C for 20 s respectively. The pre-aged sheets were artificially aged at 170 °C for 30 min to stimulate paint-baking cycle after 30 d delay at room temperature.

The DSC analysis was carried out using a Perkin-Elmer DSC7 instrument with a scanning rate of 10 °C/min in the temperature range of room temperature to 350 °C on the solution treated and pre-aged specimens. The Vickers hardness values of 5 samples were measured and averaged to estimate the hardening response using a ZX7M-HVS−50 with a load of 4.9 N and holding time of 20 s on the samples. The traditional TEM was performed using a JEOL-JEM−2100F on the specimens after pre-ageing and artificial ageing.

3 Results and discussion

3.1 Precipitation sequence

The precipitation sequence in Al−Mg−Si alloys has been investigated by many researchers, which includes the stages listed as follows: supersaturated solid solution (SSSS)→formation of Mg, Si clusters→dissolution of Mg clusters → formation of Mg+Si co-clusters → small precipitates of unknown structure (GP I or pre-β'') → formation of coherent β'' needles (GP II) → formation of semi-coherent β' rods + lath-like particles → formation semi-coherent β plates → formation of incoherent β.

Such sequences are not particular and valid for any temperature. Some of the phases might not occur at low temperatures or may evolve into others almost instantaneously at high temperatures and there may be ranges of co-existence with more than one phase. The exact precipitation sequence depends on the alloy compositions (excess in Mg or Si, or balanced alloy) and the possible presence of additional elements (Cu, Mn, Fe, etc) [16].

Figure 1 shows the DSC curves of the experimental alloys as-quenched and the following pre-aged at 200 °C for 20 s. The DSC curves of as-quenched alloys illustrate a slight precipitation peak A at 70 °C and a dissolution trough B at 155 °C. The exothermic peak A is ascribed to the formation of Si−Mg-vacancy clusters and nucleation of GP zones [17]. Since the clusters can dissolve and then transform to pre-β'' and β'' during the heat treatment, trough B is due to the solution of atomic clusters. The process associated with trough C is not known exactly. It is considered that the pre-β'' precipitates are formed during ageing at around 70 °C. The peak A is followed by a sharp peak D, which is supposed to be caused by random precipitates, exhibiting irregular arrangement of bright dots in the HRTEM image [18]. According to ESMAEILI et al [16] the precipitation of β', Q'' and Q' phase. Lead to the exothermic peaks F, H and I.

The first stage in the precipitation sequence, i.e., GP zone or clusters formation, is a complex process. Based on previous studies, this stage consists of three types of clusters: clusters of Si atoms, clusters of Mg atoms, and co-clusters of Mg and Si atoms. These three types of clusters compete with each other. However, due to the ultrafine size of the clusters, the details of the clustering process are unclear. According to a recent three-dimensional atom probe study, in this stage, Cu did not have a significant effect on the chemical compositions of the GP zones [19].

The DSC curves of the alloys with 0.1% copper pre-aged at 100 °C for 2 h don't show peak A and trough B. This indicates that the atomic clusters are formed and grow into the critical size which is stable during pre-ageing. And the density of the peak D shows a significant increase as shown in Fig. 1(b).

As shown in Fig. 1(c), a peak H appears at the temperature of around 275 °C and a peak I appears at the temperature of around 340 °C in addition to the

