Rare Metal Materials and Engineering
Volume 50, Issue 1, January 2021
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Rare Metal Materials and Engineering, 2021, 50(1): 0023-0028.

ARTICLE

DICTRA® Simulation of Mg and Mn Micro-segregations in Al-Mg5.0-Mn0.5 Alloy During Homogenization Annealing

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Abstract: Micro-segregation of Mg and Mn in Al-Mg5.0-Mn0.5 alloy during homogenized annealing at 470 °C was evaluated by computational simulation in DICTRA® software, using MOB2 diffusion database and Al-based database. The segregation factor was used to predict the distribution of Mg and Mn at 470 °C annealing temperature for different annealing time. Simulation results were compared with microstructure observations. Results show that after homogenizing at 470 °C for 8.3 h, the segregation factor of Mg is about 0.94, close to 1.0; while, the segregation factor of Mn varies from 0.78 to 1.3. After homogenization annealing at 470 °C for 11.1 h, the segregation factor of Mg is close to 1.0, concentration of Mg is basically uniform, and the range of segregation factor of Mn is almost unchanged. However, almost the same segregation factor of 0.8~1.3 is observed for Mn after annealing at 470 °C for 27.8 h. According to the DICTRA calculation results, after homogenizing at 470 °C for 11.1 h, the micro-segregation of Mg is almost eliminated. While the micro-segregation of Mn cannot be eliminated, even if the annealing holding time extends to 27.8 and 30 h. The simulation can provide a reference for the selection of annealing process of Al-Mg5.0-Mn0.5 alloy.

Key words: Al-5.0Mg-0.5Mn alloy; DICTRA; segregation factor; homogenization annealing

The aluminum-magnesium alloy is one of the lightest engineered metallic materials, and has good properties such as specific strength, specific stiffness, and corrosion resistance, which has been widely used in aerospace, electrical and electronics, transportation, bridge construction, etc. In aluminum-magnesium alloys, when magnesium is the main alloying element or manganese is simultaneously added, work-hardenable alloys with medium to high strength can be achieved and the strength can be greatly enhanced compared with pure aluminum and aluminum-manganese alloys[1-3].

In Al-Mg alloy, Mg is mainly in the solid solution and room-temperature brittle phases of β (Al_3Mg_2 and Al_8Mg_5) are mainly distributed at the dendrites of the as-cast microstructure, usually as a brittle fracture resource. In addition, during casting process, intra-grain and regional segregations easily occur, leading to the elemental segregation and decreasing plasticity and deformation ability of the alloy, thereby adversely affecting mechanical properties of the aluminum alloy [4,5]. Therefore, homogenization annealing of an Al-Mg alloy ingot is very important. The homogenization process maximizes the α (Al) fraction of the matrix, increases solubility of Mg and Mn in the matrix and strongly prevents segregation of these elements. The homogenization process leads to a uniform chemical composition for the ingot, improves morphology and distribution of the second phase, increases the plasticity,

Received date: May 25, 2020
Foundation item: National Natural Science Foundation of China (51661004); Innovation Drive Development Foundation of Guangxi (GKAA17202011, GKZ14122001-3); Guangxi Natural Science Foundation (2018GXNSFAA050048, 2017GXNSFAA198271); Guangxi Key Laboratory Project for Processing Non-ferrous Metals and Characteristic Materials (GXYSSF1809)
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of the second phase, increases the plasticity, and modifies the process properties.

The annealing temperature and holding time are fundamental parameters and have been given extensive attentions during the homogenization of aluminum-magnesium alloy [6-8]. The non-uniform distribution of precipitated phase containing Mg and Mn in A5083 aluminum alloy after casting was reported by Sheppard[9]. The non-uniformity is closely related to the solute distribution pattern of the as-cast alloy and the distributions of Mg and Mn can be greatly uniform after appropriate homogenization holding time. Birol et al [10,11] reported that the yield strength and tensile strength of aluminum alloy increase with the increase of homogenization temperature, due to the more uniform diffusion of magnesium and the precipitation of manganese as a dispersion phase at higher homogenization temperature, which greatly improves the strength of the aluminum alloy. Li et al[12] further reported that the volume fraction of phase containing Mn in 3003 aluminum alloy is dependent on the concentration of Mn in solid solution during homogenization, and prolonging the holding time is conducive to the dispersion and precipitation of phase containing Mn.

