Homogenization heat treatment of 2099 Al–Li alloy

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Abstract The microstructure evolution and composition distribution of as-cast and homogenized 2099 aluminum–lithium (Al–Li) alloy were studied by optical microscopy (OM), differential thermal analysis (DTA), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), area and line scanning, X-ray diffraction (XRD), and Vickers microhardness test methods. The results show that severe dendrite exists in the as-cast alloy. Cu, Zn, Mn, and Mg distribute unevenly from the grain boundary to inside. The low-melting point nonequilibrium eutectic phases dissolve into the matrix during the first-step homogenization, whereas the melting point of residual eutectic phases is elevated. After the second-step homogenization, most of the remaining eutectic phases dissolve into the matrix, except a small amount of Al–Cu–Fe phases. An optimized homogenization process of the 2099 Al–Li alloy is developed ($515\text{ }^{\circ}\text{C} \times 18\text{ h} + 525\text{ }^{\circ}\text{C} \times 16\text{ h}$), which shows a good agreement with the homogenization kinetic analysis results.

Keywords 2099 Al–Li alloy; Homogenization treatment; Nonequilibrium eutectic; Kinetic analysis

1 Introduction

Aluminum–lithium (Al–Li) alloys are used commercially in military aircraft and space vehicles in several critical

applications. However, there is still an interest in developing the next generation of Al–Li alloy with improved specific strength and damage tolerance and reduced mechanical property anisotropy [1]. This interest stemmed from the fact that each 1 % lithium added to the alloy reduced its density by 3 % and increased the elastic modulus by $\sim 5\%$ [2, 3]. A representative third-generation Al–Li alloy is the AF/C 458 alloy, which was developed in 1997 and designated as AA 2099 by the Aluminum Association in 2004 [4]. When compared to its predecessor of 2090, 2099 has fewer planar anisotropy, higher transverse ductility, superior stress corrosion cracking resistance, and excellent toughness, and like 2090, it has superb cryogenic properties [5, 6].

Studies showed that [7–11] interdendritic segregation during direct chill semicontinuous casting is a serious problem, which has low-melting temperature and dendritic networks morphology and thus, seriously deteriorates the properties of the alloys. Hence, to improve the composition homogeneity and the properties, the ingots of this kind of alloys need homogenization treatment after casting. Homogenization treatment is a crucial process to remove the microsegregation and dissolve large soluble nonequilibrium intermetallic phases, which are formed in rapid solidification processing [12].

Owing to the high content of alloying elements in 2099 Al–Li alloy, it is important to investigate its evolution of eutectic phases and to develop an appropriate homogenization process for actual industrial application. In the present work, microstructure evolution and composition distribution of as-cast and homogenized 2099 Al–Li alloy were studied; the soaking time and temperature of the first-step and second-step homogenization processes were determined, respectively; the kinetic equation of the homogenization was derived.

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Table 1 Chemical composition of 2099 Al–Li alloy (wt%)

Cu	Li	Zn	Mg	Mn	Zr	Al
2.60	1.75	0.64	0.29	0.30	0.08	Bal.

2 Experimental

The semicontinuous 2099 ingot was provided by Southwest Aluminum (Group) Co., Ltd. The ingot dimension is Φ 540 mm $\times$ 1,000 mm, and the chemical composition is given in Table 1. The specimens with the size of 50 mm $\times$ 100 mm $\times$ 20 mm were extracted from the half position between the circular boundary and the center of the ingot.

First, some specimens were homogenized by the first-step homogenization treatment at 515 °C for 10, 14, 18, 22, 26, 30, 34, and 38 h and selected a reasonable soaking time (18 h). Then, the others were homogenized by the second-step homogenization treatment at 515 and 525 °C for 16 h and at 535 and 545 °C for 8 h based on 515 °C $\times$ 18 h, respectively. The purpose of the first-step homogenization is to eliminate the low-melting point nonequilibrium eutectic phases [13, 14], and the second-step homogenization is trying to reduce or eliminate the residual high-melting point nonequilibrium eutectic phases [15].

The nonequilibrium eutectic phases melting temperature were examined by differential thermal analysis (DTA) from room temperature to 700 °C with a heating rate of 10 °C $\cdot$ min^{−1}. Microstructures of as-cast and homogenized specimens were observed by optical microscopy (OM) and scanning electron microscopy (SEM). Intermetallic phases and chemical composition of the alloy were analyzed by X-ray diffraction (XRD) and energy dispersive spectrometry (EDS), respectively. Area and line scanning analysis was performed to observe the distribution of the alloying elements in the materials. Vickers microhardness under different homogenization conditions were measured.