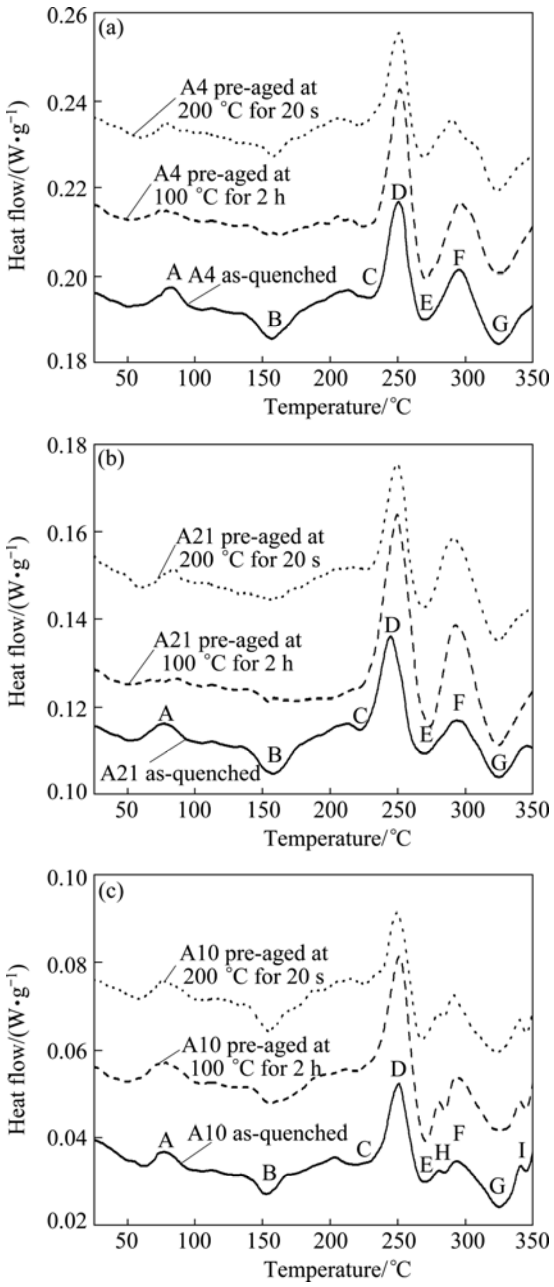

Fig. 1 DSC curves of as-quenched, pre-aged at 100 °C for 2 h and pre-aged at 200 °C for 20 s of AA6016 based alloy with out Cu (a), 0.1% (b) and 0.3% (c) Cu

corresponding peak A and trough B are found in the DSC curves of the pre-aged alloy with 0.3% Cu. These two peaks mean the formation of Q'' and Q' phases [16]. Figure 1(c) suggests that the addition of 0.3% Cu leads to the formation of Q'' and Q' precipitates, but has no obvious effect on the formation of the atomic clusters in Al−Mg−Si system alloys, which may be attributed to the low diffusion coefficient of copper in aluminum matrix.

3.2 Vickers hardness measurement

Figure 2 shows the Vickers hardness evolution during pre-aging, natural aging and final artificial ageing. The hardness values of specimens pre-aged at 100 °C for 2 h and then artificially aged are higher than those pre-aged at 200 °C for 20 s and then artificially aged, which suggests that clusters in the specimens after pre-ageing at 100 °C for 2 h become more stable and effective to develop into β'' precipitates (confirmed by larger peak D in corresponding DSC curves in Fig. 1).

