Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 23(2013) 2543−2550
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Microstructural evolution during homogenization of Al−Cu−Li−Mn−Zr−Ti alloy

Hong-ying LI[1,2], Xiong-jie SU[1], Hao YIN[1], De-sheng HUANG[1]

1. School of Materials Science and Engineering, Central South University, Changsha 410083, China;
2. Key Laboratory of Nonferrous Materials, Ministry of Education, Central South University, Changsha 410083, China

Received 25 May 2013; accepted 22 July 2013

Abstract: The microstructure evolution of Al−Cu−Li−Mn−Zr−Ti alloy during homogenization was investigated by optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX), and differential scanning calorimeter (DSC) methods. The results show that severe dendritic segregation exists in the experimental alloy ingot. Numerous eutectic phases can be observed in the grain boundary, and the distribution of the main elements along the interdendritic region varies periodically. The main secondary phase is Al_2Cu. The overburnt temperature of the alloy is 520 °C. The second phases are gradually dissolved into the matrix, and the grain boundaries become spare and thin during homogenization with increasing temperature or prolonging holding time. Homogenization can be described by a constitutive equation in exponential function. The suitable homogenization treatment for the alloy is (510 °C, 18 h), which agrees well with the results of homogenization kinetic analysis.
Key words: Al−Cu−Li−Mn−Zr−Ti alloy; homogenization; microstructure; kinetics

1 Introduction

For high fuel efficiency and low operation cost, Al−Cu−Li alloys are widely used in aviation and aerospace industries because of their low density and high elastic modulus [1−3]. Li is the lightest metal in nature, and each 1% (mass fraction) boost of Li content in aluminum alloy contributes to about 3% density reduction and about 5% elastic modulus increase [4−6]. Adding Li to Al−Cu alloys forms the main strengthening T1 phase, which contributes to higher strength, better corrosion resistance and fatigue resistance performance than conventional 2xxx series aluminum alloys for aerospace applications [7−10]. Thus, Al−Cu−Li−Mn−Zr−Ti alloys are regarded as a competitive structural material for aerospace in the 21st century, and their development is receiving increasing attention [11−13].

The microstructures and mechanical properties of Al−Cu−Li alloys are sensitive to the microstructure of as-cast alloys, heat treatment, and subsequent processing. During casting, the microsegregation of main elements cannot be avoided, along with a considerable amount of massive undissolved secondary phases in the ingot. These factors weaken the workability of the cast structure and ultimately affect the mechanical properties of aluminum alloys [14−16]. By homogenization treatment, these residual phases can be redissolved into the matrix; microsegregation can also be reduced or even completely eliminated. Thus, homogenization is a primary and important step for the manufacture of Al−Cu−Li alloys. Numerous studies on homogenization prior to extrusion or rolling have been reported [17−20]. However, reports on the effects of homogenization heat treatment on the microstructure of Al−Cu−Li alloys are limited. Therefore, the microstructure evolution of Al−Cu−Li alloys during homogenization must be studied because the results can significantly contribute to the understanding of Al−Cu−Li alloy homogenization.

In this work, the effects of homogenization on the microstructure and composition distribution of an Al−Cu−Li−Mn−Zr−Ti alloy were investigated. The homogenization kinetic equation of the experimental alloy was established, and the results can provide indispensable information in optimizing the parameters of homogenization treatment.

2 Experimental

The materials used in this study were prepared with

Corresponding author: Hong-ying LI; Tel: +86-731-88836328; Fax: +86-731-88836328; E-mail: lhying@csu.edu.cn
DOI: 10.1016/S1003-6326(13)62766-1

high purity ingot of Al, pure Li, pure Cu, pure Mg and binary intermediate alloys of Al−Mn, Al−Zr and Al−Ti. The alloy was melted in a graphite crucible heated in a resistance furnace, and the liquid metal was then poured into a steel mold. The ingot dimensions were 25 mm× 60 mm×130 mm. The nominal composition of the ingot was Al−2.8Cu−1.4Li−0.3Mn−0.2Mg−0.12Zr−0.12Ti−0.1Fe−0.1Si (mass fraction, %). Slices with dimensions of 10 mm×10 mm×10mm were cut from the half position between the surface and the center of as-cast ingot. Homogenization was performed at 485, 500, 510, 520, 530 °C for 24 h, respectively. And then at the optimized temperature, the specimens were homogenized for 6, 12, 18 and 24 h. All the homogenized samples were air-cooled to room temperature.

The microstructure characteristics of as-cast and homogenized samples were examined by optical microscopy (OM), scanning electron microscopy (SEM), and energy dispersive X-ray spectrometry (EDX). The specimens for OM observation were etched with Keller reagent (1 mL HF, 1.5 mL HCL, 2.5 mL HNO_3 and 95 mL H_2O). For SEM examination, the samples were mechanically polished but kept unetched. SEM observation was conducted using a JSM−6360LV microscope with energy dispersive X-ray spectroscopy (EDX). Differential scanning calorimetry (DSC) analyses were conducted using a SDT-Q600 differential scanning calorimeter with a heat-up rate of 10 K/min.

