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ARTICLE

Microstructure and Property Evolution of Al-Zn-Mg-Cu Alloy with Ho Addition During Homogenization

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Abstract: Homogenization treatment for Al-Zn-Mg-Cu alloy with Ho addition was investigated by scanning electron microscope (SEM), optical microscope (OM), and differential scanning calorimeter (DSC). Electrical conductivity and micro-hardness were tested during different homogenization processes. The results show that there are four kinds of second phases in as-cast alloy: T (AlZnMgCu), Al_7Cu_2Fe, Al_8Cu_4Ho and S (Al_2CuMg), which cause severe micro-segregation in microstructure. After homogenization treatment at 475 °C for 20 h, T phase is completely dissolved back into matrix and no S phase is observed, with Al_7Cu_2Fe and Al_8Cu_4Ho remaining. Micro-hardness and electrical conductivity are associated with vibration of T phase, dissolution of which can increase micro-hardness and decrease electrical conductivity. Besides, precipitation of Al_3Ho also contributes to the increase in both micro-hardness and electrical conductivity during homogenization at 475 °C for 5~20 h. Finally, through homogenization kinetic analysis, the appropriate homogenization parameter is determined as 470~475 °C/20~25 h.

Key words: Al-Zn-Mg-Cu alloy with Ho addition; homogenization treatment; micro-hardness and electrical conductivity; homogenization kinetic analysis

Al-Zn-Mg-Cu alloy (7xxx series) has been extensively applied in plenty of manufacturing industries, including aerospace components, automobile parts and weapon systems, due to its low density, high strength and high ductility[1-4]. In the case of precipitation strengthening Al-Zn-Mg-Cu alloy, the mechanical properties are strongly related to the distribution and the volume fraction of precipitates formed during the homogenization and aging treatments [5-8]. Consequently, new types of 7xxx alloys with high alloying element contents are constantly developed, intending to enhance the precipitation behavior.

As micro-alloying elements, RE (Y, Tb, Dy, Ho, Sc and Er) has been widely added into aluminum alloys to form thermal stable coherent $L1_2$-structured Al_3RE nanoparticles, which can facilitate grain refinement, improve mechanical properties and have proven to be effective in pinning dislocation and sub-boundaries to inhibit recrystallization and grain growth during post-homogenization thermal processing of the aluminum alloys[9-11]. Filatov [10] showed that the mechanical properties of Al-Mg alloys with Er addition are strongly improved by the presence of the fine dispersed Al_3Er particles after heat treatment. Pang et al[12] indicated that the addition of Ho not only refines the microstructure but also purifies grain boundaries. Pang[13] proposed homogenization heat treatment of Al-6.5Zn-2.1Mg-2Cu-*x*Ho alloy. Liu et al[14] investigated the effect of minor Sc and Zr on recrystallization behavior and mechanical properties of novel Al-Zn-Mg-Cu alloys. The results showed that abundant nano-scale sized Al_3(Sc, Zr) particles can effectively pin dislocations and sub-grain boundaries, exhibiting excellent anti-recrystallization behavior and precipitate strengthening effect.

It is well known that homogenization treatment is an indispensable process for aluminum alloys to achieve desired comprehensive performances. Generally speaking, 7xxx alloys are subjected to homogenization treatment right after casting, aiming to eliminate microsegregation and to dissolve the large soluble eutectic intermetallic particles back into the matrix[14-17]. Meanwhile, homogenization treatment is also applied to precipitate Al_3RE particles with reasonable volume fraction and size[18]. As a result, it is an essential process to

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develop an optimum homogenization treatment for 7xxx aluminum alloys.

However, to our best knowledge, there is little report about microstructure evolution and Al_3Ho precipitation behavior of Al-Zn-Mg-Cu alloy with Ho addition during homogenization. Therefore, the main goals of present study include: (1) optimization of homogenization parameters for high Zinc Al-Zn-Mg-Cu alloy with Ho addition; (2) characterization of microstructure evolution and phase transformation of the studied alloy during homogenization; (3) discussion of the effect of the phase dissolution and transformation on evolution of electrical conductivity and micro-hardness; (4) homogenization kinetic analysis of the experimental homogenization parameters.

