

Microstructural evolution of ultra-high strength Al-Zn-Cu-Mg-Zr alloy containing Sc during homogenization

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Received 8 October 2010; accepted 28 March 2011

Abstract: The microstructural evolution and composition distribution of an Al-Zn-Cu-Mg-Sc-Zr alloy during homogenization were investigated by optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The results show that severe dendritic segregation exists in Al-Zn-Cu-Mg-Sc-Zr alloy ingot. There are a lot of eutectic phases at grain boundary and the distribution of the main elements varies periodically along interdendritic region. The main eutectic phases at grain boundary are Al_7Cu_2Fe phase and T ($Al_2Mg_3Zn_3$). The residual phases are dissolved into the matrix gradually during homogenization with increasing temperature and prolonging holding time, which can be described by a constitutive equation in exponential function. The overburnt temperature of the alloy is 473.9 °C. The optimum parameters of homogenization are 470 °C and 24 h, which is consistent with the result of homogenization kinetic analysis.

Key words: Al-Zn-Cu-Mg-Sc-Zr alloy; homogenization; microstructural evolution; overburnt temperature; homogenization kinetics

1 Introduction

High strength aluminum alloys of Al-Zn-Cu-Mg series are widely used in aviation and aerospace field due to their high specific strength, toughness and fatigue durability [1–3]. The common feature of these alloys is high volume fraction of alloying elements, which leads to severe dendrite and grain boundary segregation in the as-cast alloy. In order to obtain good processing properties and service performance, the as-cast alloys should be homogenized before subsequent processing. The homogenization temperature and time play a very important role in the dissolution of the residual phases during the homogenization. Usually, the residual coarse particles of Fe-rich or Cu-rich phases will result in a decrease of toughness and strength, and reduce fatigue properties [4–8].

It is well known that the type and intrinsic characteristic of residual phases will differ in different alloys and change with different heat treatment conditions. MONDAL and MUKHOPADHYAY [9] studied the phases in the as-cast and homogenized 7055

aluminum alloys, and revealed that the major residual phases were η ($MgZn_2$), T ($Al_2Mg_3Zn_3$), S (Al_2CuMg) and θ ($CuAl_2$). The microstructure of the cast 7050 alloy consists of dendrites, high angle grain boundaries, and inter-dendritic eutectic regions containing phases such as Al_2CuMg , $MgZn_2$ and Mg_2Si [10].

Despite detailed studies of microstructural evolution in the as-cast and homogenized 7050 and 7055 alloys, less attention has been paid to the evolution of eutectic structure in the Al-Zn-Cu-Mg-Sc-Zr alloy, and the transformation of primary eutectic structure to coarse residual particles is not yet clear.

The present study was designed to examine the microstructural evolution of Al-Zn-Cu-Mg-Zr alloy containing Sc during homogenization. The effects of temperature and holding time on the microstructural evolution during the homogenization were also investigated, from which the practicable treatment of homogenization was concluded.

2 Experimental

The nominal composition of the studied alloy was

Al-8.1Zn-2.05Mg-2.3Cu-0.21Sc-0.12Zr (mass fraction, %). The cast ingot was prepared with pure Al, pure Zn, pure Mg and Al-Cu, Al-Sc, Al-Zr master alloys by ingot metallurgy in a crucible furnace and then poured into a copper plate-shape mould (260 mm×150 mm×30 mm). Specimens with dimensions of 20 mm×20 mm×5 mm were cut from the central position of the cast ingot. In this region, the ingot enriched in major alloying elements. The specimens were homogenized at 450, 460, 465, 470, 480 and 485 °C for 24 h, respectively. And then at the optimized temperature, the specimens were homogenized for 8, 16, 24 and 32 h. All the homogenized specimens were air-cooled to room temperature.

The melting temperature of eutectic phase was determined with DSC analysis on DUPONT9900. The microstructures of specimens were analyzed by optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectrometry. The SEM specimens were prepared through a conventional mechanical grinding and polishing, and followed by etching with Keller reagent (2 mL HF+3 mL HCl+5 mL HNO₃+190 mL H₂O). The analyses of SEM and EDX were carried out on Philips Sirion 20 and Finder-1000.