3 Results and discussion

3.1 As-cast microstructure

Figure 1 shows the microstructures of as-cast alloy, and Table 1 shows the results of EDX analysis. Severe dendritic segregation exists in the ingot, and a considerable number of intermetallic phases exist at the grain boundaries. The EDX results reveal that the bright phase is Al_2Cu. The lamellar eutectics are defined as Fe- and Mn-containing phases.

Figure 2 presents the line scanning analysis of as-cast alloy. As illustrated in Fig. 2, the distribution of main elements along interdendritic region varies periodically. Therefore, in order to investigate the distribution of elements during the homogenization, the key is to study the diffusion law along interdendritic region.

Figure 3 presents SEM microstructure along with the distribution of the main elements Cu, Mg, and Mn in the as-cast alloy. The segregation of Cu, Mg, and Mn at the grain boundaries differs from one another. It is obvious that the segregation of Cu is great, while the segregation of Mg and Mn is not obvious. The concentration of elements decreases from the grain boundary to the interior. Therefore, homogenization is necessary to remove severe dendritic segregation in the as-cast alloy. Generally, the relationship between the diffusion coefficient of element and the temperature can be expressed as

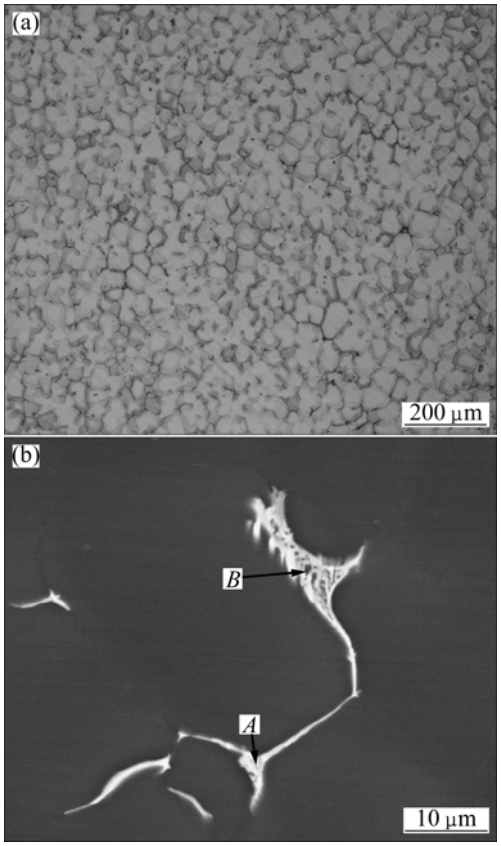

Fig. 1 As-cast microstructures of experimental alloy: (a) OM; (b) SEM

Table 1 Chemical composition of secondary phases in experimental alloy (mole fraction, %)

Phase	Composition/%				
	Al	Cu	Mg	Mn	Fe
A	77.98	22.02			
B	79.78	17.80	1.30	1.69	0.87