1 Experiment

The as-cast Al-Zn-Mg-Cu alloy with Ho addition was fabricated by DC casting with pure Zn, pure Cu, pure Mg and Al-Ho master alloy. Chemical composition of the studied ingot was tested by SPECTROLAB optical emission spectroscopy, as listed in Table 1.

Samples with the dimension of 10 mm×10 mm×10 mm were directly obtained from the center part of the ingot. The following homogenization treatment was performed in Nabertherm Gmbh furnace. As-cast samples were divided into two groups (Fig. 1). Group 1 was subjected to single-stage homogenization at 460~485 °C for 10, 20 and 30 h; group 2 was subjected to single-stage homogenization at 475 °C for different soaking time ranging from 5 h to 35 h; the homogenized samples were designated as G1 and G2, respectively. Fig.1 illustrates the schematic diagram of the homogenization treatments. To retain the homogenized microstructures, samples were immediately water quenched, once taken out of the furnace.

A OLYMPUS GX53 optical microscope (OM) and a Phenom XL scanning electron microscope (SEM) attached with energy dispersive spectroscopy (EDS) were used for microstructure characterization and composition analysis of both the as-cast and homogenized samples. Sheets with a diameter of 3 mm and a thickness of 1 mm were prepared for differential scanning calorimeter (DSC) tests by NETZSCH DSC204 in a range from 25 °C to 590 °C with a heating rate of 10 °C/min. Electrical conductivity tests was conducted by a SIGMASCOPE SMP350 meter within 5 min after water quenching. Micro-hardness was obtained by a WILSON VH1102 micro-hardness tester. Both electrical conductivity and micro-hardness tests were carried out at ambient temperature.

Table 1 Chemical composition of Al-Zn-Mg-Cu alloy with Ho addition (wt%)

Zn	Mg	Cu	Fe	Si	Ho	Al
9.04	1.95	2.46	0.21	0.04	0.18	Bal.

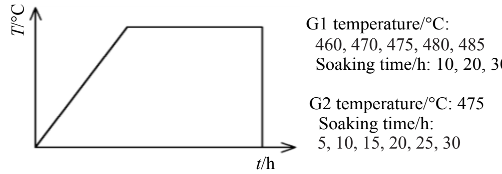

Fig.1 Schematic diagram of the homogenization treatment

2 Results and Discussion

2.1 Characterization of as-cast microstructure

Fig.2 shows the OM as well as SEM microstructures of the as-cast alloy. After solidification, a great amount of non-equilibrium eutectic and intermetallic phases are distributed in interdendritic spaces and grain boundaries (Fig. 2a), which result in severe composition segregation, deterioration of comprehensive performance and discount to precipitation strengthening effect. Combing SEM and EDS, it can be seen from Fig.2b and Table 2 that there are four different identified phases: light gray A and D as Al_7Cu_2Fe and S (Al_2CuMg), respectively; bright white B as Al_8Cu_4Ho; net-shaped C as T (AlZnMgCu). Fig.3 shows the selected area of EDS analysis (Fig. 3a) and corresponding element distribution of Al, Zn, Mg, Cu in the as-cast alloy. It can been seen that the main alloying elements of Zn, Mg and Cu are enriched at grain boundaries and form severe segregation. A suitable homogenization treatment is necessary to alleviate the phenomenon.

Fig.4 elucidates that T (AlZnMgCu) phase begins to melt at 478.5 °C[19]. Therefore, the homogenization temperature should be lower than the inflection point to avoid formation of detrimental overheated holes. Yet, excessively low homogenization temperature cannot achieve the expected goals.

2.2 Microstructural evolution during homogenization

To optimize the homogenization parameters, i. e., temperature and soaking time, DSC experiments were conducted with five various temperatures and soaking time. The results

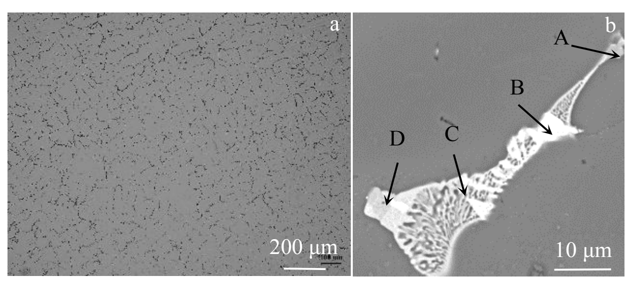

Fig.2 OM (a) and SEM (b) images of as-cast Al-Zn-Mg-Cu alloy with Ho addition

Table 2 EDS results of intermetallic phases (point A~D) in as-cast Al-Zn-Mg-Cu alloy with Ho addition in Fig.2 (at%)

