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ARTICLE

Determination of Thermo-physical Properties of 7XXX Aluminum Alloys by Equivalency Method

Huang Yuanchun[1,2], Zhao Jianye[1], Hu Jiawei[1], Xiao Zhengbing[1,2], Huang Shita[3]

[1] Light Alloy Research Institute, Central South University, Changsha 410012, China; [2] State Key Laboratory of High Performance Complex Manufacturing, Central South University, Changsha 410083, China; [3] Department of Materials, Antai New Energy Technology Co., Ltd, Zhangzhou 363999, China

Abstract: Based on the equivalency method (the impact of all alloying elements on the thermo-physical properties can be expressed through the equivalent impact of a reference element), Zn was regarded as a reference element, and the parameters required for equivalency calculation were obtained through the numerical fitting of the Al-rich liquidus line in the binary phase diagram of 7XXX series aluminum alloys. The sum of the equivalent concentration of other elements and the actual concentration of the reference element was used to calculate the liquidus temperature and latent heat of materials. The calculation results are in good agreement with the measured data by differential scanning calorimetric (DSC) apparatus. Compared with Jmatpro software, the equivalency method shows better accuracy.

Key words: 7XXX aluminum alloys; zinc equivalency; thermo-physical properties; DSC; Jmatpro

7XXX (Al-Zn-Mg-Cu) aluminum alloys have ultra-high strength, good toughness, and fine corrosion resistance[1,2], therefore playing an indispensable role in the aerospace industry as one of the main structural materials. The element composition of these alloys has a significant influence on their structure and thermo-physical and mechanical properties. The effects of some essential alloying elements are presented as follows: Zn and Mg are the dominant strengthening elements, which can greatly improve the strength and hardness but reduce the plasticity, corrosion resistance, and fracture toughness of alloys; Cu can improve not only the tensile strength, plasticity, and fatigue strength, but also the stress corrosion resistance within a certain range; a small amount of transition elements Mn and Cr can improve the structure and properties of alloys; the impurity elements Fe and Si lead to the premature development of cracks, which decreases the plasticity and fracture toughness; the trace elements, such as Zr, Ti, and B, can refine the grains and improve the hardenability, weldability, and stress corrosion resistance. It is well known that there is a synergy between chemical composition and various thermo-physical and structural properties[3-8]. However, due to the high alloying degree of 7XXX aluminum alloys, the synergistic effect becomes complex. Therefore, a simple approach to control the quality and optimize the properties is necessary.

In response to the requirements for an integrated quality control program, an analysis method based on the equivalency was proposed in this research. The equivalency method has been applied to many kinds of alloys, so its feasibility and effectiveness have also been proved. For ferroalloys, there are various carbon equivalency (CE) formulae to express the weldability[9-11]. The conventional CE formulae are widely used to determine the weld metal properties and practicability of welding without expensive and time-consuming test procedures[12]. In addition, the concept of zinc equivalency was proposed for copper alloys. The calculation formulae of Zn content in the polybasic brass have been discussed from different perspectives. Xia et al[13] found that the current calculation formula is not accurate, while Zheng et al[14] believed that the zinc equivalency coefficients for elements and formula are in an integrated system. Yang et al[15] established the relationship between the structure and chip-

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Corresponding author: Xiao Zhengbing, Ph. D., State Key Laboratory of High Performance Complex Manufacturing, Central South University, Changsha 410083, P. R. China, E-mail: xiaozb@csu.edu.cn