3 Results and discussion

3.1 Characterization of as-cast microstructure

Figure 1a shows the microstructure of 2099 Al–Li alloy. It is a typical as-cast eutectic structure exhibiting serious dendritic segregation. The average grain size of as-cast alloy is $\sim$ 479 μ m. The nonequilibrium eutectic distributes along grain boundaries present continuous networks morphology, which greatly deteriorates the strength and toughness properties of the alloy due to microstructure hereditary. The alloy mainly consists of solid solution α (Al) and binary phases Al₂Cu, Al₆Mn, Al₃Zr, and MgZn₂ and ternary phases Al₂CuLi, Al₆CuLi₃, and AlMg₄Zn₁₁ (Fig. 1b), which are distributed in grains and along grain boundaries.

As shown in Fig. 2, the alloying elements Cu, Mg, and Zn are significantly enriched in grain boundaries, and the element concentration decreases from the grain boundary to inside. Therefore, a homogenization treatment is required to reduce or eliminate severe segregation in the as-cast alloy.

3.2 First-step homogenization

DTA curves of as-cast and the first-step homogenization are shown in Fig. 3. As shown in Fig. 3a, two endothermic peaks are observed in the as-cast alloy, sited at 532 and 645 °C, which are corresponding to the melting temperature of nonequilibrium eutectic and matrix, respectively. The peak at 532 °C is generally considered as the overheating temperature of the as-cast alloy, so the homogenization treatment temperature of this kind of alloy is always below 532 °C. In the present study, the first-step homogenization temperature is designed at 515 °C, and the soaking time from 10 to 38 h at intervals of 4 h.

As shown in Fig. 4, after the first-step homogenization, most of the nonequilibrium eutectic phases dissolve into

Fig. 1 OM image **a** and XRD pattern **b** of as-cast alloy

Fig. 2 Area SEM images of as-cast alloy: **a** SEM image, **b** Cu, **c** Mg, and **d** Zn

Fig. 3 DTA curves of **a** as-cast and **b** homogenized ($515\text{ }^{\circ}\text{C} \times 18\text{ h}$) alloy

the matrix, the grain boundaries are no longer continuous and become thinner, but a small amount of dendrites still exist and there are also some second phases inside the grains. Moreover, the peak sited at $532\text{ }^{\circ}\text{C}$ vanishes, but another endothermic peak sited at $569\text{ }^{\circ}\text{C}$ emerges (Fig. 3b). It can be inferred that the low-melting point nonequilibrium eutectic phases are dissolved into the matrix at $515\text{ }^{\circ}\text{C} \times 18\text{ h}$, and the residual eutectic melting point rises to $569\text{ }^{\circ}\text{C}$. Besides with the increase of the soaking time, the change of residual eutectic phases is slightly (Fig. 4a–d), especially over 18 h. This phenomenon indicates that when the soaking time exceeds a certain value, homogenization treatment cannot reduce microstructure segregation effectively.

Vickers microhardness (a load of 500 g for 20 s) was measured on specimens after the first-step homogenization,

as shown in Fig. 5. With the increase of soaking time, the hardness value is increased sharply within 18 h. This can be ascribed to the solid solution strengthening for non-equilibrium eutectic phases dissolved into the matrix efficiently during this period. Continue to increase the soaking time (exceed 18 h), the hardness value is increased slightly or even decreased. According to the second Fick's law [16, 17], with the increase of soaking time at a certain temperature, the diffusion flux will be reduced with the decrease of the concentration gradient. When the solute atoms distribute evenly, continuing to increase the soaking time will have little effect on the composition segregation, and the segregation extent will not have a further improving. Combining OM observation and microhardness analysis, a proper first-step homogenization process is determined as $515\text{ }^{\circ}\text{C} \times 18\text{ h}$.

Fig. 4 OM images of alloy homogenized at 515 °C for different time: **a** 10 h, **b** 18 h, **c** 26 h, and **d** 34 h

3.3 Second-step homogenization

After the first-step homogenization treatment, the residual nonequilibrium eutectic melting point rises to 569 °C. Hence, the temperature for the second-step homogenization should be elevated to further reduce or eliminate the dendrite segregation. As shown in Fig. 6a, b, with elevating the temperature from 515 to 525 °C, the remaining non-equilibrium eutectic decreases, and the dendrite almost eliminates. Moreover, the residual nonequilibrium eutectic phases dissolve sustainably at 535 °C, as shown in Fig. 6c, but a small amount of melting balls appear in the local areas and grain boundaries tend to melt. Further increasing temperature to 545 °C, the number of melting balls increase continuously, and the grain boundaries show

intermittent punctuates, which are typical overheating features (Fig. 6d).