Point	Al	Zn	Mg	Cu	Fe	Ho	Phase
A	78.80	2.03	2.03	8.54	7.60	-	Al_7Cu_2Fe
B	54.43	-	-	40.37	-	5.20	Al_8Cu_4Ho
C	61.78	24.01	15.60	9.73	-	-	T (AlZnMgCu)
D	77.29	6.93	7.72	7.57	-	0.50	S (Al_2CuMg)

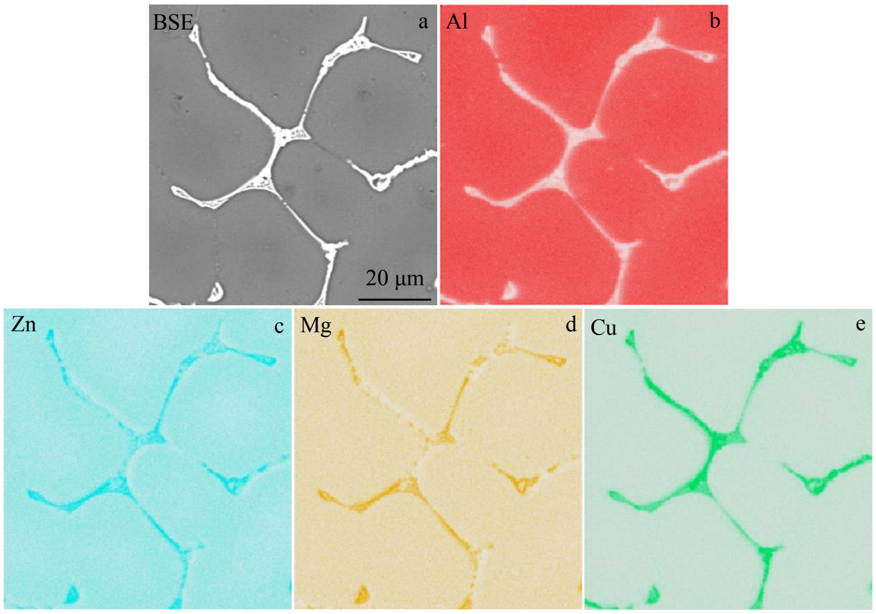

Fig.3 SEM image (a) and corresponding element distribution of Al (b), Zn (c), Mg (d), and Cu (e) of as-cast alloy

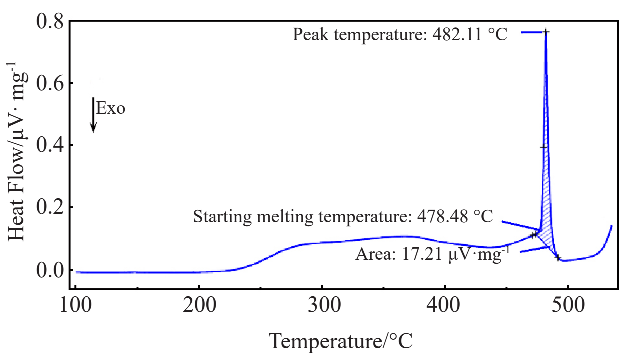

Fig.4 DSC curve of the as-cast alloy

(Fig. 5) indicate that the endothermic peak area keeps shrinking with increasing the homogenization temperature for 20 h or with increasing soaking time at 475 °C until it totally vanishes when the temperature is higher than 475 °C (Fig.5a) or when the soaking time is more than 20 h (Fig.5b).