Although researches on the diffusion or segregation of Mg and Mn during the homogenization of aluminum alloys have been carried out in large quantities, studies combining experimental research and simulation to characterize the distribution of elements in aluminum alloy are still few. DICTRA is flexible software for simulation of diffusion controlled transformations in multicomponent alloys. It is closely linked with the Thermo-Calc software, which provides all necessary thermodynamic calculations [13,14]. In this research, DICTRA was used to fully understand the segregation of Al-Mg5.0-Mn0.5 aluminum alloy during solidification and the effect of diffusion annealing on reducing segregation. SCHEIL model is used to study the re-distribution rule of elements in the process of non-equilibrium solidification of Al-Mg5.0-Mn0.5 aluminum alloy. The segregation factor of alloying elements of Mg and Mn during solidification and following diffusion annealing of the aluminum alloy was calculated by DICTRA to survey the effect of diffusion annealing time on the micro-segregation of Mg and Mn. To verify the emulation, the mapping of alloying elements of Mg and Mn was characterized by scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS).

1 Experiment

The main components of the examined alloy were 5.0wt% Mg and 0.5wt% Mn, and the balance Al. Industrially pure aluminum, magnesium, and Al-10Mn master alloy were used as raw materials for melting. Before melting, the dried pure aluminum and the master alloy were placed in a graphite crucible at a melting temperature of 780 °C until the metal was soft-crushed and then covered with a coating agent (10.8% calcium fluoride+72.8% magnesium chloride+16.4% chlorinated calcium). However, in the melting process, the content of Mg was high and it was easy to be burned. Pure magnesium was added when the temperature dropped to 700 °C, and then the covering agent was added to reduce the loss of magnesium. Thereafter, hexachloroethane refined at 720 °C was added, stood for 20 min, and poured into a pre-heated steel mold to obtain a square sample with the casting volume of 160 mm×100 mm×12 mm. For the experiments, six sets of massive samples with the dimensions of 19.5 mm×6 mm×4.5 mm were taken from the center of the ingot at the same height. The technological parameters for homogenization annealing were kept at 470 °C for 0, 2.7, 8.3, 11.1, 27.8, and 30 h followed by air-cooling. After polishing, surface of the sample was etched for 10~15 s with Keller's etchant (95 mL water, 2.5 mL HNO_3, 1.5 mL HCl, and 1.0 mL HF) and the sample involving surface corrosives and etching solution was rinsed with warm water. Then, the samples were dried, the microstructure was observed by a Leica microscope, and morphology and types of various compounds were identified by a SUS-8220 field emission scanning electron microscope (FESEM) operated at a voltage of 15.0 kV and equipped with an Oxford EDS.

2 Results and Discussion

2.1 Theoretical calculation of equilibrium solidification microstructure

DICTRA simulates the dynamics by combining a multicomponent diffusion equation with Thermo-Calc software. The main parameters of thermodynamics come from Thermo-Calc, and the parameters about atomic mobility are stored in MOB database. The diffusion coefficients related with temperature and solubility can be calculated by atomic mobility and related thermodynamic parameters [15,16]. The diffusion equations are follows:

$$J_k = \sum_{j=1}^{n-1} D_{kj}^{n} \frac{\partial c_j}{\partial z} \quad (1)$$

where J_k is the diffusion coefficient of element k; D_{kj}^{n} is the $(n-1)\times(n-1)$ diffusion coefficient matrix; $\frac{\partial c_j}{\partial z}$ is the solubility gradient of element j.

It is assumed that the system is 3 element system (5.0wt% Mg, 0.5wt% Mn, and the balance Al) and the total length of the system is 0.1 mm. By the above-mentioned dynamic simulation calculation, the relationship between the solidification temperature and solid phase fraction of Al-5.0Mg-0.5Mn aluminum alloy is calculated (Fig.1), and the changes of the solid-liquid phase interface position with solidification time are also obtained (Fig.2). Fig.1 and Fig.2 show that solidification of the examined aluminum alloy

begins when it is cooled to 636.5 °C. When the temperature drops to 339 °C, the solidification process is basically completed. The aluminum melting requires 381 s from the casting temperature to completion of solidification. In addition, since the software calculation is under the conditions of thermodynamic equilibrium, the actual solidification temperature has to be greater than the calculated value.