3 Results and discussion

3.1 As-cast microstructure

Figure 1 shows the microstructure of the as-cast

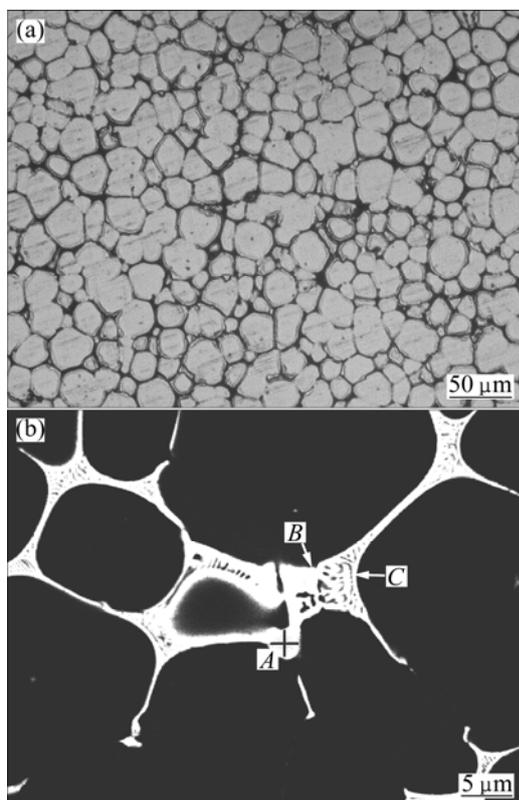


Fig. 1 Microstructures of as-cast alloy: (a) Metallography; (b) SEM image

alloy. The results of EDX analysis are listed in Table 1. It can be seen that a large number of residual phases exist at the grain boundaries. These phases in Fig. 1(b) show different shapes with different contrast. The energy dispersive X-ray analysis reveals that the deep grey phases contain Cu and Fe, and the constituent is close to Al₇Cu₂Fe phase in composition (spot A in Fig. 1(b)), while the lamellar eutectics are *T* (Al₂Mg₃Zn₃) phase (spot B and spot C in Fig. 1(b)) with solute of Cu [11–13].

Table 1 Chemical composition of secondary phases in studied alloy

Phase	<i>x</i> (Al)/%	<i>x</i> (Zn)/%	<i>x</i> (Mg)/%	<i>x</i> (Cu)/%	<i>x</i> (Fe)/%
<i>A</i>	80.45	–	–	13.92	5.62
<i>B</i>	51.43	17.66	20.19	10.72	–
<i>C</i>	62.43	13	16.55	8.02	–

Figure 2 shows the SEM microstructure and the composition maps of Cu, Mg, and Zn (brightness is proportional to elemental concentration) in as-cast Al-Zn-Cu-Mg-Sc-Zr alloy. The composition maps exhibit the relative Cu, Mg, and Zn concentrations. It can be seen that the segregation degrees of Cu, Mg and Zn at grain boundaries are different. The differences of brightness show that the segregation order of elements is Cu>Mg>Zn. The concentrations of the elements decrease from grain boundary to grain interior. Therefore, the homogenization treatment is required to eliminate severe dendritic segregation in the as-cast alloy. Generally, the relationship between the diffusion coefficient and the temperature can be described as:

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

where D_0 is the diffusion coefficient; R is the mole gas constant; Q is the diffusion activation energy; T is the thermodynamic temperature.

Figure 3 shows the DSC curves of as-cast ingot and specimens homogenized at different temperatures for 24 h. Two endothermic peaks are observed in the as-cast alloy, sited at 473.9 °C and 622.7 °C respectively. The endothermic peak at 473.9 °C disappears gradually after homogenization at an elevated temperature. It may be corresponding to the dissolution of some non-equilibrium phases during homogenization. The endothermic peak at 622.7 °C is ascribed as the melting point of the alloy. These results reveal that the homogenized temperature of the alloy should not surpass the temperature of 473.9 °C, which is generally called the overburnt temperature of the alloy.

