SOLIDIFICATION CURVES OF Al–Cu, Al–Mg AND Al–Cu–Mg ALLOYS

S.-W. CHEN and C.-C. HUANG
Department of Chemical Engineering, National Tsing-Hua University, Kuang-Fu Road, Hsin-Chu, Taiwan 30043, R.O. China
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Abstract—Three different methods have been utilized to determine the solidification curves of the Al-rich Al–Cu, Al–Mg and Al–Cu–Mg alloys. These three methods, i.e. a conventional quenching and image analysis method, calculations using two simplistic solidification models, and a proposed DTA coupled with mathematical modeling method, have been illustrated. Obtained by the three different methods, the solid fractions versus solidification temperatures of the solidifying samples are compared with one another, and the three different methods are discussed. Advantages of using the proposed DTA coupled with mathematical modeling method to determine the solidification curves are demonstrated. A ~20°C undercooling of these Al-rich alloys during solidification has been observed by using DTA. The primary solidification phases are α-Al phase for all seven alloys. The secondary solidification phases have also been identified by using metallography, SEM (Scanning Electron Microscopy) and EPMA (Electron Probe Microanalysis).

1. INTRODUCTION

Casting processes are the most important methods in the manufacturing of aluminum alloys [1–4]. Due to the good fluidity and low melting point of most aluminum alloys, they are adaptable to many of the most commonly used casting processes. Viscosity of alloys is enormously reduced whilst melting, thus much less shear stress is required when using casting than when using the solid-state forming processes. This has made casting an economically preferable process in most occasions. The microstructures and microsegregations of the cast developed during solidification greatly affect the products’ properties [1–7]. This is obvious if the casting process is the product’s last forming process. Even through many after-cast treatments, the aluminum alloys still retain the cast structures in most cases. Controlling solidification process is no doubt very important. Understanding of the solidification curves of aluminum alloys, i.e. the solidification sequences and solid fractions versus temperatures during solidification, are crucial for the control of solidification processes [5–10]. The solidification curves are also believed to be related to the castability of alloys [8–11]. Al–Cu, Al–Mg and Al–Cu–Mg alloys are the base alloys of many important cast alloys and many high strength commercial wrought alloys, such as 2090, 6061 and 7075, which are of importance in aerospace applications. In this study, different methods have been used to determine the solidification curves of the Al-rich Al–Cu, Al–Mg and Al–Cu–Mg alloys.
thermodynamic models. The authors have studied the aluminum-rich end of the Al-Cu–Mg ternary system previously [20], and the assessed parameters for the thermodynamic models have been adopted in this study and are listed in Table 1. The thermodynamic parameters used in this study for the three binary constituent systems, Al–Cu, Al–Mg and Cu–Mg systems are based on Chen’s [6], Murray’s [21] and Zuo’s [22] assessments, respectively, and are also shown in Table 1. A solution model has been used to describe the α-Al and liquid phases. The excess Gibbs energy is represented by the following equation:

\[
\Delta^\text{E} G = \frac{1}{2} \sum_{i=1}^{3} \sum_{j=1}^{3} \{w_i \ln (x_i) + \{x_j \ln (x_j) - w_i w_j \} x_i x_j \}
\]

The two intermetallic phases at the Al-rich corner, θ-AlCu and S-AlCuMg phases, reveal only small ranges of homogeneity and are treated as line compounds. Their integral Gibbs energies of formations are represented by a three-term and two-term equation, respectively:

\[
\Delta G_i = A + BT + CT \ln T, \\
\Delta G_i = A + BT.
\]

The Scheil model [12] has four basic assumptions: (1) the interfaces are in equilibrium; (2) there is no diffusion in the solid phase; (3) the compositions are homogeneous through the entire liquid phase; and (4) the densities are equal for the solid and liquid phases. Based on the above four assumptions, mass balance equations can be derived for the solidification processes. The derived mass balance equations and the numerical solving procedures have been described previously [6]. The distribution coefficients of the Al–Cu, Al–Mg and Al–Cu–Mg systems are obtained from the thermodynamic models mentioned above [20–22].