2.2 Theoretical calculation of elemental segregation

SCHEIL model and Al-based database of Thermo-Calc software were used to simulate the solidification of Al-5.0Mg-0.5Mn alloy. It is assumed that the total length of the system is 0.1 mm, and the aluminum melt is cooled down to 339 °C at the cooling rate of 0.2 °C/s, then increased to 470 °C and held for different time. In order to calculate conveniently, liquid phase component of solidification interface is regarded as the inter-dendritic composition, taken before solidification at 636.5 °C (Fig.1.). Fig.3 shows the concentration distributions of Mg and Mn elements just after solidification to different positions of solid-liquid interface or annealing for different time. The distribution of Mg atom during the solidification is extremely inhomogeneous.

When the solidification time is 100 s, the content of Mg in the solidified liquid-solid interface at the beginning is less than 2.0wt%; while, at a distance of 3.9×10^{-5} m from the interface, where the initial molten aluminum is solidified, the content of Mg reaches 7.8wt%. When the solidification time is 381 s, the solidification is basically completed and the solubility of Mg is still not uniform. When the diffusion time reaches 100 000 s after solidification, the Mg atoms are uniformly dispersed and approach the theoretical content of 5.0wt%. Both Mn and Mg atoms are involved in the substitutional solid solution atoms. However, the diffusion rate of Mn in the solid phase is much lower than that of Mg atoms. Therefore, the required time of Mn for homogenization is longer than that of Mg atoms. From Fig.3b, even if the solidification and diffusion time reaches 100 000 s, the distribution of Mn is still not uniform and the segregation of Mn component is not eliminated.

In order to further analyze the distribution of Mg and Mn at 470 °C for different annealing time, the segregation factor after diffusion annealing was quoted [17]. The segregation factor (SM) is defined as

$$SM = \omega M(\text{partial}) / \omega M(\text{average}) \quad (2)$$

where M represents certain element; $\omega M(\text{partial})$ represents local content of element M; $\omega M(\text{average})$ represents the theoretical content of element M, which is 5.0% for Mg and 0.5% for Mn.

Fig.4 shows the segregation of Mg and Mn elements at different positions of solid-liquid interface at different annealing time from 381 s to 27.8 h. When the solidification

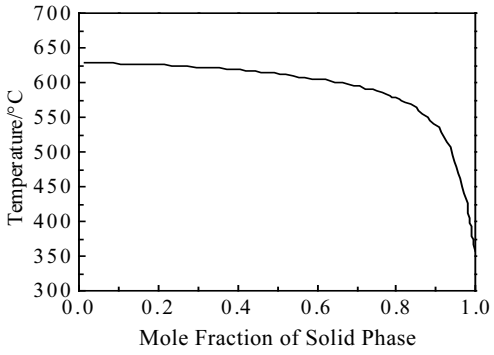

Fig.1 Relationship between solidification temperature and solid phase fraction for Al-5.0Mg-0.5Mn alloy