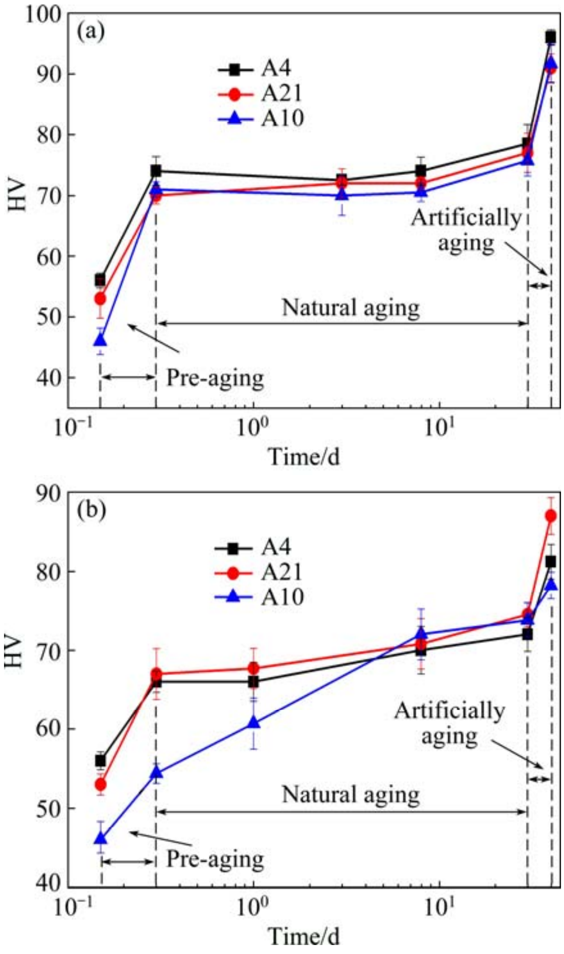

Fig. 2 Vickers hardness evolution curves of three alloys during processing with pre-aging at 100 °C for 2 h (a) and pre-aging at 200 °C for 20 s (b)

It is considered that nucleation of Q'' and Q' phases occurs in the alloy with 0.3% Cu, particularly at the temperature about 200 °C (Fig. 1(c)). The influence of copper addition on the growth of clusters is weakened accordingly and results in high density of the clusters. Therefore, the amount of β'' precipitates decreases, which results in decreasing paint-baking response in the alloys as shown in Fig. 2(b).

3.3 Microstructural aspects

Figures 3 and 4 show TEM bright field images and the $[001]_{\text{Al}}$ selected area diffraction patterns (SADPs) obtained from those pre-aged at 100 °C for 2 h or pre-aged at 200 °C for 20 s, and then artificially aged at 170 °C for 30 min, respectively. No clusters, which are