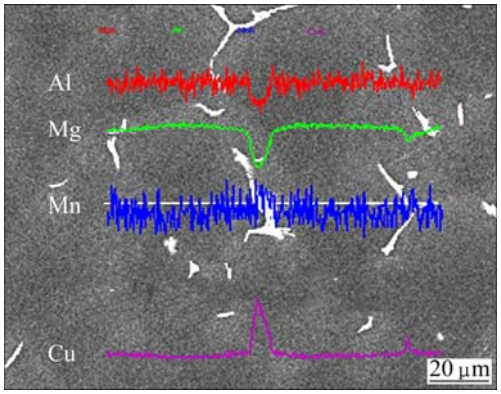

Fig. 2 Line scanning of as-cast alloy

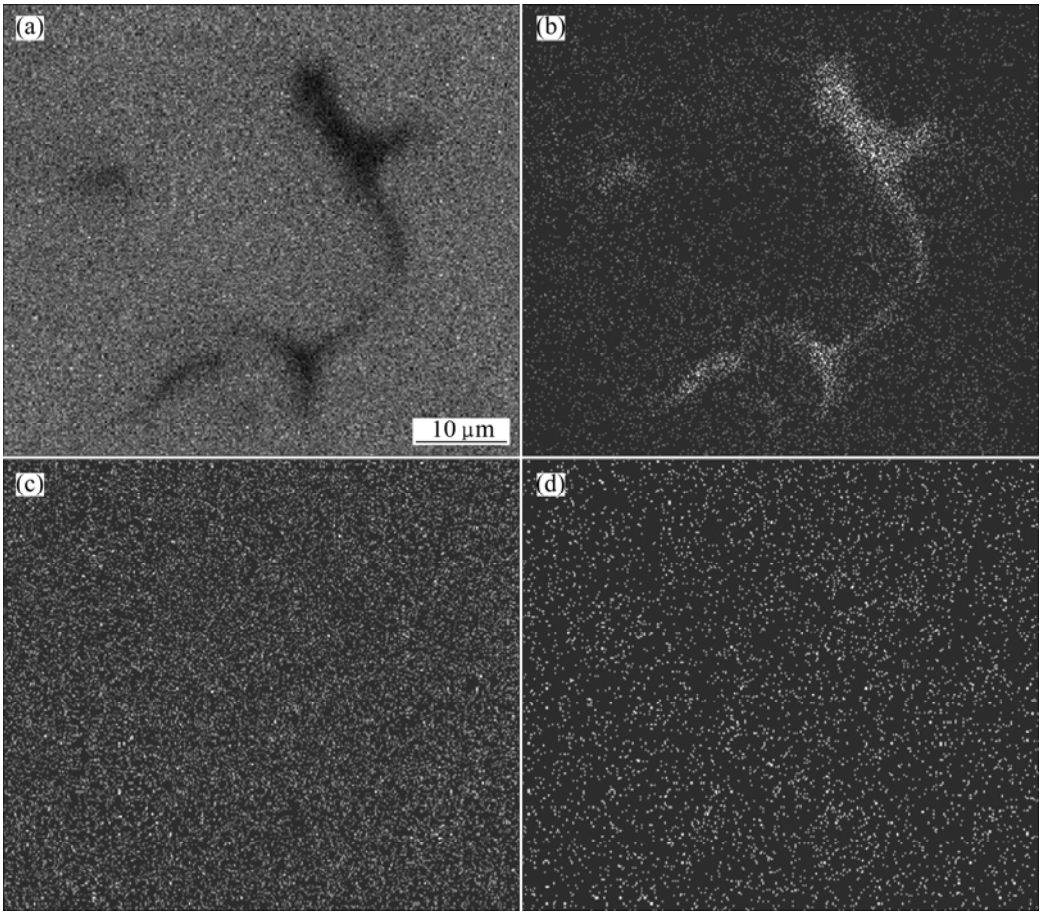

Fig. 3 SEM microstructure and element distribution of as-cast Al−Cu−Li alloy: (a) SEM image; (b) Cu distribution; (c) Mn distribution; (d) Mg distribution

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (1)$$

where D_0 is the diffusion coefficient, Q is the diffusion activation energy, R is the gas constant, and T is the thermodynamic temperature. Based on Eq. (1), a higher temperature obviously corresponds to a quicker diffusion speed. However, alloy overburn is fairly common at higher temperatures. Thus, obtaining the appropriate temperature for homogenization is necessary.

Figure 4 shows the DSC curve of as-cast Al−Cu−Li alloy. Two endothermic peaks are observed in the as-cast alloy, sited at 522.5 °C (point *C*) and 656.7 °C (point *D*), respectively. The temperature of point *C* can be the melting point of eutectic phase. The endothermic peak at 656.7 °C (point *D*) corresponds to the melting point of as-cast alloy. Thus, the homogenization temperature should not surpass 522.5 °C.

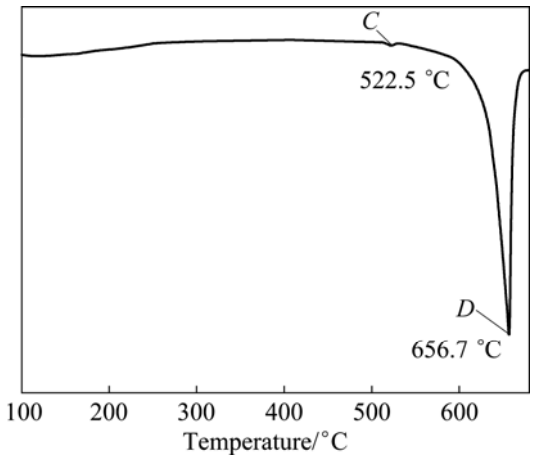

Fig. 4 DSC curve of as-cast Al−Cu−Li alloy

3.2 Microstructure of homogenized alloy

The optical microstructures of the experimental alloy homogenized at different temperatures show that the residual phases gradually dissolve with increased homogenization temperature (Fig. 5). In addition, the grain boundaries become thinner and clearer with increased temperature, and the residual phase distribution along the grain boundaries develops a discontinuous pattern. Upon homogenization at 510 °C for 24 h (Fig. 5(b)), most of the residual phases dissolve and the dendritic network structure is reduced. When the temperature is increased to 520 °C, some of the melting compounds and triangular constituents are observed