It can be extracted from SEM images (Fig. 6) that the inter-connected net frameworks of T (AlZnMgCu) phase in as-cast alloy start to break down, as the alloy is homogenized at 460 °C for 20 h. With increasing the homogenization temperature, the T (AlZnMgCu) phases gradually transform into S (Al_2CuMg) phase (Fig. 7), leaving behind undecomposable and dispersed Al_8Cu_4Ho and Al_7Cu_2Fe phase (Table 3). To quantitatively count the area fraction variation of intermetallic phases during different homogenization process, IPP (Image-Pro Plus) was applied to calculate the residual phase in SEM images. The results (Fig. 8) suggest that when homogenization soaking time is fixed at 20 h, area fraction of second phases keeps declining until it reaches a stable value of 2% at 475 °C (black line), which is corresponding to peak area transformation in Fig. 5a. While the homogenization temperature is set as constant value of 475 °C (Fig. 8, red line), at the initial stage, area fraction of second phases dramatically reduces to 63.7%, since higher temperature leads to greater transformation kinetic.

2.3 Micro-hardness and electrical conductivity evolution during homogenization

Fig. 9 shows the micro-hardness and electrical conductivity

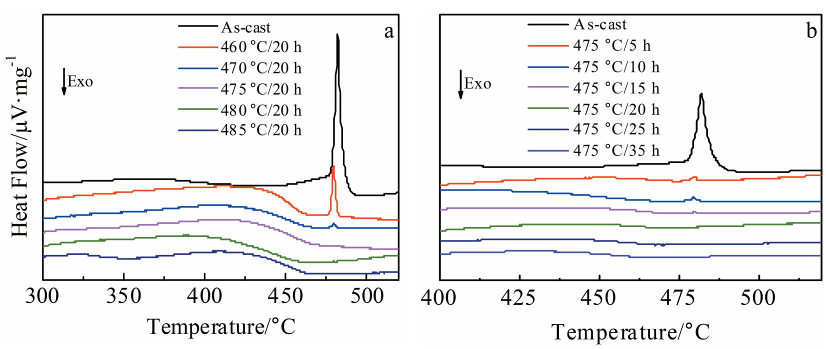

Fig.5 DSC curves of the alloy homogenized at different temperatures for 20 h (a) and for different time at 475 °C (b)

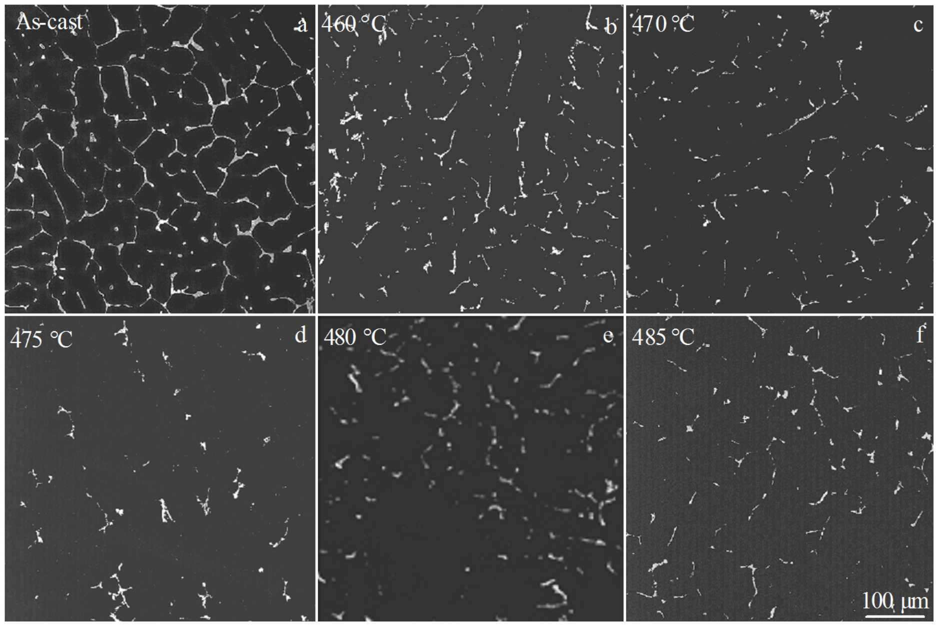

Fig.6 SEM images of second phases in as-cast alloy (a) and the alloys homogenized at different temperatures for 20 h