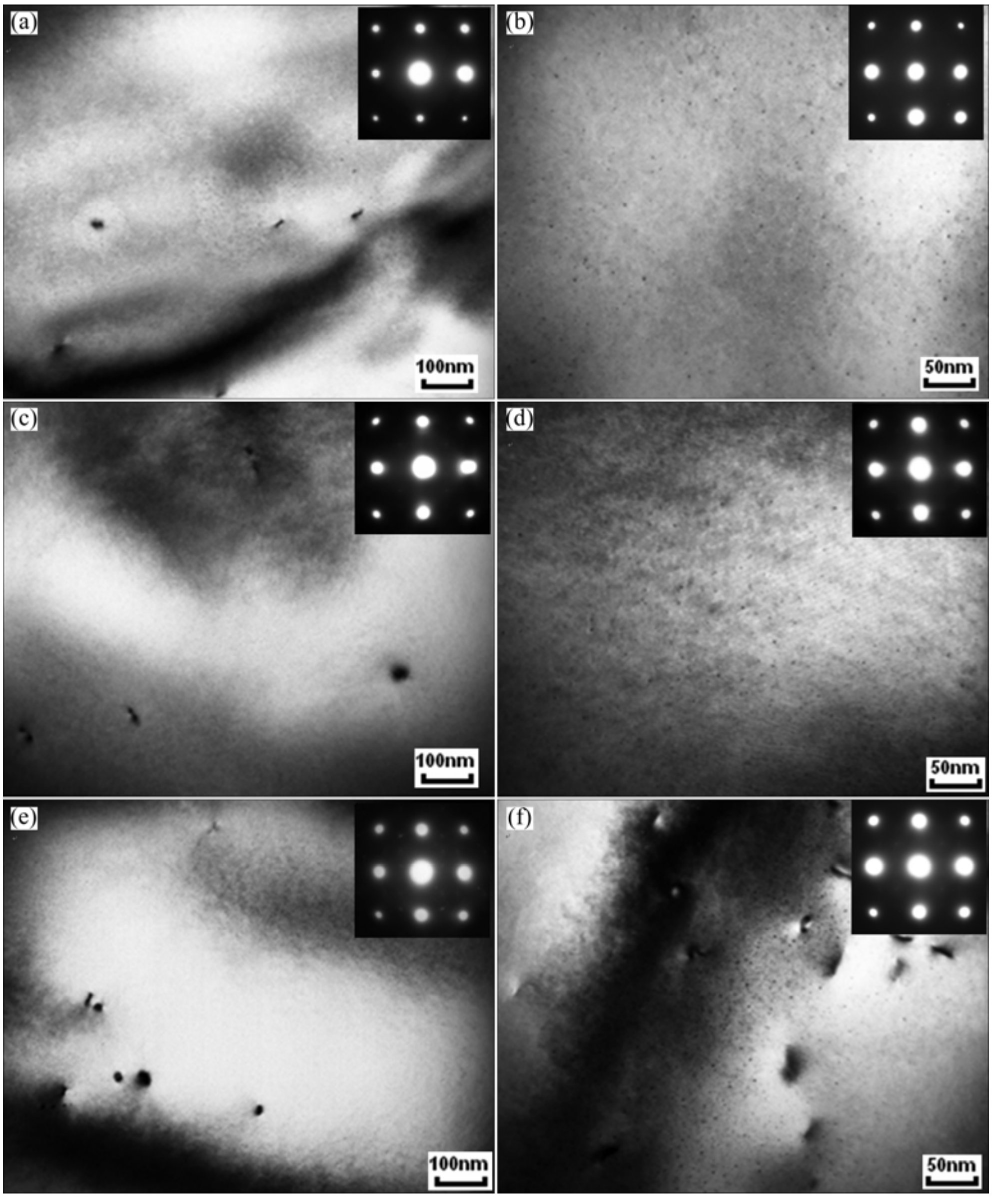

Fig. 3 TEM bright field images and selected area diffraction patterns with B=$[001]_{\mathrm{Al}}$ obtained from alloys; (a) alloy A4 pre-aged at 100 °C for 2 h; (b) Alloy A4 pre-aged at 100 °C for 2 h and aged at 170 °C for 30 min; (c) Alloy A21 pre-aged at 100 °C for 2 h; (d) Alloy A21 pre-aged at 100 °C for 2 h and aged at 170 °C for 30 min; (e) Alloy A10 pre-aged at 100 °C for 2 h; (f) Alloy A10 pre-aged at 100 °C for 2 h and aged at 170 °C for 30 min

indicated in the DSC results, are found in the pre-aged samples. But the distribution of the precipitates in the artificially aged 6016 based alloy differs. This is due to the fact that the clusters with a lower solute concentration and undefined morphology are not large enough to give contrast in TEM images. For the artificially aged alloy, the precipitates with 0.1% Cu pre-aged at 100 °C for 2 h are denser than those in the copper-free one or the one with 0.3% Cu. This suggests that copper addition has an adverse effect on the kinetics of the subsequent artificial ageing in the case of copper less than 0.3% and pre-aging at 100 °C for 2 h. Mg and Si clusters are present in the as-quenched alloys, but Mg and Si atoms aggregate during natural aging to form Mg−Si co-clusters. By aging at 100°C, spherical GP zones with Mg, Si atoms similar to the co-clusters. GP zones give contrast in TEM images but the co-clusters are formed, because the former has a higher solute concentration than the later. The precipitation products after artificial aging for 30 min at 170 °C are GP zones regardless of the prior aging conditions, but the number density of the GP zones is significantly affected by the pre-aging conditions. Natural aging suppresses the precipitation kinetics of the GP zones in artificial aging, but pre-aging at 100 °C increases the number density of the GP zones in the artificially aged alloy. This suggests