breaking performance by adjusting the zinc equivalent of silicon brass. Yang et al[16] developed a silicon brass alloy with excellent comprehensive performance and chip-breaking performance which is close to that of the free-cutting lead brass. With regard to Al alloys, Djurdjevic[17,18] and Hernandez[19] et al proposed an alternative approach for the simulation of cast Al-Si alloys based on the silicon equivalency Si_{EQ}, which numerically expressed the impact of all the alloying and impurity elements through the equivalent content of Si. This approach is applied to calculate the characteristic solidification temperatures (liquidus temperature and Al-Si eutectic temperatures). Based on this approach, Mitrašinović et al[20] calculated the physical and structural parameters, such as latent heat, solid fraction, grain growth restriction factor (GRF), and grain size of multi-component hypoeutectic Al-Si alloys. The statistical analysis of the results shows that the calculated value has a good correlation with the measured value. However, it is uncertain whether the approach is suitable for 7XXX aluminum alloys. Besides, the calculation of equivalency method for 7XXX aluminum alloys is rarely investigated. Therefore, this research established the algorithm of zinc equivalency Zn_{EQ} based on the equivalency method and the chemical composition of 7XXX aluminum alloys. Through representing the amount of all alloy elements with Zn_{EQ}, the online quality control and prediction of the thermo-physical properties (liquidus temperature and latent heat) during solidification of multi-component 7XXX alloys can be realized. The accuracy of this algorithm was evaluated by comparing the calculated results with the measured values obtained by the differential scanning calorimetric (DSC) apparatus and the simulated values from the commercially available Jmatpro software.

1 Establishment of Zn_{EQ} Algorithm

The typical aluminum binary phase diagrams of several major alloying elements in 7XXX aluminum alloys are shown in Fig. 1[21]. It can be distinctly seen that in every Al-*X* (*X* represents the alloying element) system, with increasing the content of added elements in pure aluminum, the liquidus temperatures are all decreased and finally reach the minimum value at a specific content. Therefore, the liquidus of any eutectic binary Al-*X* phase diagram can be accurately expressed by Eq.(1)[22], as follows:

$$T_{\mathrm{LIQ}}^{\mathrm{Al}-X} = A - BX_i - CX_i^2 \quad (1)$$

where $T_{\mathrm{LIQ}}^{\mathrm{Al}-X}$ is the liquidus temperature of binary Al-*X* system (°C), *i* represents the element content (wt%), X_i represents the alloy content of specific alloying element *X* (wt%), *A* is the melting point of pure aluminum (660.452 °C), and *B* and *C* are the polynomial coefficients.

Zn was regarded as a reference element for 7XXX aluminum alloys, because it is one of the main elements with massive content and has an influence on the casting properties, such as fluidity, latent heat, and shrinkage. Therefore, the liquidus of the Al-Zn binary system can be expressed by Eq.(2), as follows:

$$T_{\mathrm{LIQ}}^{\mathrm{Al}-\mathrm{Zn}} = 660.452 - 1.704\mathrm{Zn}_i - 0.005\,88\mathrm{Zn}_i^2 \quad (2)$$

Two liquidus lines in binary Al-Zn and Al-*X* systems can be visualized for analysis, as shown in Fig.2. The two curves are similar: the liquidus temperature is decreased with increasing the content of alloying elements. Therefore, the isothermal concentration difference between Zn and *X* elements can be expressed by Eq.(3), as follows:

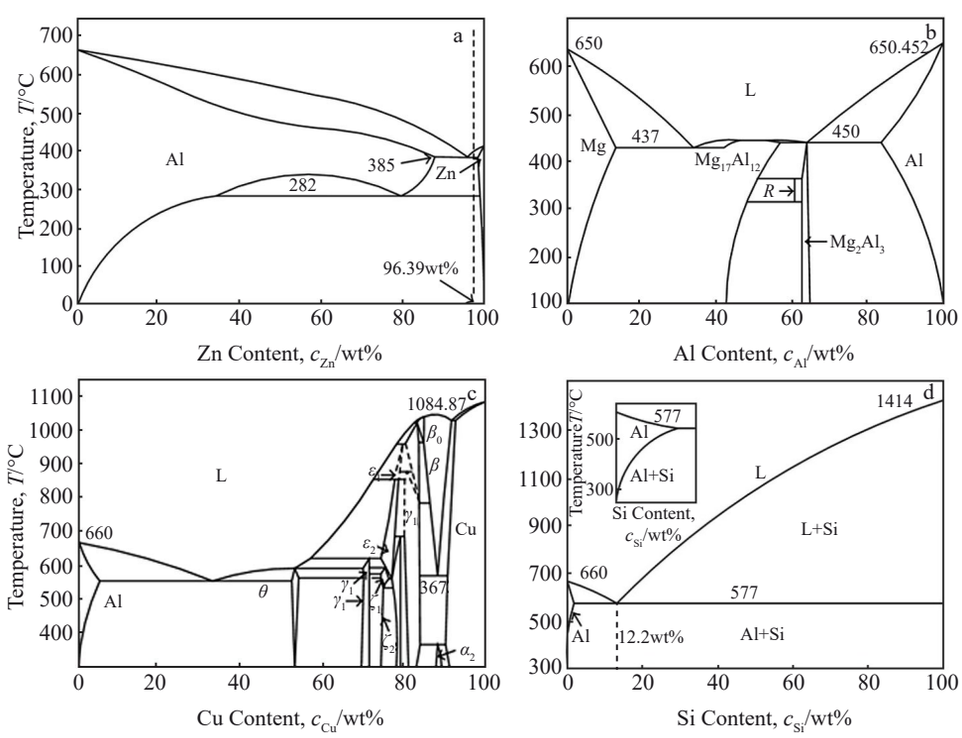

Fig.1 Aluminum binary phase diagrams of different major elements in 7XXX aluminum alloys[21]: (a) Al-Zn, (b) Mg-Al, (c) Al-Cu, and (d) Al-Si

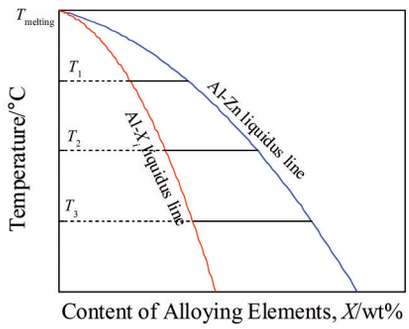

Fig.2 Liquidus lines of Al-Zn and Al-X_i binary systems

$$Zn_{EQ,@T}^{X_i} = \left| Zn_i - X_i \right| \quad (3)$$

where $Zn_{EQ,@T}^{X_i}$ is the isothermal concentration difference between Zn and alloying element X of i content (wt%). Thus, the influence of different alloying elements in the aluminum melt on the liquidus temperature is equivalently related to the effect of Zn with equivalent amount.

Considering the whole temperature range between the melting point of the pure aluminum and the eutectic temperature of the observed binary alloying element, the quadratic equation to describe the relationship between $Zn_{EQ}^{X_i}$ with the alloying element X of i content can be constructed, as follows:

$$Zn_{EQ}^{X_i} = a_0^{X_i} + b_0^{X_i} X_i + c_0^{X_i} X_i^2 \quad (4)$$

where $Zn_{EQ}^{X_i}$ is the zinc equivalency of alloying element X of i content (wt%); $a_0^{X_i}$, $b_0^{X_i}$, and $c_0^{X_i}$ are polynomial coefficients.

The value of X_i and the corresponding $Zn_{EQ,@T}^{X_i}$ at a fixed temperature can be obtained by the liquidus curve. Then the polynomial parameter can be obtained by fitting the X_i value with the corresponding $Zn_{EQ}^{X_i}$ at different temperatures.

The effect of various major and minor solute elements in 7XXX aluminum alloys derived from the binary phase diagrams on $Zn_{EQ}^{X_i}$ can be expressed by Eq. (4), and all the necessary coefficients (a_0, b_0, and c_0) are listed in Table 1. In addition, Fig. 3 summarizes the effect of several major and minor elements on Zn_{EQ}. When X_i=0, the value of $Zn_{EQ}^{X_i}$ should also be 0, leading to a_0=0.

Table 1 Polynomial coefficients for Zn_{EQ} calculation derived from different binary Al-X systems

Al-X	a_0	b_0	c_0
Al-Mg	0	2.254 56	−0.025 43
Al-Cu	0	0.436 06	0.007 43
Al-Si	0	2.152 09	0.023 23
Al-Fe	0	4.908 79	−0.023 37
Al-Mn	0	5.537 78	−0.155 63
Al-Ti	0	−0.339 9	0.035 24
Al-B	0	−0.991 76	0.000 281 2
Al-Zr	0	−0.682 2	0.002 95

The Zn_{EQ} for any multi-component 7XXX cast alloys can be determined as the sum of the equivalent concentration of other elements and the actual zinc concentration, as follows:

$$Zn_{EQ} = Zn_i + \sum Zn_{EQ}^{X_i} \quad (5)$$

The application of Zn_{EQ} provides a simple and reliable way to acquire high-quality materials, and improves the simulation accuracy. The liquidus temperature and latent heat of different alloys were studied through DSC (NETZSCH STA 449C) synchronous thermal analyzer.