As shown in Fig. 7, with the increase of temperature from 515 to 525 °C, the microhardness increases and the maximum value is obtained at 525 °C. However, the hardness decreases as the temperature rises to more than 525 °C. Combining OM observation and microhardness analysis, an optimized second-step homogenization process is determined as 515 °C × 18 h + 525 °C × 16 h.

Line scanning traces of the as-cast and homogenized alloy are shown in Fig. 8. The peak of the line scanning has two peaks corresponding to a coarse eutectic phase in Fig. 8a, which shows that the alloying elements distribution is uneven within an eutectic phase. Besides, the distribution is also uneven in the dendrite and the extent of segregation is Cu > Mn > Zn (Figs. 4b–d and 8a), especially that impurity element Fe shows a significant segregation in the as-cast structure that has a negative impact on processing and properties. After the first-step homogenization, Zn segregation is eliminated, Mn distribution is homogeneous from the grain boundary to inside, and only a small amount of Cu and Fe is enriched on the grain boundaries (Fig. 8b). After the second-step homogenization, all the alloying elements distribution is homogeneous from the grain boundary to inside and only small segregation of Cu still exists (Fig. 8c). Therefore, we can conclude that the main alloying elements diffusion velocity is Zn > Mn > Cu, and the homogenization temperature to eliminate the main alloying elements segregation is Cu > Mn > Zn.

Fig. 5 Vickers microhardness at 515 °C with different homogenization times

Fig. 6 OM images of alloy homogenized at 515 °C × 18 h+ **a** 515 °C × 16 h, **b** 525 °C × 16 h, **c** 535 °C × 8 h, and **d** 545 °C × 8 h

Fig. 7 Vickers microhardness at different temperatures for 16 h

The evolution of eutectic phases of the 2099 alloy during homogenization treatment based on XRD and EDS analyses can be concluded as follows:

After the first-step homogenization as shown in Fig. 9a, the amount of AlCu phase decreases, Al₆Mn phase nearly disappears, most of the ternary phases dissolve into the matrix, and some new phases form, such as AlLi and Al₇Cu₃Mg₆. Chemical composition analysis (rhombus Nos. 1 and 2 in Fig. 9b), as shown in Fig. 9c, d, indicates that the selected areas are composed of Al–Cu–Fe enriched eutectic phases, such as Al₂Cu and Al₁₃Fe₄, which are formed during the casting process.

After the second-step homogenization, most of the nonequilibrium eutectic phases dissolve into the matrix. Some phases, such as Al₆CuLi₃ and AlMg₄Zn₁₁, are precipitated in the cooling process after homogenization

(Fig. 10a). It can be seen from Fig. 10c, d, the residual eutectic phases (triangle Nos. 1 and 2 in Fig. 10b) are composed of Al–Cu–Fe and Al–Cu. In addition, Al₃Zr particles are appearing under this homogenization condition. They are not detected by X-ray due to low content.

3.4 Homogenization kinetic analysis

As shown in Fig. 8, the distribution of the main alloying elements along the interdendritic region varies periodically. This variation law can be approximately represented in Fig. 11, where L is the wavelength (interdendritic spacing), Δw_0 is the initial amplitude of the composition segregation, and $\bar{w}$ is the average concentration of the element. Therefore, the studies of diffusion law along dendrite region are important to the investigations of elements distribution during homogenization.

According to Ref. [11], the initial concentration of the elements along the interdendritic region can be approached by Fourier series components in a cosine function:

$$w(x) = \bar{w} + A \cos(2\pi x/L) \quad (1)$$

where $A = 0.5\Delta w_0$.

According to the second Fick's law [18, 19] and the boundary conditions, $w(x, t)$ is given as

$$w(x, t) = \bar{w} + 0.5\Delta w_0 \cos\left[\frac{2\pi x}{L}\right] \exp\left[-\frac{4\pi^2}{L^2}Dt\right] \quad (2)$$

where D is the diffusion coefficient of the alloying elements in the matrix and t is the diffusion time.