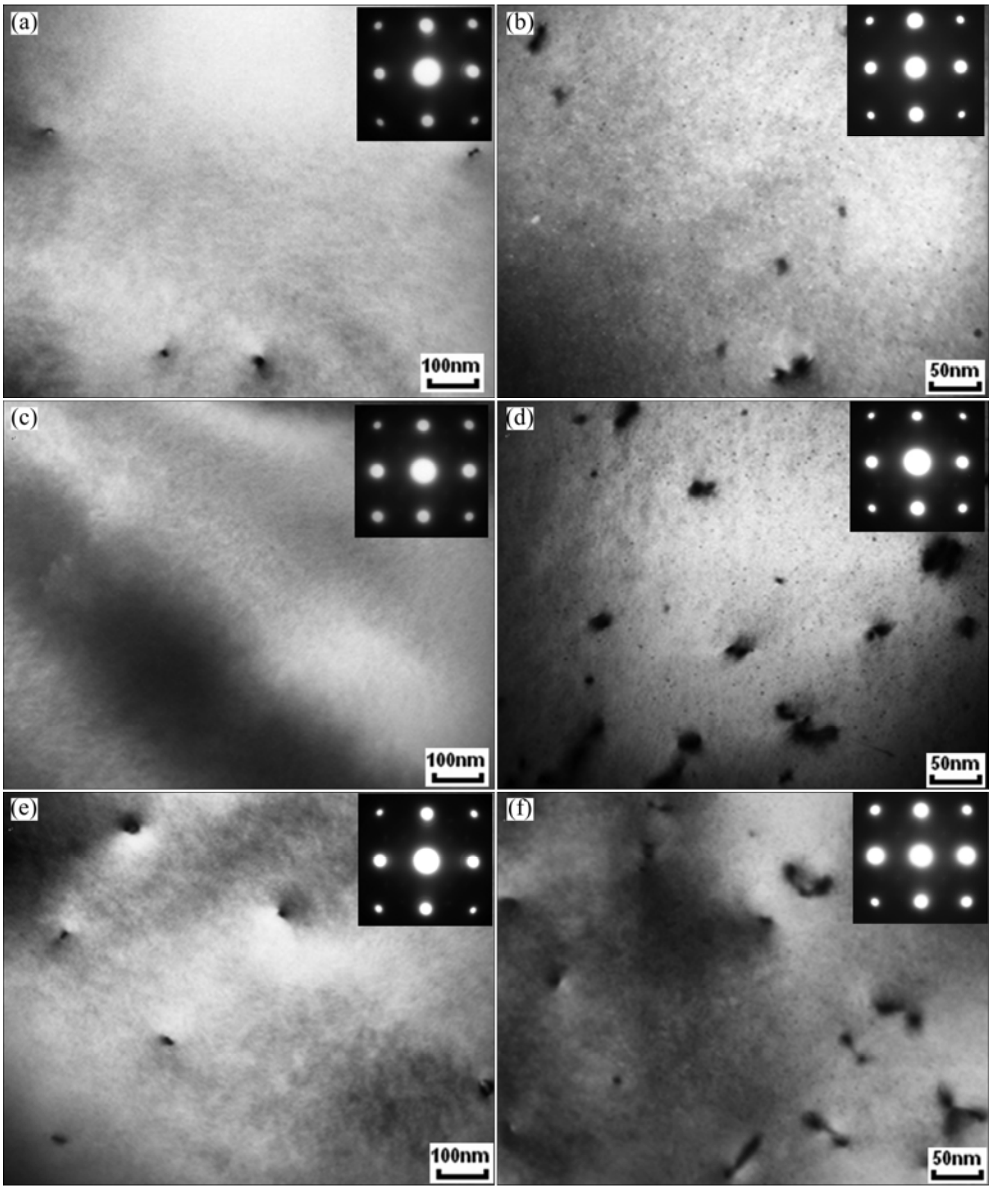

Fig. 4 TEM bright field images and selected area diffraction patterns with $B=[001]_{\mathrm{Al}}$ obtained from alloys: (a) Alloy A4 pre-aged at 200 °C for 20 s; (b) Alloy A4 pre-aged at 200 °C for 20 s and aged at 170 °C for 30 min; (c) Alloy A21 pre-aged at 200 °C for 20 s; (d) Alloy A21 pre-aged at 200 °C for 20 s and aged at 170 °C for 30 min; (e) Alloy A10 pre-aged at 200 °C for 20 s; (f) Alloy A10 pre-aged at 200 °C for 20 s and aged at 170 °C for 30 min