The thermal analysis specimens were in the form of metal powder with average mass of 10~15 mg, and they were placed into an alumina crucible. The experiments were performed at the same heating and cooling rate of 10 °C/min in the temperature range of 25~700 °C. Besides, the argon was used as the protective gas to prevent alloy oxidation in the whole experiment. DSC apparatus was calibrated with ultra-high purity aluminum standard specimen to obtain the baseline before the experiments. DSC experiments for each alloying element were repeated three times and the average value was used for analysis.

2 Results and Discussion

2.1 Calculation of liquidus temperature

During the solidification of multi-component alloys, the liquidus temperature is important for research[23,24]. After the content of all solute elements is equivalized to the corresponding Zn_{EQ} value, the liquidus temperatures of 7XXX

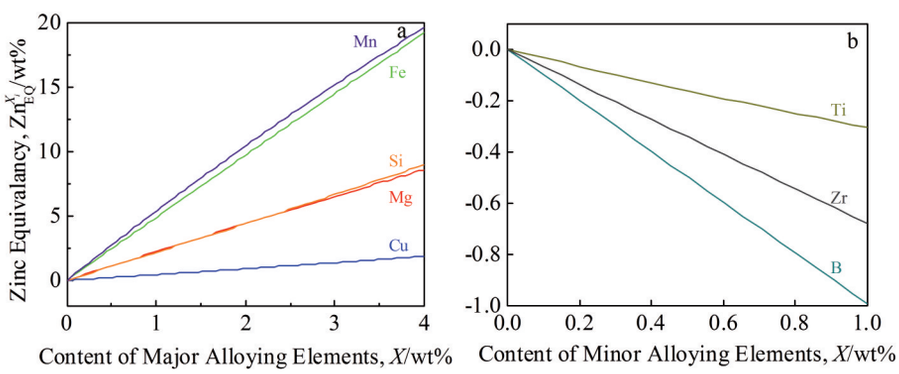

Fig.3 Effect of content of major alloying elements (a) and minor alloying elements (b) on corresponding zinc equivalency

aluminum alloys can be obtained, as follows:

$$T_{\mathrm{LIQ}}^{\mathrm{Al-Zn-}\sum X_i} = 660.452 - 1.704\mathrm{Zn_{EQ}} - 0.005\,88\mathrm{Zn_{EQ}^2} \quad (6)$$

In order to evaluate the accuracy of the calculation formulae, fifteen alloys were prepared, and their corresponding parameters are also obtained, as listed in Table 2. The liquidus temperatures of all these alloys were determined by the thermal analysis technique with accuracy of ±1 °C[24,25]. Fig.4 shows the comparison between the calculated/simulated and DSC measured liquidus temperatures of the aluminum alloys.

The results of Fig. 4 and Table 2 all demonstrate that both the calculations based on equivalency method and the simulation by Jmatpro software alloys show good accuracy for prediction of liquidus temperatures. The statistical analysis reveals that the application of Zn_{EQ} algorithm presents smaller standard deviations ($R^2_{Zn_{EQ}}$=0.94) and smaller scatter range, compared with those obtained by Jmatpro software ($R^2_{Jmatpro}$= 0.82), i.e., the calculation based on the equivalency method is more accurate.

The slight discrepancies between measured and predicted liquidus temperatures mainly originate from two aspects: the precision of the coefficients for conversion of equivalent content and the neglect of the interactions among alloying elements in aluminum melts. The analytical approach in this research is generally based on the binary alloying systems (Fig.1). By repeatedly measuring the liquidus lines on the zinc-rich side of each binary system and considering the interactions among the elements in the aluminum melt, the calculated values may be closer to the measured values.

2.2 Calculation of latent heat

The latent heat of solidification indicates the energy released by a substance during the transition from liquid to solid phase without temperature change. The latent heat of solidification of each alloy depends primarily on the alloy composition, which consequently affects the macro/micro structures under the given solidification conditions. Therefore, the latent heat is important in the solidification process and has an influence on the casting quality. Besides, the application of latent heat is essential in the modelling and simulation of the solidification process, which directly affects the calculation accuracy.