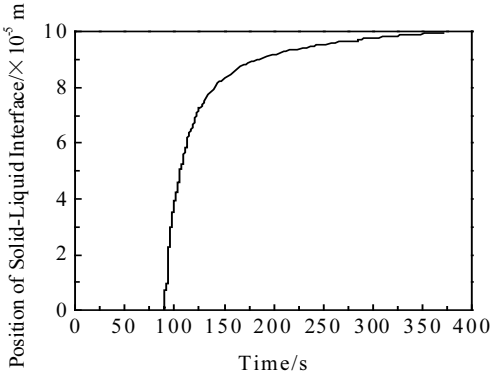

Fig.2 Change of the position of liquid-solid interface with solidification time

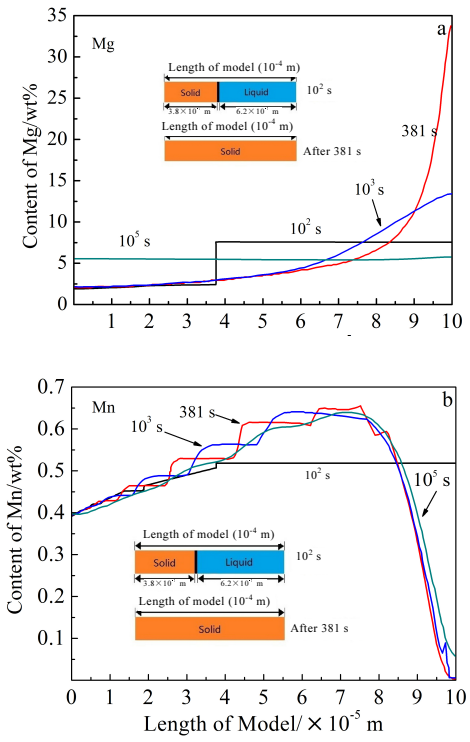

Fig.3 Concentration distribution of Mg (a) and Mn (b) in Al-5.0Mg-0.5Mn alloy after solidification and holding at 470 °C for different time

is just completed (381 s), the segregation factor of Mg varies from 0.4 (at start position of the system) to 2.5 (at terminated position), and the element-depleted region appears; Mn varies from 0.78 (at start position) to 1.3 (at the position of 7.5×10^{-5} m). After completing solidification, the segregation factors of Mg and Mn show different changes in the subsequent diffusion annealing process. The maximum segregation factor of Mg is about 1.4 after 2.7 h annealing at 470 °C; whereas, the segregation factor of Mn ranges from 0.78 to 1.3 and a certain amount of component segregation is observed. After annealing for 8.3 h, the segregation factor of Mg is about 0.94 (at start position), close to 1.0; while the segregation factor of Mn alters from 0.78 to 1.3. After annealing for 11.1 h, the segregation factor of Mg is still close to 1.0, and the concentration of Mg is basically uniform; while, the range of segregation factor for Mn is mainly unchanged. Even after annealing for 27.8 h, the segregation factor of Mn varies from 0.8 (at start position) to 1.3 (at the position of 7.5×10^{-5} m), with only minor changes. As shown in Fig.4b, the segregation factor curves of different annealing time are basically coincident, and the segregation of Mn is still unavoidable. The main factors affecting the microscopic segregation are cooling rate, solute element distribution coefficient and diffusion coefficient. The simulation process assumes that the cooling rate and the solute element distribution coefficient are constant. Considering that the diffusion of Mn in Al matrix is difficult and the diffusion coefficient is low, according to the literature, the diffusion coefficient of Mn in Al matrix at 470 °C is nearly 1.0×10^{-16} $m^2\cdot s^{-1}$ [18] and the diffusion coefficient of Mg in Al matrix at 450 °C is nearly 6.24×10^{-15} $m^2\cdot s^{-1}$[19]. The total length of the system (10^{-4} m) is too long for Mn to diffuse. The peak value appears at the position of 7.5×10^{-5} m, not at the terminated position of the system. Therefore, segregation factor of Mn is meaningless between 7.5×10^{-5} m and 10×10^{-5} m in the curve (Fig.4b). Therefore, the microscopic segregation of Mg during casting can be eliminated by the diffusion annealing process. However, the microscopic segregation of Mn cannot be eliminated even after prolonging the diffusion annealing.

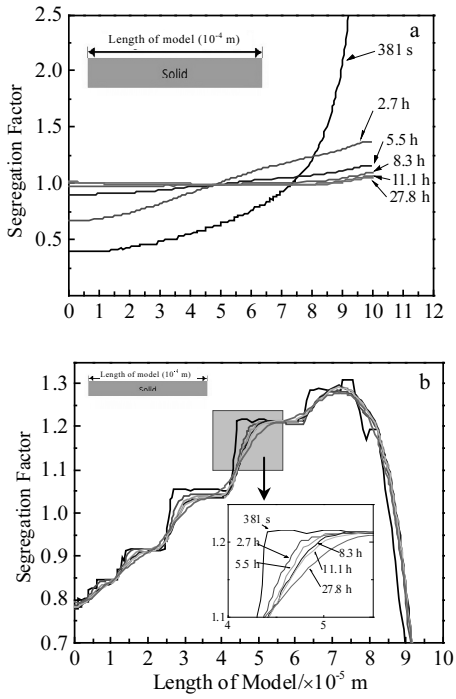

Fig.4 Segregation factors of Mg (a) and Mn (b) in Al-5.0Mg-0.5Mn aluminum alloy after different annealing time