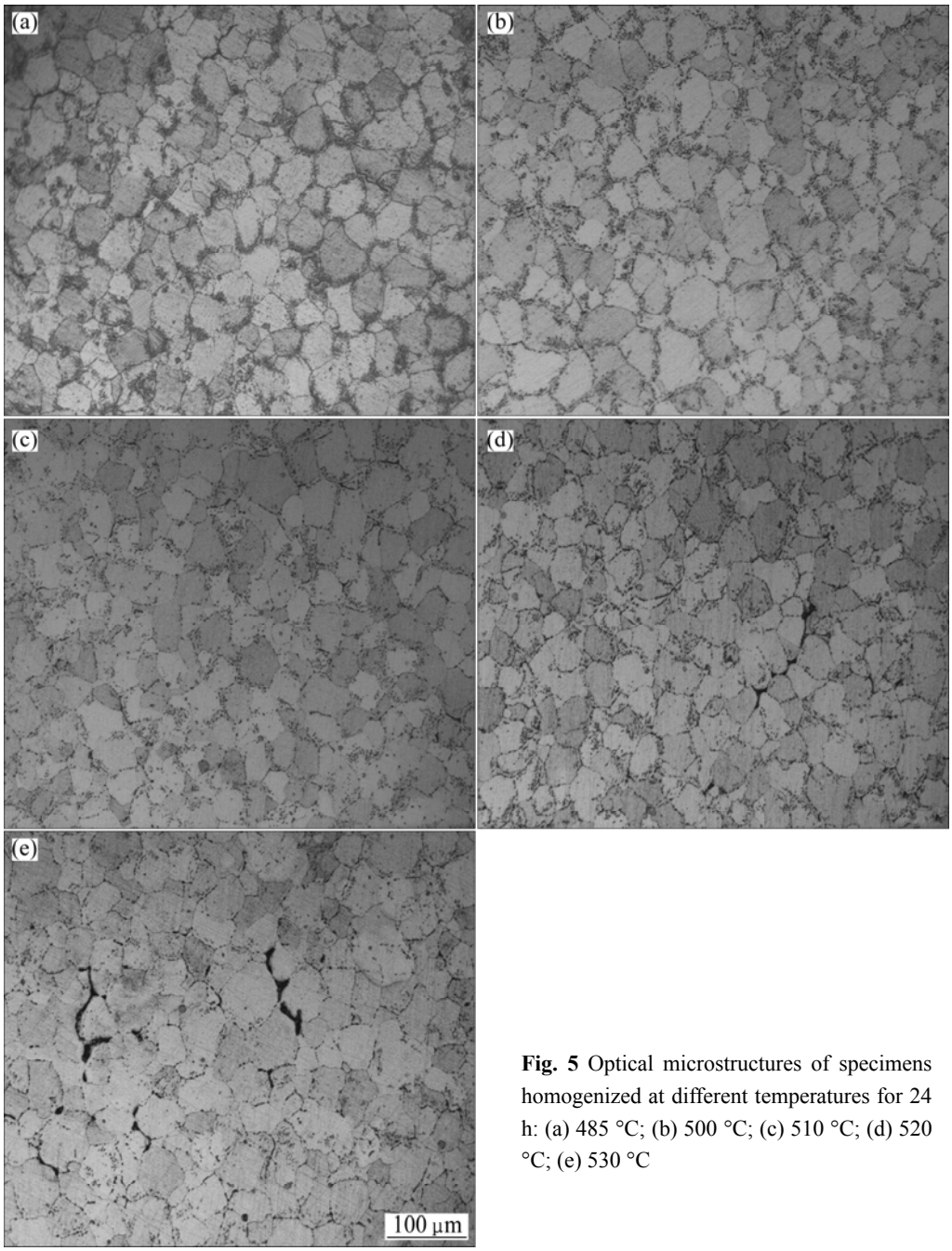

Fig. 5 Optical microstructures of specimens homogenized at different temperatures for 24 h: (a) 485 °C; (b) 500 °C; (c) 510 °C; (d) 520 °C; (e) 530 °C

at the grain boundaries (Fig. 5(d)), indicating that the specimen is slightly overburnt. By further increasing the homogenization temperature, more triple conjunctions are observed, indicating the specimen is seriously overburnt. In conclusion, 510 °C is determined to be the upper homogenization temperature limit.

Figure 6 shows the SEM backscattered images of the specimen homogenized at different temperatures. The second phase gradually dissolves into the matrix after homogenization at an elevated temperature. When the temperature is increased to 510 °C, the residual phases in the grain boundaries decrease significantly. The number of second phases in the grain boundaries does not show significant reduction with increased homogenization temperature. This observation indicates that the appropriate temperature for homogenization is 510 °C.

Figure 7 shows the SEM images of the specimen homogenized at 510 °C for different time. The interdendritic second phases are gradually reduced, and the residual phases become smaller and sparser with prolonging holding time. When the holding time is increased to 18 h, the residual phase is almost dissolved into the matrix (Fig. 7(c)). Figure 7(d) shows that the residual phase does not decline with the prolonging holding time.