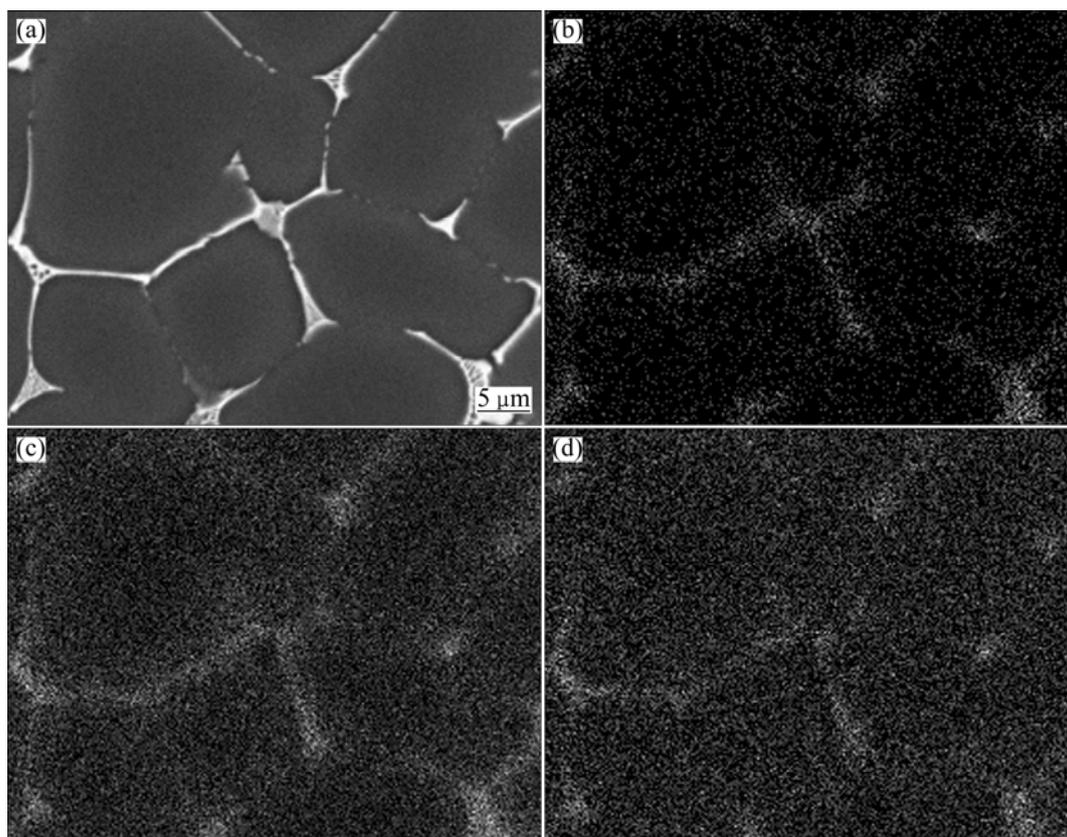


Fig. 2 SEM microstructure (a) and composition maps of Cu (b), Mg (c) and Zn (d) in as-cast studied alloy

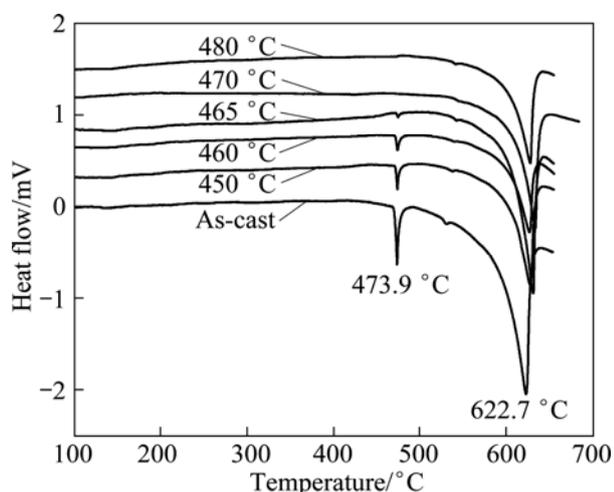


Fig. 3 DSC curves of as-cast ingot and specimens homogenized at different temperatures

3.2 Effect of homogenization temperature on microstructures

Figure 4 shows the microstructures after homogenization at different temperatures for 24 h. It can be seen from Fig. 4 that the non-equilibrium eutectics with low melting point dissolved gradually when the temperature increased. The continuous residual phases along the grain boundaries have turned to be

uncontinuous ones, and the grain boundaries become thin and clear. Most of the non-equilibrium eutectics with low melting point have dissolved after homogenization at 470 °C for 24 h. When the temperature increases up to 480 °C, some spherical phases and redissolved triangular constituents at the grain boundaries can be observed (Fig. 4(e)), which indicates the occurring of overburnt microstructures. It can be concluded that the suitable upper limit of homogenization temperature is 470 °C. The DSC analysis in Fig. 3 shows the same conclusion.