that the GP zones formed in the pre-aging condition grow in the subsequent artificial aging process, but the co-clusters formed by natural aging are completely reverted. Thus, it can be concluded that the major contributor for age hardening in the paint-baking cycle is the GP zones. An increase in the number density of β'' precipitates by artificial aging after 100 °C pre-aging indicates that the spherical GP zones provide heterogeneous nucleation sites for the β'' precipitate. On the other hand, a low number density of β'' precipitates with natural aging suggests that co-clusters are reverted at the temperature of artificial aging, resulting in reduced precipitation kinetics. This study also reveals that the atom ratio in the co-clusters, GP zones and β'' is close to that of the alloy composition. This finding suggests that excess Si causes a higher number density of precipitates [18]. When pre-aged at 200 °C for 20 s, coarser and lower density precipitates are formed, especially after aging at 170 °C for 30 min (Fig. 4).

The addition of Cu has a large effect on the artificial age-hardening kinetics and a small but noticeable effect on the maximum hardness and the higher copper alloy shows evidence of Q'' and Q' precipitates. The distribution of the precipitates in the alloy with 0.1% Cu after pre-ageing and artificial ageing is denser than that in the artificially aged alloys with copper-free or 0.3%

Cu, revealing that the corresponding paint bake responses of the alloys present a significant difference shown in Fig. 2.

4 Conclusions

1) Clusters in the specimens after pre-ageing at 100 °C for 2 h become more stable and thus more effective to develop into β'' precipitates during final artificial ageing, which is beneficial to paint-bake responses.

2) Copper addition accelerates ageing precipitation at above room temperature and retards room temperature natural ageing. However, the density of copper atoms in the Al−Mg−Si system with copper addition of 0.3% decreases, which means no acceleration of nucleation of the clusters.

References

[1] HIRSCH J, AL-SAMMAN T. Superior light metals by texture engineering: Optimized aluminum and magnesium alloys for automotive applications [J]. Acta Materialia, 2013, 61(3): 818−843.

[2] JANSE J E, ZHUANG L, MOOI J, de SMET P. Evaluation of the effect of Cu on the paint bake response of preaged AA6xxx [J]. Materials Science Forum, 2002, 396−402: 607−612.

[3] EDWARDS G A, STILLER K, DUNLOP G L, COUPER M J. The precipitation sequence in Al−Mg−Si alloys [J]. Acta Materialia, 1998, 46(11): 3893−3904.

[4] MARIOARA C D, ANDERSEN S J, ZANDBERGEN H W, HOLMESTAD R. The influence of alloy composition on precipitates of the Al−Mg−Si system [J]. Metallurgical and Materials Transactions A, 2005, 36(3): 691−702.

[5] TAMIZIFAR M, LORIMER G W. The effect of copper on the aging response of an aluminium-magnesium-silicon alloy [C]//Third International Conference on Aluminium Alloys: Their Physical and Mechanical Properties, 1992: 220−225.

[6] MURAYAMA M, HONO K. Pre-precipitate clusters and precipitation processes in Al−Mg−Si alloys [J]. Acta Materialia, 1999, 47(5): 1537−1548.

[7] ZHEN L, FEI W D, KANG S B, KIM H W. Precipitation behaviour of Al−Mg−Si alloys with high silicon content [J]. Journal of Materials Science, 1997, 32(7): 1895−1902.