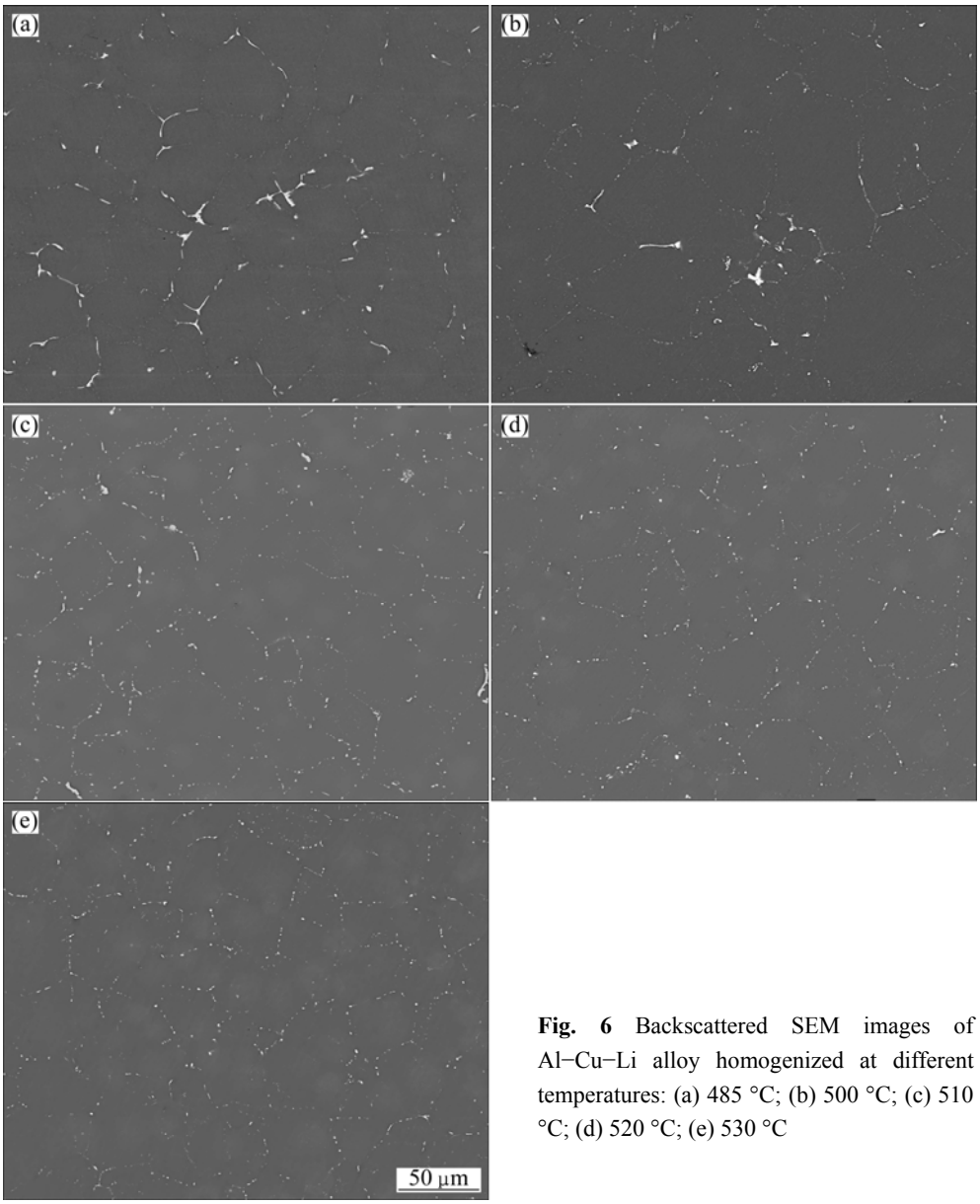

Fig. 6 Backscattered SEM images of Al−Cu−Li alloy homogenized at different temperatures: (a) 485 °C; (b) 500 °C; (c) 510 °C; (d) 520 °C; (e) 530 °C

Based on the above discussion, it can be seen that most of the residual phases at the grain boundary dissolve into the matrix. And the segregation of elements Cu, Mg, and Mn at the grain boundary and the distribution of these elements almost homogeneous when the experimental alloys are homogenized at 510 °C for 18 h. Therefore, the proper homogenization treatment is (510 °C, 18 h) based on the above experiments.