### Table 1. Parameters of thermodynamic models for the Al-Cu, Al-Mg and Al-Cu-Mg systems

<table>
<thead>
<tr>
<th>Lattice stabilities:</th>
<th>(\Delta G_i^{\text{L,L}})</th>
<th>(\Delta G_i^{\text{L,F}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta G_i^{\text{AG,AG}})</td>
<td>10795.0 – 11.564 × T</td>
<td>13054.0 – 9.615 × T</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solution parameters for the liquid phase (L) and fcc phase (a).</th>
<th>(\Delta G_i^{\text{L,L}})</th>
<th>(\Delta G_i^{\text{L,F}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(w_i)</td>
<td>(-2.3086 - 5058.51/T)</td>
<td>(-1202.79/T)</td>
</tr>
<tr>
<td>(w_j)</td>
<td>(+0.3428 - 5166.64/T)</td>
<td>(+3460.83/T)</td>
</tr>
<tr>
<td>(w_k)</td>
<td>(+0.7469 - 1165.14/T)</td>
<td>(+1120.16/T)</td>
</tr>
<tr>
<td>(w_l)</td>
<td>(+3.5926 - 13162.72/T)</td>
<td>(+2431.62/T)</td>
</tr>
</tbody>
</table>

Formation energies of θ and B phases:

\[
\Delta G_i^{\text{E}} = 22893.2 – 423.07 × T + 56.453 × T \ln (T) \\
\Delta G_i^{\text{E}} = -24500 + 11.315 × T
\]

[Standard states: Al(L), Cu(L), Mg(L)]

### 2.2. Quenching and image analysis

The binary alloys were prepared with elements of 99.99% purity. For the preparation of Al–Cu alloys, the BN (boron nitride) coated stainless steel crucible, which contained the weighed elements was kept inside a furnace at 800°C for 1 h, taken out of the furnace, and then the molten alloys were cast in a pre-warmed graphite mold to produce rods of 8 mm in diameter and 120 mm in length. For the preparation of Al–Mg alloys, aluminum was melted first and poured on top of magnesium. The aluminum-covered magnesium with aluminum was then transferred to a furnace at 800°C and kept inside for 15 min, then the same procedures as used for preparing Al–Cu alloys were followed. Ternary alloys were prepared with 99.99% purity aluminum, 99.99% purity copper and Al–Mg master alloys. The same methods as used to prepare Al–Cu alloys were applied. Pieces of Al–Cu, Al–Mg and Al–Cu–Mg rods were cast for compositions by using ICP (Inductively Coupled Plasma). Losses of the magnesium during the alloy preparation were observed. Compositions of the alloys investigated in this study are listed in Table 2.

Conventional quenching experiments were carried out. Each sample was loaded in a boron nitride crucible and encapsulated in a quartz tube. The encapsulated sample cells were held inside a heated vertical tube furnace at 700°C for 30 min. During the prolonged holding, the aluminum alloys became molten. The furnace was then cooled at a controlled cooling rate. The selected cooling rates were 1 and 5°C/min. The samples remained inside the furnace until the furnace reached a pre-determined temperature, then they were quenched into water. The solidified aluminum alloys were cut in half. One half of the sample was analyzed for the formation phases by using XRD (X-ray diffraction) and the other half was analyzed by using Leco image analyzer [23]. SEM (Scanning Electron Microscopy) and EPMA were also used to identify the primary and secondary solidification phases. The solidification curves were thus determined.

### Table 2. Compositions of alloys investigated in this study

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al-10.0 wt% Cu</td>
</tr>
<tr>
<td>2</td>
<td>Al-4.5 wt% Cu</td>
</tr>
<tr>
<td>3</td>
<td>Al-6.5 wt% Mg</td>
</tr>
<tr>
<td>4</td>
<td>Al-4.25 wt% Mg</td>
</tr>
<tr>
<td>5</td>
<td>Al-25.0 wt% Cu-4.0 wt% Mg</td>
</tr>
<tr>
<td>6</td>
<td>Al-20.0 wt% Cu-3.0 wt% Mg</td>
</tr>
<tr>
<td>7</td>
<td>Al-15.0 wt% Cu-4.0 wt% Mg</td>
</tr>
</tbody>
</table>
2.3. Using DTA and mathematical modeling