[8] CUNIBERTI A, TOLLEY A, RIGLOS M V, GIOVACHINI R. Influence of natural aging on the precipitation hardening of an AlMgSi alloy [J]. Materials Science and Engineering A, 2010, 527(20): 5307−5311.

[9] RØYSET J, STENE T, SAEER J A, REISO O. The effect of intermediate storage temperature and time on the age hardening response of Al−Mg−Si alloys [J]. Materials Science Forum, 2006, 519: 239−244.

[10] KOLAR M, PEDERSEN K O, GULBRANDSEN-DAHL S, MARTHINSEN K. Combined effect of deformation and artificial aging on mechanical properties of Al−Mg−Si alloy [J]. Transactions of Nonferrous Metals Society of China, 2012, 22(8): 1824−1830.

[11] MANSOURINEJAD M, MIRZAKHANI B. Influence of sequence of cold working and aging treatment on mechanical behaviour of 6061 aluminum alloy [J]. Transactions of Nonferrous Metals Society of China, 2012, 22(9): 2072−2079.

[12] HUANG C, DIAO J, DENG H, LI B, HU X. Microstructure evolution of 6016 aluminum alloy during compression at elevated temperatures by hot rolling emulation [J]. Transactions of Nonferrous Metals Society of China, 2013, 23(6): 1576−1582.

[13] MASSARDIER-JOURDAN V, EPICIER T. Study of the influence of a low copper addition and of an excess of silicon on the precipitation kinetics and on the precipitation sequence of Al−Mg_2Si alloys [J]. Materials Science Forum, 2002, 396: 851−856.

[14] HIRTH S M, MARSHALL G J, COURT S A, LLOYD D J. Effects of Si on the aging behaviour and formability of aluminium alloys based on AA6016 [J]. Materials Science and Engineering A, 2001, 319: 452−456.

[15] SILVA M S, BARBOSA C, ACSELRAD O, PEREIRA L C. Effect of chemical composition variation on microstructure and mechanical properties of a 6060 aluminum alloy [J]. Journal of Materials Engineering and Performance, 2004, 13(2): 129−134.

[16] ESMAEILI S, WANG X, LLOYD D J, POOLE W J. On the precipitation-hardening behavior of the Al−Mg−Si−Cu alloy AA6111 [J]. Metallurgical and Materials Transactions A, 2003, 34(13): 751−763.

[17] BRYANT J D. The effects of preaging treatments on aging kinetics and mechanical properties in AA6111 aluminum autobody sheet [J]. Metallurgical and Materials Transactions A, 1999, 30(8): 1999−2006.

[18] MATSUDA K, IKENO S, TERAYAMA K, UETANI Y. Comparison of precipitates between excess Si-type and balanced-type Al−Mg−Si alloys during continuous heating [J]. Metallurgical and Materials Transactions A, 2005, 36(8): 2007−2012.

[19] RINGER S P, HONO K. Microstructural evolution and age hardening in aluminium alloys: Atom probe field-ion microscopy and transmission electron microscopy studies [J]. Materials Characterization, 2000, 44(1): 101−131.

Cu 含量对 Al−Mg−Si 合金析出及烤漆硬化行为的影响

刘聪慧，张新明，唐建国，刘星兴，陈　亮

中南大学 材料科学与工程学院，长沙 410083

摘　要：采用 DSC、硬度测试及 TEM 研究 Al6016 铝合金中 Cu 含量对淬火及淬火预时效样品的人工时效析出和硬化行为的影响。结果表明，微量 Cu 有利于形成较大且稳定性较好的 GP I，能在随后的人工时效过程中进一步向 GP II 转化，从而提高合金的烤漆硬化能力。但是，当 Cu 含量为 0.3%时，烤漆硬化能力没有得到显著增加。对于含 Cu 合金，预时效热处理也能有效地抑制合金的自然时效行为。

关键词：Al−Mg−Si−Cu 合金；烤漆硬化行为；含 Cu 析出相

(Edited by Xiang-qun LI)