Fig. 8 Line scanning analysis under different conditions: **a** as-cast, **b** 515 °C × 18 h, and **c** 515 °C × 18 h + 525 °C × 16 h

The cosine distribution attenuation law in Eq. (2) can be described by the attenuation function [20]:

$$w(x, t) = 0.5\Delta w_0 \exp\left[-\frac{4\pi^2}{L^2}Dt\right] \quad (3)$$

Assuming the element distribution is homogeneous when the composition segregation amplitude is reduced to 1 %, then

$$1\% = \exp\left[-\frac{4\pi^2}{L^2}Dt\right] \quad (4)$$

Considering the relationship between diffusion coefficient and temperature, D is given as

$$D = D_0 \exp(-Q/RT) \quad (5)$$

where D_0 is independent coefficient, Q is the diffusion activation energy, R is the gas constant, and T is the absolute temperature.

By substituting Eq. (5) into Eq. (4), the equation can be rewritten as:

$$\frac{1}{T} = \frac{R}{Q} \ln\left[\frac{4\pi^2 D_0 t}{4.6L^2}\right] \quad (6)$$

Assuming $A = R/Q$ and $B = 4.6/4\pi^2 D_0$, we can obtain the homogenization kinetic equation:

$$\frac{1}{T} = A \ln\left(\frac{t}{BL^2}\right) \quad (7)$$

As long as the parameters of as-cast microstructure are given, the homogenization kinetic curves can be obtained.

Fig. 9 Phases analysis after the first-step homogenization: **a** XRD, **b** SEM, **c** and **d** EDS of No.1 and No.2 in **b**

Fig. 10 Phases analyses after the second-step homogenization: **a** XRD, **b** SEM, **c** and **d** EDS of No.1 and No.2 in **b**

From the results of Sect. 3.3, we can know that the diffusion coefficient of Cu is much lower than Zn and Mn at the same temperature. Therefore, the homogenization

process is believed to be controlled by the diffusion of Cu. By substitution of $D_0(\text{Cu}) = 0.084 \text{ cm}^2 \cdot \text{s}^{-1}$, $Q(\text{Cu}) = 136.8 \text{ kJ} \cdot \text{mol}^{-1}$, and $R = 8.314 \text{ J} \cdot (\text{mol} \cdot \text{K})^{-1}$ into Eq. (7),

Fig. 11 Elements distribution during process of homogenization

Fig. 12 Curves of homogenization kinetic

the homogenization kinetic curves of 2099 Al–Li alloy for different dendrite spacings can be obtained. As shown in Fig. 12, the soaking time is decreased with the increase of temperature, and microstructure refinement can also greatly shorten the soaking time.

The average dendrite spacing of as-cast and after the first-step homogenization treatment in this study is 65 and 70 μm , respectively, obtained from quantitative metallographic analysis. According to the homogenization kinetic curves, at the optimized temperatures of 515 and 525 $^{\circ}\text{C}$, the corresponding soaking time are 19.2 and 17.1 h, respectively. This is in good accordance with the experimental results. Besides, we find that there still exist a small amount of remaining eutectic phases in the local areas, and XRD and EDS analysis show that they are consisted of Al–Cu–Fe phases, owing to its high-melting point that cannot be eliminated in the homogenization process.

4 Conclusion

In the present study, 2099 Al–Li alloy homogenization treatment was carried out by performing the first-step and second-step homogenization treatment in a range of times and temperatures. Severe dendrite segregation exists in the

as-cast alloy. The segregation extent of main alloying elements is $\text{Cu} > \text{Mn} > \text{Zn}$.

Low-melting point nonequilibrium eutectic phases dissolve into the matrix at 515 $^{\circ}\text{C}$ for 18 h, and maximum value (129 HV0.5) of microhardness is obtained at 515 $^{\circ}\text{C}$ for 18 h. The further increase of soaking time has little effect on the microstructure evolution and microhardness changes. Most of residual nonequilibrium eutectic phases dissolve and the dendrite almost eliminates at 525 $^{\circ}\text{C}$ for 16 h. With the increase of the temperature, some melting balls appear, which is typical overheating features. The optimized second-step homogenization process is determined at 515 $^{\circ}\text{C} \times 18 \text{ h} + 525 \text{ }^{\circ}\text{C} \times 16 \text{ h}$. The segregation is eliminated basically after second-step homogenization. The homogenization kinetic curves have a good consistent with the first-step and second-step homogenization treatment process parameters.

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