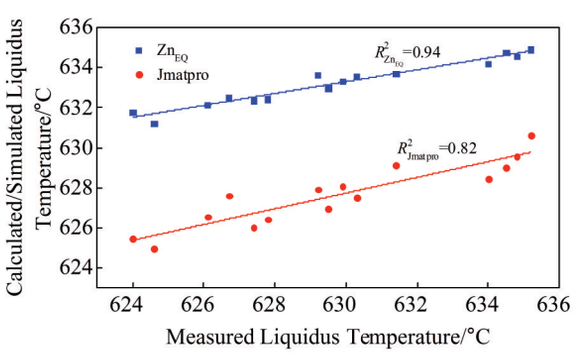

Fig.4 Comparison between calculated/simulated and measured liquidus temperatures of 7XXX aluminum alloys

Table 2 Chemical composition of 7XXX aluminum alloys and corresponding liquidus temperatures obtained by different methods

No.	Chemical composition/wt%			Liquidus temperature, T_{LIQ}/°C		
	Zn	Mg	Cu	Zn_{EQ}	Jmatpro	DSC
1	8.7	2.1	2.3	634.76	629.01	634.5
2	8.7	2.4	2.3	633.56	627.52	630.3
3	8.7	2.7	2.3	632.36	626.03	627.4
4	9.0	2.1	2.3	634.20	628.47	634.0
5	9.0	2.4	2.3	632.99	626.98	629.5
6	9.0	2.7	2.3	631.79	625.48	624.0
7	9.3	2.1	2.3	633.64	627.92	629.2
8	9.3	2.4	2.3	632.43	626.43	627.8
9	9.3	2.7	2.3	631.22	624.94	624.6
10	9.0	2.1	1.9	634.55	629.54	634.8
11	9.0	2.4	1.9	633.34	628.05	629.9
12	9.0	2.7	1.9	632.14	626.55	626.1
13	9.0	2.1	1.5	634.90	630.61	635.2
14	9.0	2.4	1.5	633.69	629.11	631.4
15	9.0	2.7	1.5	632.49	627.61	626.7

The latent heat of common pure metals is available from Ref. [26-28]. However, for most of the multi-component alloys, the latent heat of solidification is rarely reported. Fortunately, several processing methods of latent heat release during casting have been widely used, such as enthalpy method, temperature compensation method, and equivalent specific heat method[29,30]. All these methods usually assume that the amount of latent heat is proportional to the increase of solid fraction in the alloy during casting. Then, the calculation is conducted under the condition of equilibrium and non-equilibrium solidification with the lever rule and Schell's equation, respectively[19,20].

The main alloy phases in Al-Zn-Mg-Cu system include α phase (single-phase solid solution), T phase (AlCuMgZn), S phase (Al_2CuMg), M phase ($MgZn_2$), and θ phase (Al_2Cu). However, the multi-component aluminum alloys can be regarded as pseudo-binary Al-Zn_{EQ} alloys by the zinc equivalency method. Thus, the solidification path of these alloys can be described through the formation of primary α-Al solid solution and followed by the precipitation of the primary β-zinc from α-Al solid solution. As for this transformed Al-Zn_{EQ} pseudo-binary system, it is assumed firstly that the latent heat of solidification of the precipitated α-aluminum solid solution is the same as that of the pure aluminum. Then, the amount of primary α-aluminum and primary zinc can be calculated by the lever rule and Schell's equation. In conclusion, the total latent heat of solidification can be expressed by Eq.(7), as follows:

$$L_{\mathrm{Heat\ of\ solidification}}^{\mathrm{Al-Zn}} = f_{\mathrm{Primary}}^{\alpha\text{-Al}} L_{\mathrm{Heat\ of\ pure\ Al}} + f_{\mathrm{Primary}}^{\beta\text{-Zn}} L_{\mathrm{Heat\ of\ pure\ Zn}} \quad (7)$$

where $L_{\mathrm{Heat\ of\ pure\ Al}}$ is the latent heat of Al (396 J/g); $L_{\mathrm{Heat\ of\ pure\ Zn}}$ is the latent heat of Zn (112 J/g); $f_{\mathrm{Primary}}^{\alpha\text{-Al}}$ and $f_{\mathrm{Primary}}^{\beta\text{-Zn}}$ represent the

solidification fraction of α-Al and β-Zn, respectively.