2.3 Effect of annealing time on the homogenized microstructure of Al-5.0Mg-0.5Mn alloy

The element distribution and evolution of the precipitation of Mg and Mn in Al-5.0Mg-0.5Mn alloy annealed at 470 °C for different time are shown in Fig.5. The unbalanced phase forms in the as-cast structure without homogenization due to the segregation of Mg and Mn. The phases are mainly spherical, chain-type and strip, as shown in Fig.5. According to the mapping of Al, Mg and Mn and relative literatures[20-22], the above phases should be Al-Mg and Al-Mn phases. When the annealing time is 2.7 h (Fig.5b), the distribution of Mn is long strip, almost unchanged compared with as-cast microstructure (Fig.5a). Furthermore, the distribution of Mn gradually becomes chain-type or short strip, when the annealing time increases to 8.3 and 11.1 h (Fig.5c and 5d). With the increase of annealing time, Mn partially diffuses into the matrix around the origin long strip phases and the degree of segregation is reduced. However, according to the mapping of the long strip phase, the segregation of Mn does not substantially change when the annealing time increases to 27.8 and 30 h. Therefore the diffusion of the alloying element Mn is relatively difficult even if prolonging the holding time to 30 h, which is in accordance with the foregoing simulation, as shown in Fig.3b and Fig.4b. Fig.6 shows morphologies of spherical phases and Table 1 shows the results of EDS analysis. Noticeably, the spherical phases are Al-Mg phase. The homogenization annealing at different holding time affects the diffusion of alloying element of Mg. When the holding time is longer than 8.3 h at 470 °C, a large amount of Mg is dissolved into the Al matrix due to the sufficient diffusion of Mg, and then dispersed particles containing Mg form which are mainly distributed in matrix (Fig.5b and 5c). With prolonging the annealing holding time to 11.1, 27.8 and 30 h (Fig.5d and 5f)), the shape of the spherical phases is hardly changed to ensure minimum surface energy under high-temperature thermal activation, but they are distributed continuously along the boundaries. Mg reaches a more uniform level, which is basically consistent with the previous simulation results.

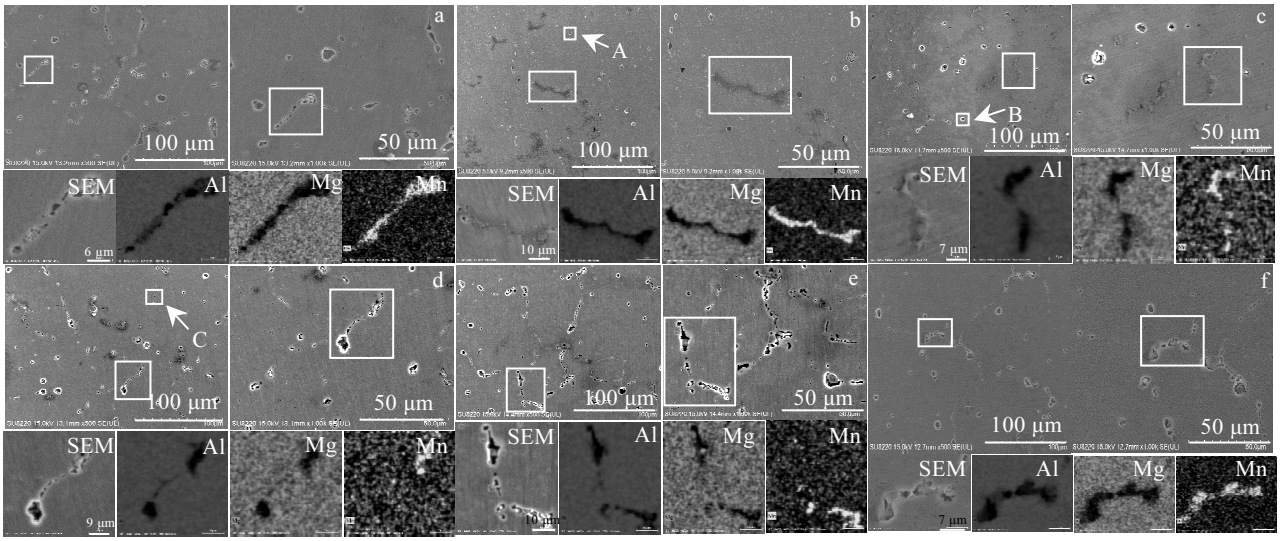

Fig.5 Microstructures and EDS mapping of various elements in Al-5.0Mg-0.5Mn alloy annealed at 470 °C for different time: (a) 0 h, (b) 2.7 h, (c) 8.3 h, (d) 11.1 h, (e) 27.8 h, and (f) 30 h

