J. Shanghai Jiaotong Univ. (Sci.), 2012, 17(3): 286-290
DOI: 10.1007/s12204-012-1270-4

Thermodynamic Analyse on Equilibrium Precipitation Phases and Composition Design of Al-Zn-Mg-Cu Alloys

*YU Jing-jing** (于晶晶), *LI Xiao-mei* (李晓梅), *YU Xin-quan* (余新泉)
(School of Materials Science and Engineering, Southeast University, Nanjing 211189, China)

Abstract: The solidification paths of Al-Zn-Mg-Cu alloys and its precipitation behavior are analyzed using software package JMatPro 6.0 for material property simulation of Al-base alloys. The microstructures of the experimental alloys are analyzed; the experimental results of microstructural analysis are in agreement with the thermodynamic prediction. Through orthogonal experimental method, this paper designs the composition of Al-Zn-Mg-Cu alloys by studying the variation of η ($MgZn_2$) phase, S (Al_2CuMg) phase, T (AlZnMgCu) phase amount and precipitation temperatures with different Zn, Mg and Cu contents. It is found that with the optimum mass fraction of Zn of 6.7%, Mg of 2.2%—2.5% and Cu of 1.6%—2.0%, the mass fraction of η phase can be up to 8.7%—9.22% and that of S phase and T phase can be lower than 0.5%.
Key words: Al-Zn-Mg-Cu alloys, thermodynamic calculation, composition design
CLC number: TG 135 **Document code:** A

0 Introduction

Possessing high strength and toughness, 7xxx series aluminum alloy is a vital structural material, which can be applied widely in the aviation and aerospace fields. In recent years, many internationally recognized scholars have done much research on the composition design and the relationship between the microstructure of the precipitation phases and the properties of the material[1-2]. By controlling the content of the main phases such as η ($MgZn_2$) phase, S (Al_2CuMg) phase and T (AlZnMgCu) phase, the strength and stress corrosion resistance of Al-Zn-Mg-Cu alloys can be greatly improved[3-4].

In resent years, the use of thermodynamic modelling via the multi-platform software has been extensively applied to the complex alloys of many types, including Al-based alloys. Many software packages were developed for multicomponent phase equilibrium calculation in the past few decades, such as Thermo-Cal, Pandat and JMatPro. These software packages were developed based on the CALPHAD approach, which can be used to calculate the phase equilibrium and model the properties of multicomponent alloys by incorporating various theoretical models and relevant thermodynamic database[5-6]. In this paper, we use the CALPHAD method and JMatPro software to calculate the solidification paths of Al-Zn-Mg-Cu alloys and optimize the alloy composition of Al-Zn-Mg-Cu alloys by using the orthogonal experimental design. Moreover, the simulations are compared with the microstructural analysis to verify the reliability of the thermodynamic calculations.

1 Experimental Details

In this study, within the composition window of 7xxx series aluminum alloy, Zn mass fraction is set as 5.1%, 5.5%, 5.9%, 6.3% and 6.7% respectively, Mg mass fraction 1.9%, 2.2%, 2.5%, 2.7% and 2.9% respectively, Cu mass fraction 1.2%, 1.6%, 2.0%, 2.3% and 2.6% respectively. Other mass fraction of minor alloying elements Fe, Si and Zr is set as 0.1%, while Ti and Mn as 0.05%. Altogether 25 alloys are designed by using the orthogonal experimental method, as shown in Table 1. Incorporating the Scheil model, the JMatPro program is used to calculate the amount of η, S and T phases without considering the solid state diffusion process.

To verify the accuracy of the calculated results by thermodynamic models, we observe and analyze the solidification structure of 7150 alloy, which has the chemical composition as listed in Table 2. The measurement of this alloy is performed using differential scanning calorimeter (DSC) (DSC-Q10, TA instruments) at a constant heating rate of 10 ℃/min. Phase analysis is investigated using X-ray diffractometer (D8 Discover type, Bruker-AXS) operating at 35 kV and 20 mA. Microstructure observation is carried out by a scanning electron microscope (SEM) (XL30, Philips) fitted with an energy dispersive X-ray spectroscopy (EDS) analysis

Received date: 2012-03-30
∗**E-mail:** yjjseu@gmail.com

system to measure the chemical compositions of various particles.