DTA is one type of TA (thermal analysis). There are two cells inside a DTA furnace. One of the cells is for holding the sample and the other is for the reference. The differences in the temperatures between the two cells are recorded, and are resulted mainly from phase transformations in the sample during the heating or cooling scan. In most cases, references are chosen so that there are no phase transformations of the standard in the working temperature range. DTA is a well-developed technology. Theories and applications of DTA have been widely investigated [24-35]. Most often, DTA are used for the determinations of phase transformation temperatures, heat capacities of materials and compositions of alloys. Gray [30] proposed a simplistic mathematical model describing the heat transfer of DTA. Simulations of the determined cooling curves of DTA have been carried out in this study by using Gray's model. The models can then be used to calculate the solidification curves of samples. Backerud [3] used a traditional TA method with mathematical models to determine the solidification curves of many commercial aluminum alloys. However, TA does not have a reference cell and the results are not as sensitive as those determined using DTA.

The DTA samples were 1 mm in diameter and 8 mm in length, and were loaded inside BN crucibles and encapsulated in 3 mm ID quartz tubes. Both experiments of heating and cooling scanning modes were carried out. The heating rates were at 10, 4 and 1°C/min, while the cooling rates were at 10 and 4°C/min. Microstructures of the samples from DTA experiments were then examined by using optical microscopy. SEM and EPMA were also used for the identification of the phases.

Gray's model was used to simulate the DTA curves determined experimentally [35]. A schematic diagram of the DTA cell as shown in Fig. 1, consisting of a sample cell at a temperature $T_s$, a reference cell at a temperature $T_r$, a source of thermal energy at $T_p$, and a path having a thermal resistance, $R$, through which the thermal energy runs to or from the sample and the reference. By assuming that the sample temperature $T_s$ and the reference temperature $T_r$ were uniform and equal to those of their containers, Gray gave the thermal balance equations for the DTA cells [30]. The temperature differences of the two cells were derived from the thermal balance equations for the DTA cells and are given in the following:

$$T_s - T_r = R \frac{dh}{dt} + R(C_f - C_s) \frac{dT_p}{dt} + PC_s \frac{d(T_s - T_r)}{dt}.$$  

(3a)

It is assumed that the term $R(C_f - C_s) \frac{dT_p}{dt}$ is negligible. The validity of this assumption is verified by the fact that the DTA is adjusted so that the baseline is flat in the usual practice. The term $\frac{dh}{dt}$ is directly related to the rate of the phase transformation, i.e. $\frac{df}{dt}$ in this solidification case. For simplicity, the heat of solidification is assumed to be constant. Equation (3a) can thus be rewritten as

$$T_s - T_r = RH \frac{df}{dt} + RC_s \frac{d(T_s - T_r)}{dt}.$$  

(3b)

The temperature differences $(T_s - T_r)$ are determined from the DTA cooling curves, and $R$, $H$ and $C_s$ are parameters of the DTA instrument and samples. However, direct measurements of $R$, $H$ and $C_s$ are difficult. In this study, $RH$ and $RC_s$ were determined from the cooling curves as the two system parameters by the following procedures. According to Gray's model, the cooling curves of the after-reaction part depend only on $RC_s$ because there is no longer any reaction heat input or output in the sample cell [35]. Equation (4) can be derived from equation (3b) with the boundary condition, at the end of the reaction $t = t_{end}$, the temperature difference $\Delta T = \Delta T_{max}$.

$$\Delta T = \Delta T_{max} \exp \left[ -\frac{(t - t_{end})}{RC_s} \right].$$  

(4)

Once $RC_s$ has been determined by simulating the after-reaction curve with equation (4), $RH$ can be obtained by integrating over the entire reaction range by using equation (3b).