3.3 Homogenization kinetic analysis

According to section 3.1, the dissolution of elements Cu, Mg and Mn along interdendritic region varies periodically. Based on the previous study, the key of investigating the distribution of the elements during the homogenization is to study the diffusion law along interdendritic region [20]. The initial concentration of the elements along the interdendritic region can be approached by Fourier series components in a cosine function [21].

$$c(x) = \bar{c} + A_0 \cos\frac{2\pi x}{L} \tag{2}$$

where L is the interdendritic spacing, $\bar{c}$ is the average concentration of the element, and A_0 is the initial amplitude of the composition segregation, which can be expressed as

$$A_0 = \frac{1}{2}\left(c_{\max} - c_{\min}\right) = \frac{1}{2}\Delta c_0 \tag{3}$$

According to the second Fick's law and the boundary conditions, $A(t)$ can be expressed by

$$A(t) = A_0 \exp\left(-\frac{4\pi^2}{L^2}Dt\right) \tag{4}$$

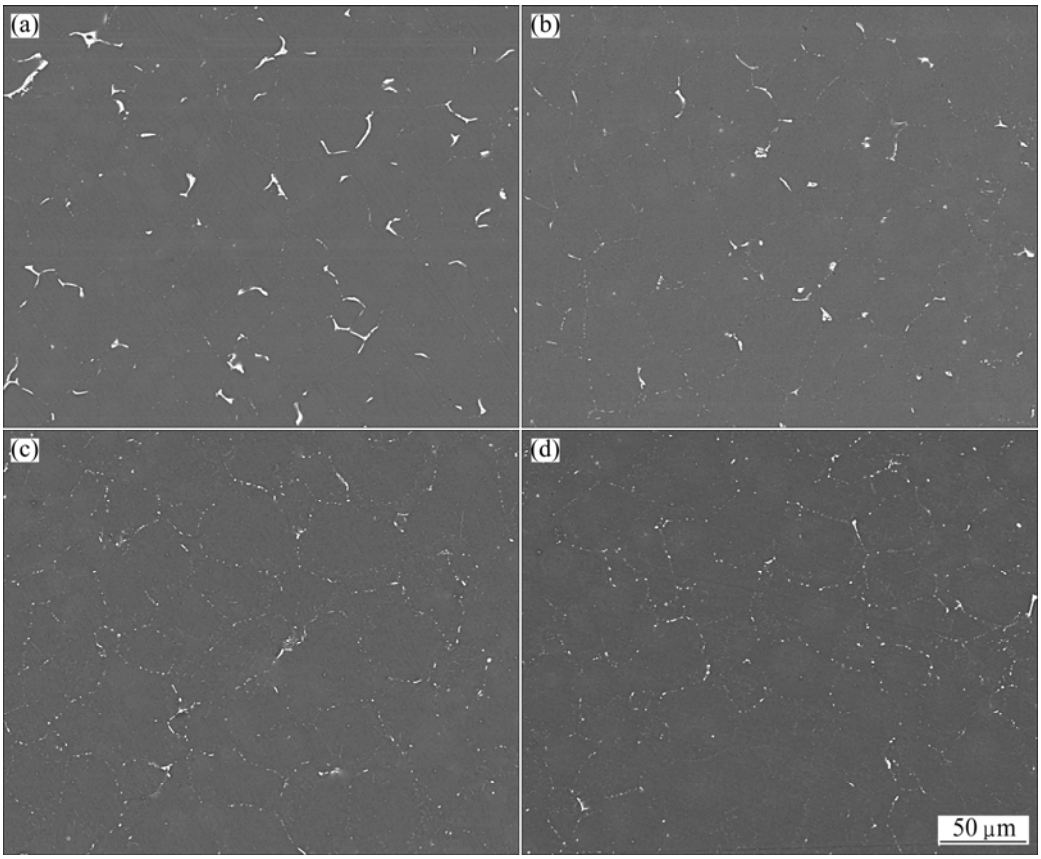

Fig. 7 Backscattered SEM images of Al−Cu−Li alloy homogenized at 510 °C for different time: (a) 6 h; (b) 12 h; (c) 18 h; (d) 24 h

It can be seen from Eq. (4) that, the amplitude of composition segregation decreases by increasing the holding time during homogenization.

From Eq. (1) and Eq. (4), $A(t)$ can be rewritten as

$$A(t) = A_0 \exp\left[-\frac{4\pi^2 D_0 t}{L^2}\exp\left(-\frac{Q}{RT}\right)\right] \tag{5}$$

Based on Eq. (5), it can be seen that the segregation along the interdendritic region decreases with the increase of homogenization temperature or the holding time, which is consistent with the experimental results in this work.