Table 1 Alloy composition design

No.	w/%		
	Zn	Mg	Cu
1#	5.1	1.9	1.2
2#	5.1	2.2	1.6
3#	5.1	2.5	2.0
4#	5.1	2.7	2.3
5#	5.1	2.9	2.6
6#	5.5	1.9	1.6
7#	5.5	2.2	2.0
8#	5.5	2.5	2.3
9#	5.5	2.7	2.6
10#	5.5	2.9	1.2
11#	5.9	1.9	2.0
12#	5.9	2.2	2.3
13#	5.9	2.5	2.6
14#	5.9	2.7	1.2
15#	5.9	2.9	1.6
16#	6.3	1.6	2.3
17#	6.3	2.2	2.6
18#	6.3	2.5	1.2
19#	6.3	2.7	1.6
20#	6.3	2.9	2.0
21#	6.7	1.9	2.6
22#	6.7	2.2	1.2
23#	6.7	2.5	1.6
24#	6.7	2.7	2.0
25#	6.7	2.9	2.3

Table 2 Composition of 7150 Al alloy

Composition	w/%	Composition	w/%
Zn	6.72	Si	0.04
Mg	2.38	Ti	0.04
Cu	1.84	Mn	0.02
Zr	0.09	Al	Bal.
Fe	0.12		

2 Results and Discussion

2.1 Thermodynamic Calculation of Solidification Path of 7150 Alloy

Using the Scheil model, the solidification path of 7150 alloy is calculated by JMatPro software, and the curve of solid fraction (mass) changing with temperature is shown in Fig. 1. It is exhibited that the liquidus temperature of 7150 alloy is 633 ℃, the solidus temperature is 470 ℃, and the transition temperature of lower melting point eutectic phase is 475 ℃. With the decrease of temperature, Al_3Zr, Al_3Fe, Mg_2Si, Al_7Cu_2Fe, $MgZn_2$ and Al_2CuMg phases are gradually generated in the casting solidification processes.

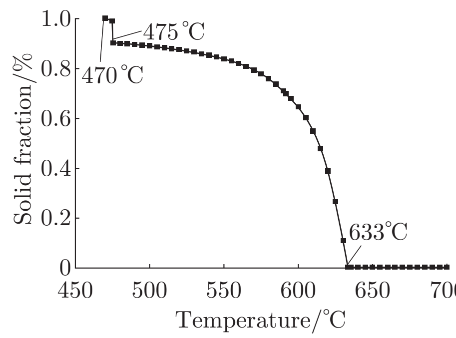
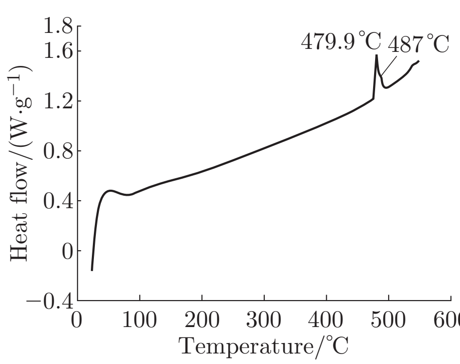
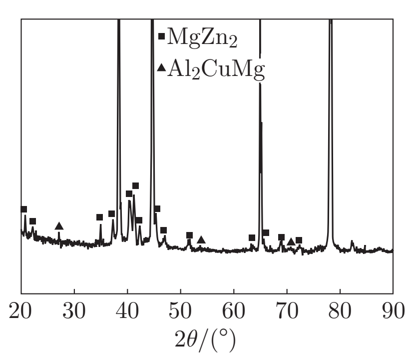


Fig. 1 Solidification path of 7150 alloy by thermodynamic calculation

Figure 2(a) shows the DSC curve of 7150 alloy simultaneously heated at 10 ℃/min to 550 ℃. There is an obvious endothermic peak at 479.9 ℃, which corresponds to the dissolution of low melting point eutectic phase. The result is consistent with the thermodynamic calculation. The phase analysis results of the alloy indicate that $MgZn_2$ and Al_2CuMg phases are the main crystalline phases in as-cast structure, as shown in Fig. 2(b). Because the content of Fe and Si is very low in the alloy, the diffraction peaks of Al_3Fe, Al_7Cu_2Fe and Mg_2Si phases are not detected in the X-ray diffraction (XRD) pattern. The experimental results are close to the thermodynamic calculation which can prove the accuracy of the thermodynamics.