3. RESULTS AND DISCUSSION

Two binary Al-Cu alloys and two binary Al-Mg alloys were examined. As listed in Table 1, the compositions were Al-10.0 wt% Cu, Al-4.3 wt% Cu, Al-6.5 wt% Mg and Al-4.25 wt% Mg for samples #1, #2, #3 and #4, respectively. The phase solidification sequences can be determined very easily by judging from the equilibrium Al-Cu and Al-Mg phase diagrams. For samples #1 - #4, the primary solidification phases are the $\alpha$-Al phase while the secondary phases are the binary eutectics, if there are any secondary phases. As described in the previous...
The microstructure of an Al-10.0 wt% Cu alloy solidified at a cooling rate of 10°C/min and then quenched at 630°C.

Owing to the possible deviations of the solid fractions caused by segregations, more than 30 sections were examined for every specimen in order to obtain a statistical accuracy. The solid fractions thus obtained are in comparison with the results determined by other methods and are shown in Figs 3–6 for binary alloys #1–#4, respectively. There are no data in the regions of high liquid fractions, because the samples quenched at higher temperatures with higher liquid fractions were exploded during quenching and their fraction solid could not be analyzed.
The lever rule is based on an equilibrium situation, while the Scheil model is applied to a case of no solid diffusions, thus the solid fractions calculated by using the lever rule are higher than those calculated by applying the Scheil model [6, 11]. In reality, it is more likely that the solid diffusions occur during solidification, while concentration gradients still exist, and the real solid fractions should fall between the predictions of the two models. However, as noticed in Figs 3–6, the results determined by quenching experiments and image analysis are higher than the predictions found by using the Scheil model, and in many cases even higher than those using the lever rule. Explanations will be discussed later.
The cooling curve of an Al–10.0 wt% Cu alloy is shown in Fig. 6. By using Gray’s model, the $RC_s$ was determined to be 0.6254 min and is listed in Table 3. The value of $RH$ was determined by integration over the entire reaction range and was 22.02 min·°C as also shown in Table 3. With $\Delta T$ observed from the cooling curve and the determined $RC_s$ and $RH$, the solidification curve for alloy #1 was calculated using equation (3) and is shown in Fig. 3. Superheating and undercooling were both observed during the heating and cooling scan. Undercooling is more pronounced than superheating. As shown in Figs 7 and 13, ~20°C undercooling was noticed in the cooling curve and that was the most obvious difference between the solidification curves determined using DTA and mathematical modeling and those calculated using the lever rule and the Scheil model. Grain refiners are usually added in the commercial processes of aluminum casting, and heterogeneous nucleation is practised, but undercooling effects are still encountered and cannot be ignored. It is a serious handicap to use the lever rule and the Scheil model because the undercooling effect is neglected in both of these models. More complex solidification models that are tentative of taking the undercooling effect and solid diffusion into consideration would require other physical parameters, such as viscosity, morphology and permeability, which are very difficult to obtain [16–19]. The other major obstacle for determining solidification curves by applying the lever rule and Scheil model is that the required distribution coefficients $k$, are seldom available for high order systems. The existence of thermodynamic models is very rare concerning systems with an order higher than binary. It is worth noting that at the end of the solidification, the amounts of the secondary phases determined by using DTA and modeling fall between the predictions given using the lever rule and Scheil model.

Solidification curves of three ternary alloys were studied. Their compositions are listed in Table 2 and are Al–25 wt% Cu–4 wt% Mg, Al–20 wt% Cu–3 wt% Mg, Al–15 wt% Cu–4 wt% Mg for samples #5, #6 and #7, respectively. For the solidification of binary alloys, the phase formation sequences can be very easily identified, however it is more difficult for the case of ternary alloys. The primary solidification phases are α-Al phase for all three ternary alloys judging from the calculated liquidus projection as shown in Fig. 8 [20]. The information of the secondary solidification phases could not be obtained directly from the equilibrium phase diagram and was determined by experiments. As shown in Fig. 9 for alloy #5, the secondary $\theta$-Al$_2$Cu phase grew on the dendritic primary phase and was identified by using metallography, SEM and EPMA. The secondary phases were all $\theta$-Al$_2$Cu phases for the three ternary alloys #5–#7. The solid fractions of the ternary

![Fig. 6. Solid fraction vs temperature for sample #4 during solidification.](image-url)
alloys during solidification were calculated by using the lever rule and Scheil model and also by simulating the determined DTA cooling curves, and the results are shown in Figs 10–12 for alloys #5–#7, respectively. The DTA parameters for Gray's model are shown in Table 3. A cooling curve for sample #5 is shown in Fig. 13. The first peak is for the solidification of primary α-Al phase, the second peak is for the

Fig. 7. The cooling curve for alloy #1 determined by using DTA superimposed with the simulated cooling curve.