Generally, when the composition segregation amplitude is reduced to 1%, the distribution of the element is homogeneous as shown by

$$\frac{A(t)}{A_0} = \frac{1}{100} \tag{6}$$

Then

$$\exp\left[-\frac{4\pi^2 D_0 t}{L^2}\exp\left(-\frac{Q}{RT}\right)\right] = \frac{1}{100} \tag{7}$$

By taking natural logarithms of both sides, Eq. (7) can be rewritten as

$$\frac{1}{T} = \frac{R}{Q}\ln\left(\frac{4\pi^2 D_0 t}{4.6L^2}\right) \tag{8}$$

Equation (8) is the homogenization kinetic equation. The homogenization kinetic curve can be obtained, as long as the parameters of the ingot microstructure are given. From the results of section 3.1 and previous work [20,21], we can draw a conclusion that the diffusion coefficient of Cu is much lower than that of Mg and Mn at the same temperature. As a result, it can be considered that the homogenization process is mainly affected by the diffusion of Cu. By substituting D_0(Cu)=0.084 cm^2/s, Q(Cu)=136.8 kJ/mol and R=8.31 J/(mol·K) into Eq. (8), the homogenization kinetic curve of the experimental alloy for different interdendritic spacings is obtained, as shown in Fig. 8. As illustrated in Fig. 8, the soaking time of homogenization reduces greatly with the increase of homogenization temperature.

By substituting the average interdendritic spacing L into Eq. (8), suitable homogenizing parameters are obtained. The average interdendritic spacing L in the present alloy is about 55 μm based on the quantitative metallographic analysis. According to the homogenization kinetic curves, at the temperature of 510 °C, the corresponding homogenization holding time is

about 16 h. The calculated results agree well with the experimental results.

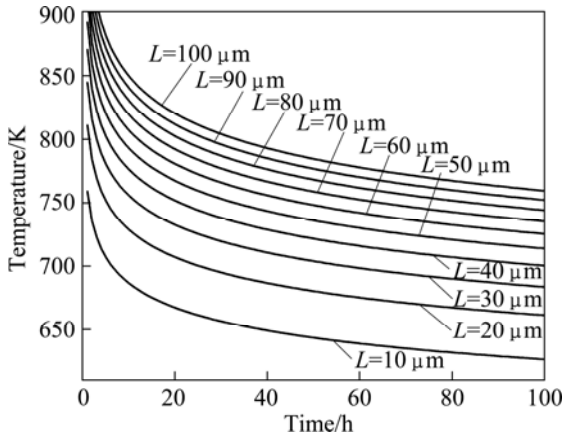

Fig. 8 Curves of homogenization kinetics

4 Conclusions

1) Serious dendritic segregation exists in the as-cast Al−Cu−Li−Mn−Zr−Ti alloy. The main elements Cu, Mg, and Mn are unevenly distributed at the grain boundary. The main secondary phase in as-cast microstructure is Al_2Cu.

2) The overburnt temperature of as-cast experimental alloy is 520 °C. With increased temperature or prolonged holding time at the temperature below overburning, the residual phases in the grain boundary gradually dissolve into the matrix. The distribution of the main elements becomes more homogenious, and the grain boundaries become sparse and thin.

3) Homogenization can be described by a constitutive equation in exponential function. According to homogenization kinetic analysis, the suitable homogenization processing for the experimental alloy is (510 °C, 18 h), which agrees well with the experimental results.

References

[1] RIOJA R J, LIU J. The evolution of Al−Li base products for aerospace and space applications [J]. Metallurgical Materials Transactions A, 2012, 43(9): 3325−3337.

[2] LI Jin-feng, ZHENG Zi-qiao, REN Wen-da, CHEN Wen-jing, ZHAO Xu-shan, LI Shi-chen. Simulation on function mechanism of T1(Al_2CuLi) precipitate in localized corrosion of Al−Cu−Li alloys [J]. Transactions of Nonferrous Metals Society of China, 2006, 16(6): 1268−1273.

[3] YOSHIMURA R, KONNO T J, ABE E, HIRAGA K. Transmission electron microscopy study of the evolution of precipitates in aged Al−Li−Cu alloys: The θ' and T_1 phases [J]. Acta Materialia, 2003, 51(14): 4251−4266.

[4] FIELDING P S, WOLF G J. Aluminum-lithium for aerospace [J]. Advanced Materials and Processes, 1996, 150(4): 21−23.

[5] LI Hong-ying, TANG Yi, ZENG Zai-de, ZHENG Feng. Exfoliation corrosion of T6- and T8-aged $Al_xCu_yLi_z$ alloy [J]. Transactions of Nonferrous Metals Society of China, 2008, 18(4): 778−783.

[6] STARINK M J, WANG P, SINCLAIR I, GREGSON P J. Microstrucure and strengthening of Al−Li−Cu−Mg alloys and MMCs: II. Modelling of yield strength [J]. Acta Materialia, 1999, 47(14): 3855−3868.

[7] AHMADI S, ARABI H, SHOKUHFAR A. Formation mechanisms of precipitates in an Al−Cu−Li−Zr alloy and their effects on strength and electrical resistance of the alloy [J]. Journal of Alloys and Compounds, 2009, 484(1−2): 90−94.

[8] XIAO Dai-hong, HUANG Bai-yun. Effect of Yb addition on precipitation and microstructure of Al−Cu−Mg−Ag alloys [J]. Transactions of Nonferrous Metals Society of China, 2007, 17(6): 1181−1185.