(a) DSC curve



(b) XRD pattern

Fig. 2 Experimental analyse of 7150 alloy (as-cast)

2.2 Microstructural Analysis of 7150 Alloy

To analyze the precipitation behavior of 7150 alloy in cast condition after rapid solidification, the experiment is carried out using the scanning electron microscope and the result is shown in Fig. 3. It is exhibited that there are a lot of non-equilibrium eutectic structures in the interdendritic region. EDS results indicate that the eutectic phases consist of η phase, S phase and coarse Al_7Cu_2Fe phase, and the overlap of phases η and S exists among the network structures. However, a certain amount of Al and Cu elements can be tested in η phase with a wide range of composition as the solid solution of the alloying elements. Because of the segregation of impurity element Si, a few of black Mg_2Si phases can be formed in the alloy, which is indicated by microscopic analysis, as shown in Fig. 3(b). In general, the microstructural observation is in accordance with the prediction in the modelling processes for this type of alloys.

2.3 Effects of Alloying Elements on Main Precipitated Phase

The result of orthogonal experiments of 25 alloys for the amount of η phase at room temperature is listed. In Table 3, K_1—K_5 are the average values of η phase amount under the levels 1—5; $R = K_{max} - K_{min}$, K_{max} is the maximum value out of the 5 values, and K_{min} is the minimum value out of the 5 values. A big R value indicates a significant influence of the factor on the result. It is obvious that the amount of η phase can be significantly influenced by Zn content and reach the maximum when Zn mass fraction is about 6.7%. The amount of η phase changing with temperature with different Zn, Mg and Cu contents is shown in Fig. 4. When Zn mass fraction increases from 5.1% to 6.7%, the amount of η phase precipitates at room temperature increases from 6.8% to 9.2%. When more Zn is available in the alloy, more η phase tends to precipitate, while the decrease in the content of Mg results in more precipitation of η phase at equilibrium state. Previous research indicates that a high Zn/Mg ratio is beneficial to the precipitation of η phase[7-8]. The change of Cu contents does not exhibit marked effects on the amount of η phase, which implies that Cu has less significant effect on the formation of η phase.

Table 3 Results of orthogonal experimental analysis for η phase at room temperature

Item	w/%		
	Zn	Mg	Cu
K_1	6.792	8.040	7.264
K_2	7.162	8.000	7.776
K_3	7.310	7.774	7.894
K_4	8.402	7.598	7.918
K_5	9.112	7.366	7.926
R	2.320	0.674	0.662

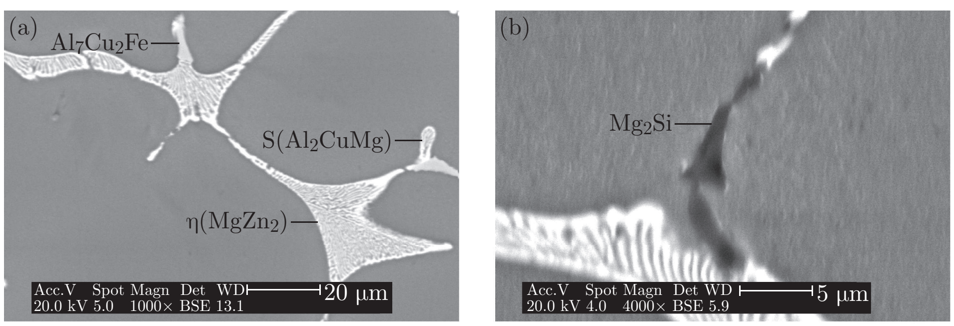
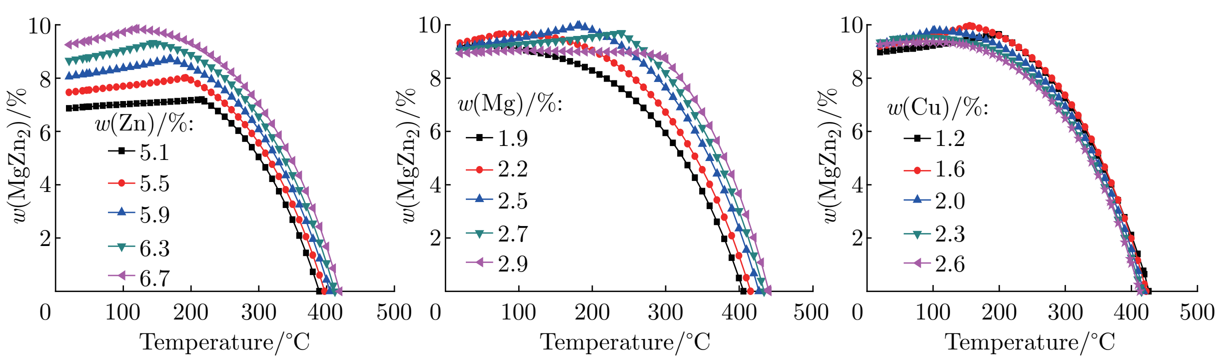