Fig. 8. The calculated liquidus projection of the Al-rich corner of Al-Cu-Mg system superimposed with the three ternary alloys investigated in this study.
co-precipitation of $\alpha$ and $\theta$, while the last peak is for the ternary eutectic, i.e. the type I reaction, $L = \alpha + \theta + S$.

Owing to experimental difficulties, quenching and image analysis experiments for ternary alloys were carried out only for alloy #5. Besides the mentioned problem of explosion for high liquid fraction specimens, there are uncertainties regarding the analysis of the successfully quenched samples due to the following reasons. First, the sample capsules have double walls and the high thermal resistance has made "rapid quenching" of the samples almost impossible. A rather slow cooling was retained for a while during quenching and the primary phase continued to grow. Second, the secondary $\alpha$-Al phase precipitated on the primary $\alpha$-Al phase, became indistinguishable, and this effect was worse because of the slow quenching rate. Third, the image analysis itself has a high degree of uncertainty when the contrast of brightness between different phases is not strong or the microstructures are too fine. This made the image analysis of "more rapid solidified" samples very unreliable. In this study, reliable results was very difficult to obtain by image analysis of the samples with cooling rates.

![Fig. 9. The microstructure of alloy #5 indicating the secondary $\theta$ phase.](image)

![Fig. 10. Solid fraction vs temperature for sample #5 during solidification.](image)
higher than 6°C/min, and this 6°C/min solidification rate is still lower than those of most commercial casting processes. These three above-mentioned effects would usually increase the measured values of solid factions given using image analysis. The high thermal resistance of the sample capsule's double walls has made the real temperatures of the samples higher than the observed readings of the furnace temperatures. On the other hand, this double-wall effect and the undercooling effect would make the real solid fractions lower than the predictions. The combination of these five major effects may explain the scatter and mostly high solid fractions of the results determined by quenching and image analysis.
The advantages of determining solidification curves by the proposed DTA coupled with mathematical modeling method have been illustrated through measurements and discussions in this study. However, more reliable results can be obtained if the simple DTA model is improved. As noticed in Figs 7 and 13, the base line changes before and after solidification and this is mainly due to the differences of heat capacities between solid and liquid phases. An improved model should take this effect into consideration, and this factor surely affects the calculated amounts of solid. The system parameters can also be more easily verified regarding their physical feasibility, if the thermal resistance and heat capacities of the samples, sample cells, furnace, etc. are considered separately.

4. CONCLUSIONS

Solidification curves of Al-rich Al–Cu, Al–Mg and Al–Cu–Mg alloys were determined by three different methods, i.e. quenching, solidification model calculation and DTA with mathematical modeling. Differences were observed between the results determined using these different methods. The most direct method, quenching and image analysis, has several experimental difficulties, such as the ability of quenching and the reliability of image analysis. Depending upon each selected solidification model used, different physical parameters are required for calculation. However, the applicability of model calculation is often restricted by the lack of physical parameters, such as viscosity and permeability of the semi-solid alloys and morphology of dendrites. Even for the most simplistic solidification models, the lever rule and Scheil model, which were used in this study, the required distribution coefficients $k$, are usually not available. Using DTA with mathematical modeling has the following advantages over the two conventional methods mentioned above.

1. DTA is a real-time measurement and does not encounter the difficulty of a change in the microstructure sample during quenching.
2. The cooling curve determined by using DTA results from the phase transformation of the entire sample. Segregation within the sample is thus not an issue in this method.
3. The solid fractions during solidification determined using the DTA coupled with mathematical modeling method are related only to the DTA cooling curves. Those physical parameters which are difficult to obtain such as viscosity, morphology and permeability are not needed in this method.

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