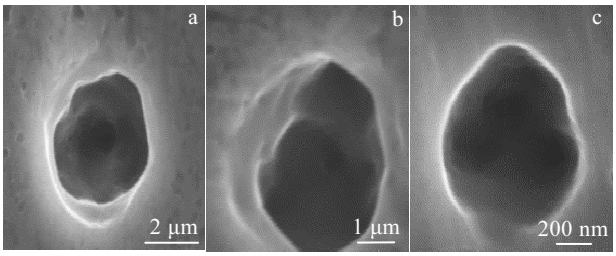

Fig.6 Local enlargement of spherical phases in Fig.5 after annealing for different time: (a) region A in Fig.5b, 2.7 h; (b) region B in Fig.5c, 8.3 h; (c) region C in Fig.5d, 11.1 h

Table 1 EDS analysis results of spherical phases in Fig.5

Spherical phase	wt%			at%		
	Mg	Mn	Al	Mg	Mn	Al
Region A -2.7 h	4.64	0.04	95.15	5.15	0.02	94.59
Region B -8.3 h	5.73	0.32	93.54	6.31	0.16	92.85
Region C-11.1 h	5.90	0.14	93.50	6.49	0.07	92.68

3 Conclusions

1) The micro-segregation of Mg and Mn during the non-equilibrium solidification of Al-5.0Mg-0.5Mn alloy is analyzed by DICTRA software. Mg-induced microsegregation can be eliminated by homogenization annealing at 470 °C with the annealing time of at least 11.1 h. However, Mn-induced micro-segregation cannot be eliminated by homogenization annealing in a short time.

2) The segregation factor is used to predict the distribution of Mg and Mn at 470 °C annealing temperature for different annealing time. After annealing for 8.3 h, the segregation factor of Mg is about 0.94, close to 1.0; while, the segregation factor of Mn varies from 0.78 to 1.3. After annealing for 11.1 h, the segregation factor of Mg is still close to 1.0, and concentration of Mg is basically uniform. However, the range of segregation factor of Mn is almost unchanged. After annealing for 27.8 h, the segregation factor of Mn shows slight changes from 0.8 to 1.3.

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Al-Mg5.0-Mn0.5 铝合金均匀化退火过程中 Mg、Mn 元素显微偏析的 DICTRA 模拟

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摘　要：基于DICTRA动力学软件的MOB2和Al基数据库，对 Al-Mg5.0-Mn0.5铝合金在470 ℃不同时间均匀化退火过程中Mg和Mn元素的显微偏析进行了模拟计算，并使用偏析因子来评价470 ℃不同时间均匀化退火过程中Mg和Mn元素的偏析程度。结果表明：在470 ℃不同退火时间后，Mg和Mn元素的偏析因子有如下变化：退火8.3 h后，Mg的偏析因子约为0.94，接近1.0，而Mn的偏析因子在0.78~1.3之间；在退火11.1 h后，Mg的偏析因子约为1.0，表示Mg的浓度基本扩散均匀，而Mn的偏析因子依然在0.78~1.3之间；退火27.8 h以后，Mn的偏析因子为0.8~1.3，与11.1 h相比只有微小的变化。根据计算结果，470 ℃下退火保温时间至少为11.1 h，Mg引起的微观偏析可通过均匀化退火消除；而Mn引起的微观偏析即使是470 ℃下退火保温时间为27.8~30 h仍然不能消除。通过对470 ℃不同均匀化退火时间合金元素的面分布对上述模拟结果进行了验证。本研究可为Al-Mg5.0-Mn0.5铝合金退火工艺的选择提供依据。

关键词：Al-5.0Mg-0.5Mn 合金；DICTRA；偏析因子；均质退火

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