Fig. 3 Backscattered electron image of the microstructure in as-cast 7150 alloy



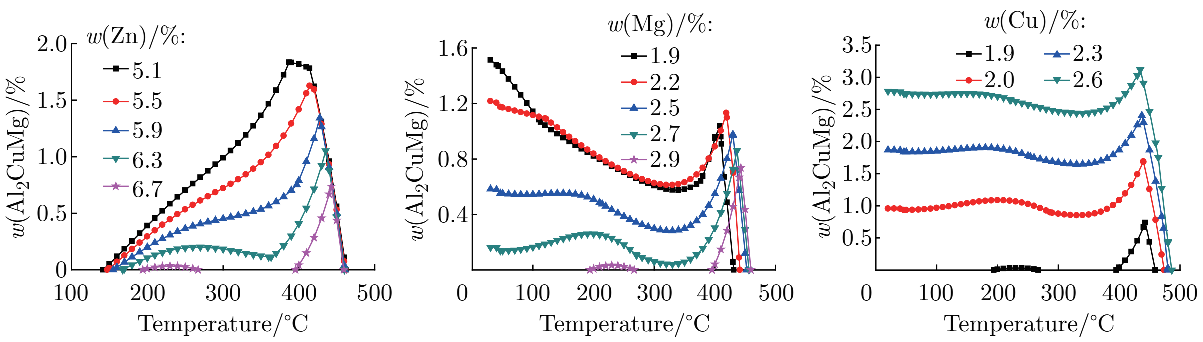
(a) $w(Mg) = 2.3\%$, $w(Cu) = 1.9\%$ (b) $w(Zn) = 6.7\%$, $w(Cu) = 1.9\%$ (c) $w(Zn) = 6.7\%$, $w(Mg) = 2.3\%$

Fig. 4 The amount of η phase changing with temperature

In order to evaluate the effects of alloying elements on S phase and T phase, which are thought to be detrimental to the toughness of the alloy, the statistics of orthogonal experiment analysis of S phase and T phase are listed in Tables 4 and 5. It is revealed that the alloy with $w(\mathrm{Cu}) = 2.6\%$ has more S phase and the amount of S phase slightly increases with the increase of Cu content, whereas Zn and Mg variations have less effects on S phase. Because T quaternary phase is formed by continuously mutual solution of $Al_2Mg_3Zn_3$ and Al_6CuMg_4 phase, it cannot be described as one or more formulas and the range of generating temperature is very wide. The dominant factor influencing the amount of T phase is Mg content and the formation of T phase favors low Cu and high Mg contents. Figure 5 shows plots of the amount of S phase changing with temperature with different Zn, Mg and Cu contents. As illustrated in Fig. 5(a), S phase is present at 460 °C, the amount increases abruptly at high temperature range and then gradually decreases as temperature goes down. There is no S phase at room temperature with different Zn contents with the composition of $w(\mathrm{Mg}) = 2.3\%$ and $w(\mathrm{Cu}) = 1.6\%$. When Mg content increases gradually, the start temperature of S phase increases, while the amount of S phase at room temperature gradually decreases (Fig. 5(b)). From Fig. 5(c), it is revealed that controlling the level of Cu content in the alloy can be an effective method to restrain the precipitation of S phase. T phase changes with temperature, as shown in Fig. 6. The variation of Mg content significantly influences the amount of T phase, and the range of temperature where T phase exists is wider with the increase of Mg addition. Zn and Cu elements have less markedly effects on the precipitation of T phase, but the increase of Zn and Cu contents is beneficial for controlling the transformation from η phase to T phase at low temperature during the aging process.