3.3 Effect of homogenization time on microstructures

Figure 5 shows the microstructures of specimens homogenized at 470 °C for different time. It can be seen that by prolonging homogenization time, the volume fraction of the dendritic-network structure is reduced gradually, and the residual phases become small and sparse. The non-equilibrium phases at the grain boundaries dissolve gradually with increasing the homogenization time. When the time increase to 32 h, no obvious dissolution of residual constituents is observed (Fig. 5(d)), and the microstructure has no significant change compared with that homogenized for 24 h (Fig. 5(c)). As a result, the reasonable homogenization time at 470 °C can be determined to be 24 h.

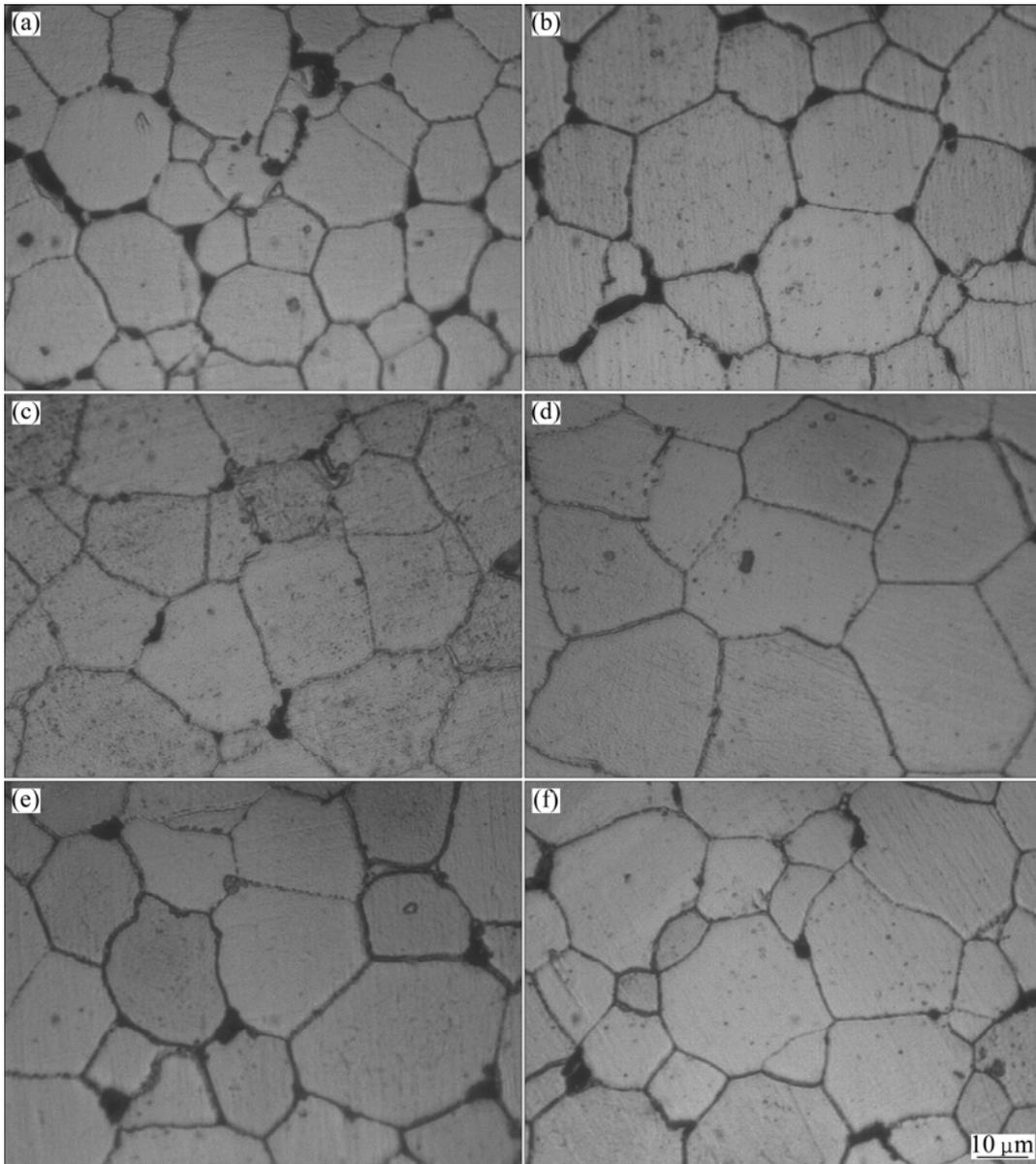


Fig. 4 Microstructures of specimens homogenized at different temperatures for 24 h: (a) 450 °C; (b) 460 °C; (c) 465 °C; (d) 470 °C; (e) 480 °C; (f) 485 °C

3.4 Line scanning analysis of homogenized alloy

Figure 6 shows the line scanning analyses of Al-Zn-Cu-Mg-Sc-Zr alloys in as-cast state and homogenized state at 470 °C for 24 h. It reveals that, after homogenization, the segregation of elements Cu, Mg, and Zn is almost eliminated and the distribution of elements is homogeneous from the grain boundary to inside. Nevertheless, a few Cu segregation still can be observed, which may be due to the low diffusion coefficient [14]. It was also reported [11] that the intermetallic phase of Al_7Cu_2Fe has high melting temperature and can not be dissolved completely during the homogenization, which leads to the small segregation of Cu at the grain boundaries after the homogenization.

3.5 Homogenization kinetic analysis

Figure 6(a) shows the line scanning analysis of as-cast Al-Zn-Cu-Mg-Sc-Zr alloy. It can be seen that the distribution of the main elements along interdendritic region varies periodically. So the studies of diffusion law along interdendritic region are important to the investigations of distribution of elements during the homogenization.

According to the diffusion kinetics of aluminum alloy during homogenizing treatment [14], the initial concentration of the elements along the interdendritic region can be approached by Fourier series components in a cosine function:

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

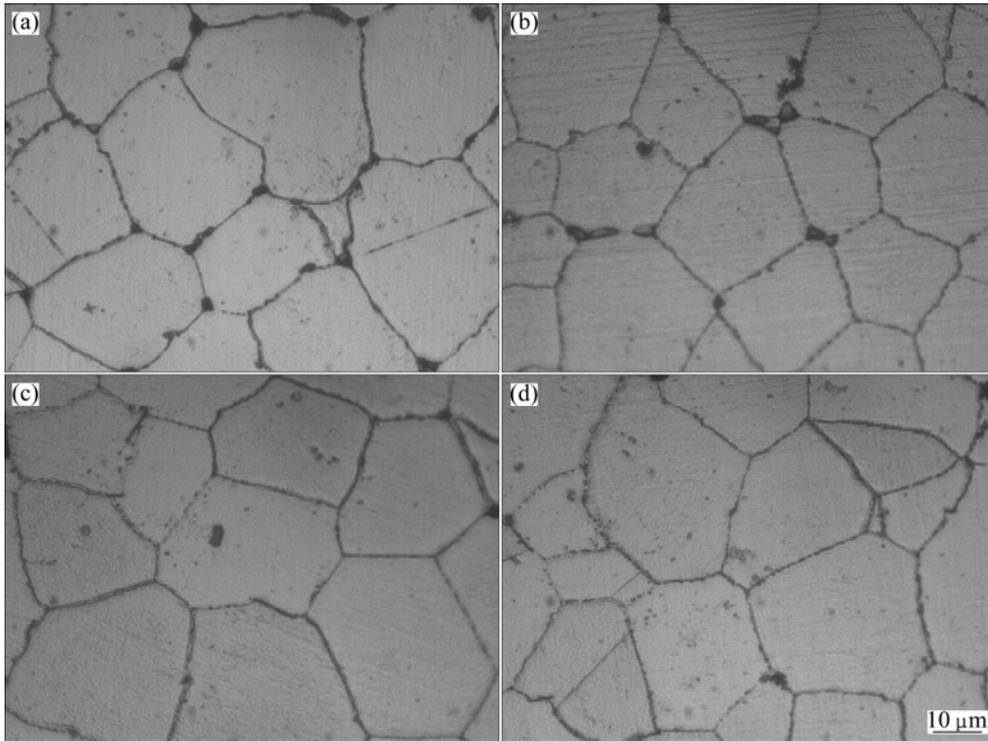


Fig. 5 Microstructures of homogenized specimens at temperatures of 470 °C for different holding time: (a) 8 h; (b) 16 h; (c) 24 h; (d) 32 h

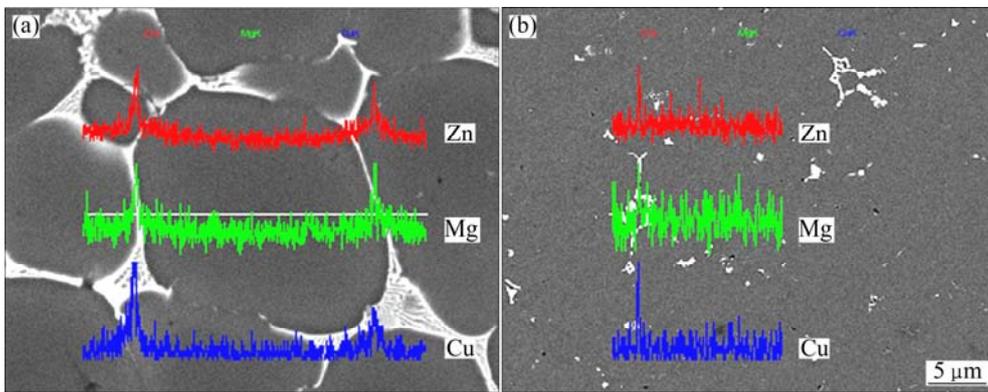


Fig. 6 Line-scan traces of elements in studied alloys: (a) As-cast; (b) Homogenized at 470 °C for 24 h

where c is the average concentration of the element; L is the interdendritic spacing; A_0 is the initial amplitude of the composition segregation which can be expressed as:

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

The variables in Eq. (2) are shown in Fig. 7. The amplitude of composition segregation decreases with the increase of the holding time during homogenization, represented as $A(t)$. According to the second Fick's law and the boundary conditions, $A(t)$ is given as:

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

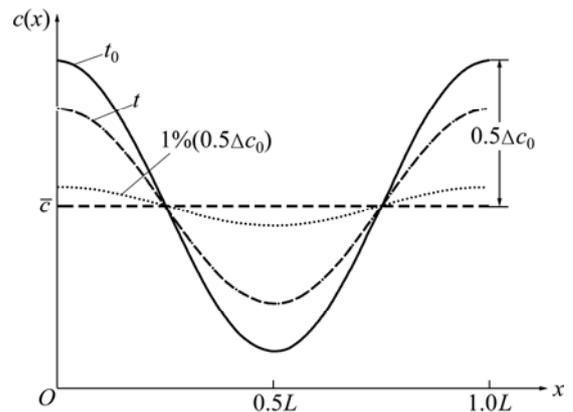


Fig. 7 Model of elemental distribution during homogenization

By substituting Eq. (1) into Eq. (4), the equation can be rewritten as:

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

It can be seen from Eq. (5) that by increasing the homogenization temperature T or prolonging the holding time t , the segregation along the interdendritic region decreases, which is consistent with the experimental result.

Assume the element distribution is homogeneous when the composition segregation amplitude is reduced to 1%, i.e.