DSC curves and the solidification paths of these alloys are obtained. Thus, the corresponding latent heat released during solidification can be determined by calculating the area between DSC curve and the baseline, which is in proportion to the latent heat of solidification.

According to Table 3, Fig. 5 shows the comparison of the practical latent heat of solidification with the calculated values by the Zn_{EQ} equivalency methods and the simulated values from Jmatpro software. It can be seen that the calculated latent heat is basically consistent with the measured values, and the higher standard correlation (0.84) also proves that this equivalency method can accurately estimate the latent heat of solidification of the 7XXX aluminum alloys.

Table 3 Zn_{EQ} contents of 7XXX aluminum alloys and corresponding latent heats obtained from different methods

No.	Zn_{EQ} content/wt%	Latent heat/kJ·kg^{-1}		
		Based on Zn_{EQ} calculation	Jmatpro simulation	DSC experiment
1	14.364 65	355.204 4	371.80	367.47
2	15.006 69	353.381 0	370.13	360.78
3	15.644 15	351.570 6	370.84	354.64
4	14.664 65	354.352 4	371.04	362.45
5	15.306 69	352.529 0	369.56	357.83
6	15.944 15	350.718 6	369.53	348.96
7	14.964 65	353.500 4	370.28	358.56
8	15.606 69	351.677 0	370.11	357.12
9	16.244 15	349.866 6	369.78	350.31
10	14.477 75	354.883 2	371.19	366.29
11	15.119 79	353.059 8	371.11	359.78
12	15.757 25	351.249 4	373.48	356.35
13	14.293 23	355.407 2	371.54	370.87
14	14.935 27	353.583 8	374.18	365.87
15	15.572 73	351.773 4	373.39	360.72

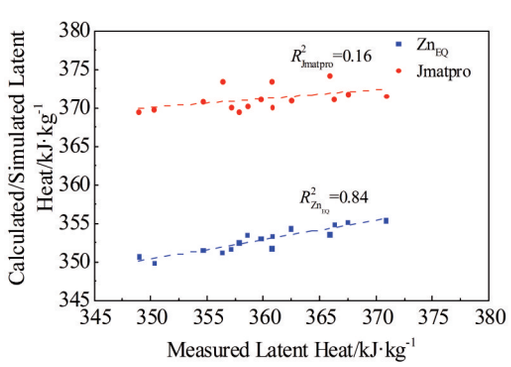

Fig.5 Comparison of calculated/simulated latent heat with measured latent heat

3 Conclusions

1) The calculation model of zinc equivalency based on the equivalency method is established, and it can predict the thermo-physical properties (liquidus temperature and latent heat) of 7XXX aluminum alloys.

2) Both the analytical methods (calculation based on Zn equivalency and Jmatpro software) can accurately predict the liquidus temperature and latent heat of solidification for the 7XXX aluminum alloys, and the equivalency method shows higher precision with simple operation.

3) This research provides guidance for the property prediction of 7XXX aluminum alloys.

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当量法测定7XXX系铝合金热物理性能

黄元春[1,2]，赵建业[1]，胡嘉伟[1]，肖政兵[1,2]，黄仕塔[3]
(1. 中南大学 轻合金研究院，湖南 长沙 410012)
(2. 中南大学 高性能复杂制造国家重点实验室，湖南 长沙 410083)
(3. 安泰新能源科技公司 材料部，福建 漳州 363999)

摘　要：基于当量的概念（所有合金元素对材料热物理性能的影响可以通过一个参考元素的等效作用来表示），以Zn为参考元素，通过对7XXX系铝合金二元相图富Al端液相线的数值拟合，得到当量算法所需参数，并将其他元素的当量浓度和参考元素的实际浓度之和用于计算材料的液相线温度和潜热。计算结果与差示扫描量热仪（DSC）测得的数据吻合。与Jmatpro软件获得的数值相比，该算法展现出更好的准确性。

关键词：7XXX铝合金；Zn当量；热物理性能；DSC；Jmatpro

作者简介：黄元春，男，1966年生，博士，教授，中南大学轻合金研究院，湖南 长沙 410012，E-mail：science@csu.edu.cn