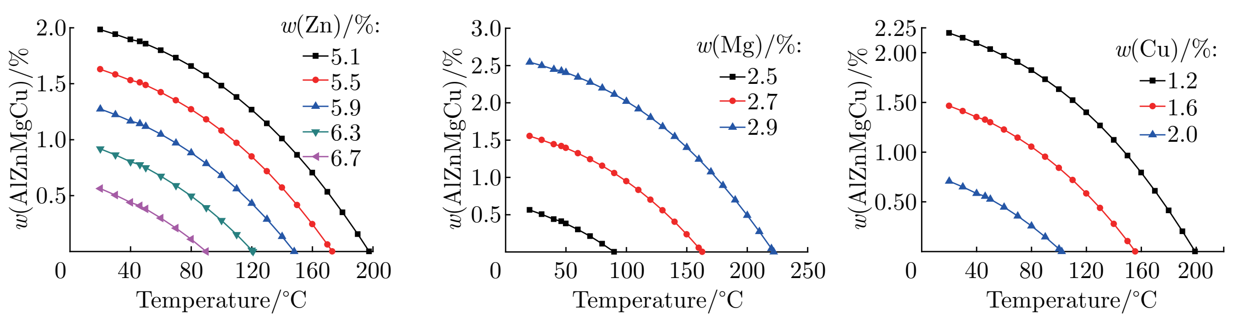
Table 4 Results of orthogonal experimental analysis for S phase at room temperature

Item	w/%		
	Zn	Mg	Cu
K_1	1.604	1.740	0.100
K_2	1.958	2.106	0.710
K_3	1.920	1.678	1.820
K_4	1.378	1.352	2.374
K_5	1.100	1.084	2.956
R	0.858	1.022	2.856



(a) $w(\mathrm{Mg})=2.3\%$, $w(\mathrm{Cu})=1.6\%$ (b) $w(\mathrm{Zn})=6.7\%$, $w(\mathrm{Cu})=1.6\%$ (c) $w(\mathrm{Zn})=6.7\%$, $w(\mathrm{Mg})=2.9\%$

Fig. 5 The amount of S phase changing with temperature



(a) $w(\mathrm{Mg})=2.5\%$, $w(\mathrm{Cu})=2.6\%$ (b) $w(\mathrm{Zn})=6.7\%$, $w(\mathrm{Cu})=2.2\%$ (c) $w(\mathrm{Zn})=6.7\%$, $w(\mathrm{Mg})=2.6\%$

Fig. 6 The amount of T phase changing with temperature

Table 5 Results of orthogonal experimental analysis for T phase at room temperature

Item	w/%		
	Zn	Mg	Cu
K_1	2.936	0.442	3.556
K_2	2.542	1.196	2.734
K_3	2.414	2.450	2.226
K_4	2.264	3.508	1.894
K_5	1.880	4.440	1.626
R	1.056	3.998	1.930

3 Conclusion

The solidification path and equilibrium phases of 7150 alloys are investigated using the JMatPro thermodynamic calculation software. It shows good agreement with the DSC and XRD experimental results. The orthogonal experimental design has been applied to the optimization of alloy composition of Al-Zn-Mg-Cu alloys by studying the effects of Zn, Mg and Cu contents on the precipitation of η, S, and T phases. It is found that with w(Zn) = 6.7%, w(Mg)= 2.2%—2.5%, w(Cu) = 1.6%—2.0%, the amount of η phase can be up to 8.7%—9.2% and that of S phase and T phase can be lower than 0.5% in the 7xxx series aluminum alloys.

References

[1] Starink M J, Wang S C. A model for the yield strength of overaged Al-Zn-Mg-Cu alloys [J]. *Acta Materialia*, 2003, **51**(17): 5131-5150.

[2] Starink M J, Li X M. A model for the electrical conductivity of peak aged and overaged Al-Zn-Mg-Cu alloys [J]. *Metallurgical and Materials Transactions A*, 2003, **34A**(4): 899-911.

[3] Li X M, Starink M J. Identification and analysis of intermetallic phases in overaged Zr-containing and Cr-containing Al-Zn-Mg-Cu alloys [J]. *Journal of Alloys and Compounds*, 2011, **509**(2): 471-476.

[4] Guo Z, Saunders N, Miodownik A P, et al. Modelling of materials properties and behaviour critical to casting simulation [J]. *Materials Science and Engineering A*, 2005, **413-414**: 465-469.

[5] Saunders N, Guo Z, Li X, et al. Using JMatPro to model materials properties and behavior [J]. *Journal of the Minerals, Metals and Materials Society*, 2003, **55**(12): 60-65.

[6] Saunders N, Miodownik A P. CALPHAD—calculation of phase diagrams: A comprehensive guide, pergamon materials series [M]. Oxford: Elsevier, 1998.

[7] Park J K, Ardell A J. Precipitate microstructure of peak-aged 7075 Al [J]. *Scripta Metallurgical*, 1988, **22**(7): 1115-1119.

[8] Yu J J, Li X M. Modelling of the precipitated phases and properties of Al-Zn-Mg-Cu alloys [J]. *Journal of Phase Equilibria and Diffusion*, 2011, **32**(4): 350-360.