[9] LI J F, LI C X. PENG Z W, CHEN W J, ZHENG Z Q. Corrosion mechanism associated with T1 and T2 precipitates of Al−Cu−Li alloys in NaCl solution [J]. Journal of Alloys and Compounds, 2008, 460(1−2): 688−693.

[10] QUAN Li-wei, ZHAO Gang, GAO S, MUDDLE B C. Effect of pre-stretching on microstructure of aged 2524 aluminium alloy [J]. Transactions of Nonferrous Metals Society of China, 2011, 21(9): 1957−1962.

[11] JIANG Na, GAO Xiang, ZHENG Zi-qiao. Microstructure evolution of aluminum-lithium alloy 2195 undergoing commercial production [J]. Transactions of Nonferrous Metals Society of China, 2010, 20(5): 740−745.

[12] LI Hong-ying, TANG Yi, ZENG Zai-de, ZHENG Zi-qiao, ZHENG Feng. Effect of ageing time on strength and microstructures of an Al−Cu−Li−Zn−Mg−Mn−Zr alloy [J]. Materials Science and Engineering A, 2008, 498(1−2): 314−320.

[13] DECREUS B, DESCHAMPS A, GEUSER F D, DONNADIEU P, SIGLI C, WEYLAND M. The influence of Cu/Li ratio on precipitation in Al−Cu−Li−x alloys [J]. Acta Materialia, 2013, 61(6): 2207−2218.

[14] HE L Z, LI X. H, LIU X T, WANG X J, ZHANG H T, CUI J Z. Effects of homogenization on microstructures and properties of a new type Al−Mg−Mn−Zr−Ti−Er alloy [J]. Materials Science and Engineering A, 2010, 527(29−30): 7510−7518.

[15] WU Yue-mei, JI Xiong, LAI Ren-ming, ZHANG Xiang-yu, GUO Zhi-xing. The microstructure evolution of an Al−Mg−Si−Mn−Cu−Ce alloy during homogenization [J]. Journal of Alloys Compounds, 2009, 475(1−2): 332−338.

[16] HUANG Hsin-wen, OU Bin-lung. Evolution of precipitation during different homogenization treatments in a 3003 aluminum alloy [J]. Materials and Design, 2009, 30(7): 2685−2692.

[17] FAN Xi-gang, JIANG Da-ming, MENG Qing-chang, ZHONG Li. The microstructural evolution of an Al−Zn−Mg−Cu alloy during homogenization [J]. Materials Letters, 2006, 60(12): 1475−1479.

[18] DENG Yun-Lai, WAN Li, WU Li-hui, ZHANG Yun-ya, ZHANG Xin-Ming. Microstructural evolution of Al−Zn−Mg−Cu alloy during homogenization [J]. Journal of Materials Science, 2011, 46(4): 875−881.

[19] TOTIK Y, SADELER R, KAYMAZ I, GAVGALI M. The effect of homogenisation treatment on cold deformations of AA 2014 and AA 6063 alloys [J]. Journal of Materials Processing Technology, 2004, 174(1): 60−64.

[20] LI Wen-bin, PAN Qing-lin, XIAO Yan-ping, HE Yun-bin, LIU Xiao-yan. Microstructural evolution of ultra-high strength Al−Zn−Cu−Mg−Zr alloy containing Sc during homogenization [J]. Transactions of Nonferrous Metals Society of China, 2011, 21(10): 2127−2133.

[21] DENG Ying, YIN Zhi-min, CONG Fu-guan. Intermetallic phase evolution of 7050 aluminum alloy during homogenization [J]. Intermetallics, 2012, 26: 114−121.

Al−Cu−Li−Mn−Zr−Ti 合金在均匀化过程中的组织演变

李红英[1,2]，苏雄杰[1]，尹 浩[1]，黄德胜[1]

1. 中南大学 材料科学与工程学院，长沙 410083；
2. 中南大学 有色金属材料科学与工程教育部重点实验室，长沙 410083

摘 要：采用光学显微镜(OM)、扫描电镜(SEM)、能谱分析(EDX)和差示扫描热分析法(DSC)研究 Al−Cu−Li−Mn−Zr−Ti 合金在均匀化过程中的组织转变。结果表明，实验合金的铸态组织中存在严重的枝晶偏析，晶界处存在大量的共晶相，主要合金元素沿枝晶区域呈周期性分布。合金中的主要未溶相为 Al_2Cu 相，过烧温度为 520 °C；均匀化过程中，随着温度的升高和时间的延长，晶界处的第二相逐渐溶入基体中，晶界逐渐变得稀疏；合金的均匀化过程可以用一指数方程描述；实验合金适宜的均匀化制度为(510 °C，18 h)，这与采用均匀化动力学方程计算的结果基本吻合。

关键词：Al−Cu−Li−Mn−Zr−Ti 合金；均匀化；显微组织；动力学

(Edited by Sai-qian YUAN)