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

Then

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

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

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

Assume $A=R/Q$ and $B=4.6/(4\pi^2 D_0)$, we can obtain:

$$\frac{1}{T} = A \ln \left(\frac{t}{BL^2} \right) \quad (9)$$

Equation (9) is the homogenization kinetic equation. If the parameters of as-cast microstructure are given, the homogenization kinetic curves can be obtained. The diffusion coefficient of Cu is much lower than that of Mg or Zn at the same temperature. So the homogenization process is believed to be controlled by the diffusion of Cu [14–16]. By substituting $D_0(\text{Cu})=0.084 \text{ cm}^2/\text{s}$, $Q(\text{Cu})=136.8 \text{ kJ/mol}$ and $R=8.31 \text{ J/(mol}\cdot\text{K)}$ into Eq. (9), the homogenization kinetic curves of Al-Zn-Cu-Mg-Sc-Zr alloy for different interdendritic spacings can be obtained, as shown in Fig. 8. It shows that the holding

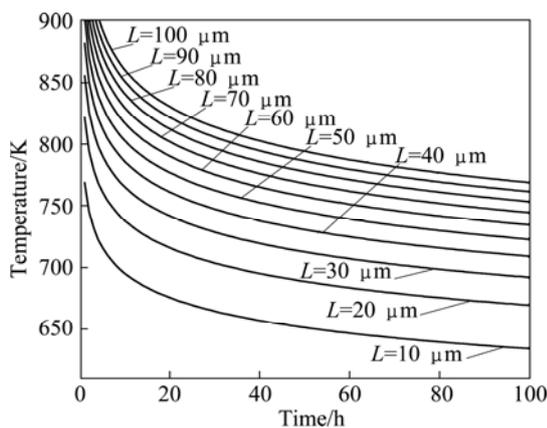


Fig. 8 Curves of homogenization kinetics

time decreases dramatically with the increase of the homogenization temperature.

The average interdendritic spacing L in the present Al-Zn-Cu-Mg-Sc-Zr alloy is $33 \mu\text{m}$ based on quantitative metallographic analysis. According to the homogenization kinetic curves, at the temperature of $470 \text{ }^\circ\text{C}$, the corresponding homogenization time is 22 h. This is in good accordance with the experimental result.

4 Conclusions

1) Severe dendritic segregation exists in Al-Zn-Cu-Mg-Sc-Zr alloy ingot. The main residual phases in this alloy are $\text{Al}_7\text{Cu}_2\text{Fe}$ and $T (\text{Al}_2\text{Mg}_3\text{Zn}_3)$ phases, which precipitate along grain boundaries. The inhomogeneous composition distributions of Cu, Mg, Zn in as-cast alloy also exist across the grain.

2) Increasing temperature and/or prolonging the holding time of homogenization, the residual phases are dissolved into the matrix gradually, which will result in thin grain boundaries and homogeneous distribution of alloying elements. A constitutive equation in exponential function can be used to describe the process.

3) The overburnt temperature of Al-Zn-Cu-Mg-Sc-Zr alloy is $473.9 \text{ }^\circ\text{C}$. The optimum homogenization treatment is $470 \text{ }^\circ\text{C}$, 24 h, which is consistent with the result of homogenizing kinetic analysis.

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含 Sc 超高强 Al-Zn-Cu-Mg-Zr 合金 均匀化过程中的组织演变

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摘要: 用光学显微镜 (OM)、扫描电子显微镜 (SEM)、能谱分析 (EDS)和 X 射线衍射技术 (XRD)分析了不同均匀化条件下 Al-Zn-Cu-Mg-Sc-Zr 铝合金的组织演变与成分分布。结果表明: Al-Zn-Cu-Mg-Sc-Zr 铝合金铸锭中存在严重的枝晶偏析, 晶界有许多共晶相, 主要元素在枝晶内部区域呈周期性分布; 晶界的主要共晶相为 $\text{Al}_7\text{Cu}_2\text{Fe}$ 相和 $T(\text{Al}_2\text{Mg}_3\text{Zn}_3)$ 相; 在合金均匀化过程中, 随着温度的升高和时间的延长, 残留相逐渐溶入基体, 这个过程可以用一指数方程来描述; 合金的过烧温度为 473.9 °C; 最佳的均匀化处理制度为 470 °C, 24 h, 这一结果与均匀化动力学方程测算的结果相符。

关键词: Al-Zn-Cu-Mg-Sc-Zr 合金; 均匀化; 组织演变; 过烧温度; 均匀化动力学

(Edited by YANG Hua)