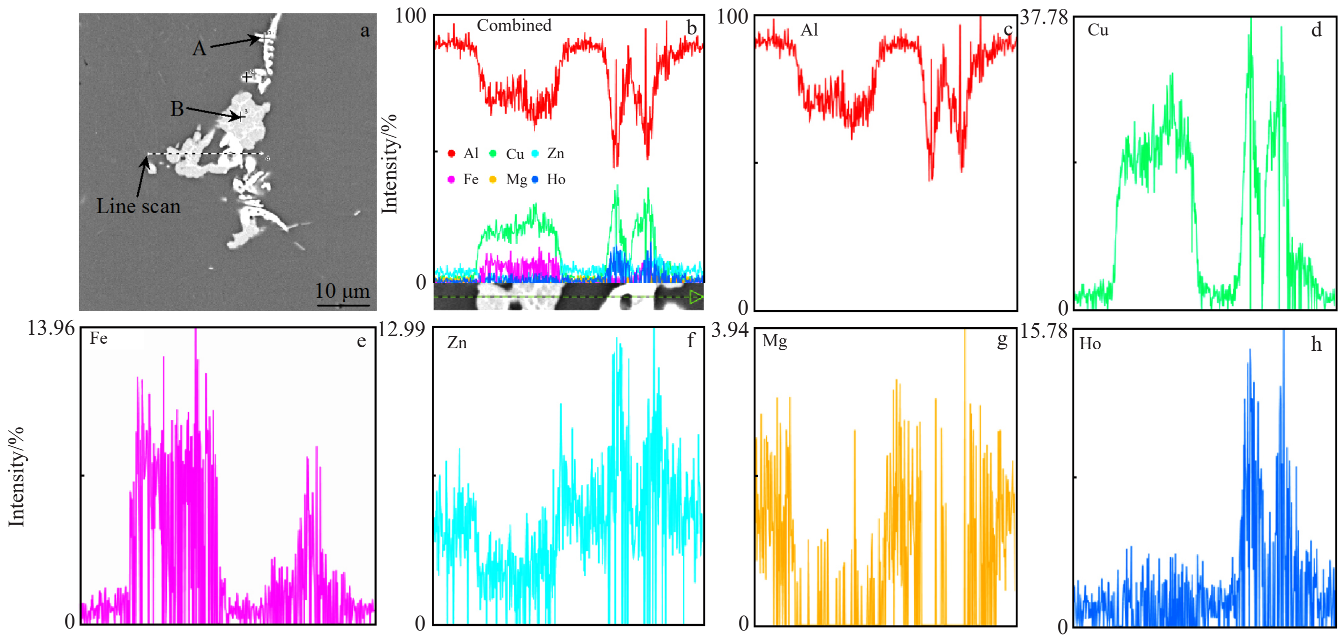

Fig.7 SEM image (a) and corresponding element distribution along marked line in Fig.7a (b~h) for homogenized alloy

of homogenized alloy at different temperatures for different soaking time. With increasing the homogenization temperature (Fig. 9a), under the combined impact of solid solution strengthening and precipitation strengthening of coherent Al_3Ho, the micro-hardness of the alloy reaches the peak value of 1517.4 MPa and increases by 33% at 475 °C. However, when the experimental temperature surpasses 478.5 °C, the micro-hardness rapidly decreases, resulting in occurrence of over-burn phenomenon and deterioration of overall performances. Meanwhile, electrical conductivity of the alloy keeps dropping, due to supersaturated solute atoms triggering proliferation of lattice distortion and electron scattering sources. With increasing the soaking time (Fig.9b), the micro-hardness of the alloy exhibits the similar changing tendency as in Fig. 9a. It should be noticed that after a reasonable sharp reduction, the electrical conductivity of the alloy starts to rise slowly, which can be related to the precipitation of Al_3Ho during the period of 5~20 h. Excessive soaking time is harmful to both micro-hardness and electrical conductivity.

Table 3 EDS results of intermetallic phases (point A and B) in homogenized Al-Zn-Mg-Cu alloy with Ho addition in Fig.7a (at%)

Point	Al	Zn	Mg	Cu	Fe	Ho	Phase
A	54.43	-	-	40.37	-	5.20	Al_8Cu_4Ho
B	78.80	2.03	2.03	8.54	7.60	-	Al_7Cu_2Fe

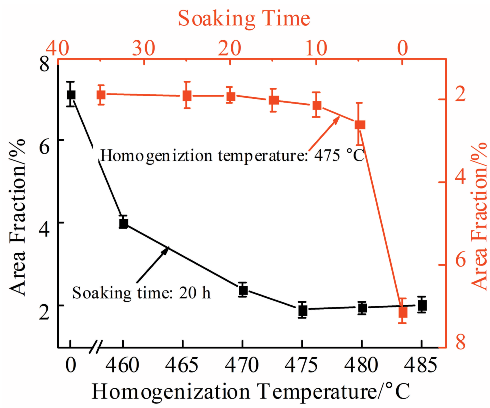

Fig.8 Area fraction of intermetallic phases after different homogenization treatments

2.4 Homogenization kinetic analysis

During homogenization, majority of T(AlZnMgCu) phase dissolves back into matrix and transforms to S (Al_2CuMg) phase[20]. Severe micro-segregation of Zn, Mg and Cu elements exists along eutectic structure at grain boundaries (Fig. 3). Based on the research of Liu[21], the homogenization kinetic equation can be expressed as

$$\exp\left(\frac{4\pi^2 Dt}{L^2}\right) = \frac{1}{100} \quad (1)$$

in which D, t and L represent solid diffusion coefficient of alloying elements in solid solution, soaking time and interdendritic spacing, respectively.

According to Mehrer' research[22], the diffusion coefficient of alloying elements can be expressed as an empirical exponential function:

$$\begin{cases} D_{Cu} = 4.8 \times 10^{-5} \exp(-16069/T) \\ D_{Mg} = 6.23 \times 10^{-6} \exp(-13831/T) \\ D_{Zn} = 2.45 \times 10^{-5} \exp(-14385/T) \end{cases} \quad (2)$$

where T is homogenization temperature (K).

Table 4 shows the calculated D results of Cu, Mg and Zn during homogenization at various temperatures. It is obvious that D_{Cu} is much lower than D_{Mg} and D_{Zn}, and Ho content, as a micro-alloying element, in the alloy is relatively low, so the diffusion of Cu element controls the homogenization process[23,24]. Meanwhile, it is also worth noticing that as the temperature increases, the value of D_{Cu}: D_{Mg}: D_{Zn} keeps dropping, meaning that the difference of D_{Cu}, D_{Mg} and D_{Zn} decreases with increasing the temperature.

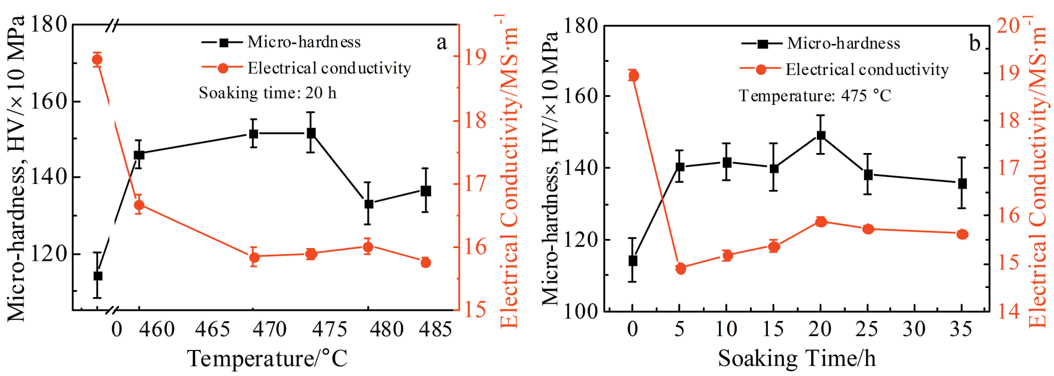

Fig.9 Micro-hardness and electrical conductivity of homogenized alloy at different temperatures (a) for different soaking time (b)

Replacing D in Eq. (1) with D_{Cu} in Eq. (2), Eq. (1) can be written as

$$T = 16069/\ln\left(\frac{1.48 \times 10^{12}}{L^2} t\right) - 273.15 \quad (3)$$

in which the units of T, t and L are °C, s and μm, respectively.

The average interdendritic spacing (L) of as-cast Al-Zn-Mg-Cu-Ho alloy measured by optical microscope in Fig. 2a is 38.1±0.3 μm. By Eq. (3), the theoretical homogenization kinetic curves for varying interdendritic spacing between 30 μm and 70 μm are constructed, as shown in Fig.9. The rationality of the experimentally optimized homogenization parameters (T=475 °C and t is 20 h, dashed line in Fig. 10) in Section 2.2 can be justified for the intersection point falling in right position. Furthermore, the experimental results (Fig. 7

Table 4 Solid diffusion coefficient D value of Cu, Mg and Zn elements in Al-matrix during homogenization ($m^2 \cdot s^{-1}$)

D	Temperature/°C				
	460	470	475	480	485
D_{Cu}	1.45×10^{-14}	1.95×10^{-14}	2.26×10^{-14}	2.60×10^{-14}	2.99×10^{-14}
D_{Mg}	3.99×10^{-14}	5.15×10^{-14}	5.83×10^{-14}	6.59×10^{-14}	7.44×10^{-13}
D_{Zn}	7.38×10^{-14}	9.58×10^{-14}	1.01×10^{-13}	1.24×10^{-13}	1.41×10^{-13}
D_{Cu}:D_{Mg}:D_{Zn}	1:2.7:5.1	1:2.6:4.9	1:2.6:4.8	1:2.5:4.8	1:2.5:4.7

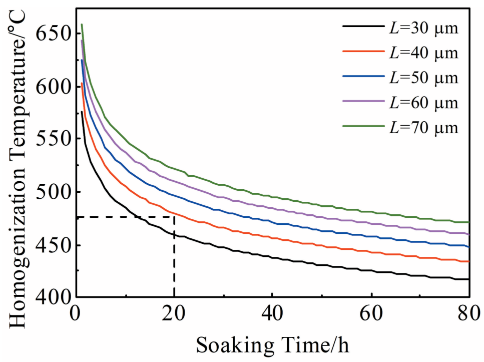

Fig.10 Homogenization kinetic curves of the alloy with different T (AlZnMgCu) phase spacing

and Table 3) also verify that no T (AlZnMgCu) phase is left after the homogenization treatment.

3 Conclusions

1) Severe micro-segregation exists in the microstructure of Al-Zn-Mg-Cu alloy with Ho addition, which is because of massive eutectic second phases, including T(AlZnMgCu), Al_7Cu_2Fe, Al_8Cu_4Ho and S(Al_2CuMg), distributed along grain boundaries.

2) Optimal single-stage homogenization parameter for the studied alloy is 475 °C/20 h. T phases are completely dissolved back into matrix and no S phase can be observed, with Al_7Cu_2Fe and Al_8Cu_4Ho remaining.

3) Micro-hardness and electrical conductivity are strongly dependent on vibration of T phase, dissolution of which will promote micro-hardness and decrease electrical conductivity. Precipitation of Al_3Ho during 5~20 h of homogenization at 475 °C increase both micro-hardness and electrical conductivity.

4) Homogenization at 470~475 °C/20~25 h is proved to be appropriate by homogenization kinetic analysis.

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Ho添加对Al-Zn-Mg-Cu合金均匀化热处理过程中微观组织和性能演变的影响

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摘　要：通过SEM、OM和DSC，研究添加Ho的Al-Zn-Mg-Cu合金均匀化热处理制度，测试不同均匀化热处理过程中合金的电导率和硬度变化。结果表明，铸态合金中存在4种第二相：T(AlZnMgCu)，Al_7Cu_2Fe，Al_8Cu_4Ho 及S (Al_2CuMg)，第二相导致合金元素分布存在严重微观偏析。合金在475 ℃均匀化热处理20 h后，T相完全回溶基体且未观察到S相，仅剩余Al_7Cu_2Fe和Al_8Cu_4Ho。硬度和电导率随T相的回溶而变化，T相的回溶使得合金硬度升高，电导率降低。同时，在475 ℃均匀化热处理5~20 h过程中，Al_3Ho相析出，这一现象引起硬度和电导率的升高。结合均匀化动力学分析，确定合金适宜的均匀化热处理制度为470~475 ℃/20~25 h。

关键词：加Ho的Al-Zn-Mg-Cu合金；均匀化热处理；硬度和电导率；均匀化动力学分析

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