INVESTIGATION THE SOLIDIFICATION OF Al-4.8 wt.% Cu ALLOY AT DIFFERENTS COOLING RATE BY COMPUTER-AIDED COOLING CURVE ANALYSIS

Mehdi Dehnavi1*, Hosein Vafaeeenezhad2, Mohsen Haddad Sabzevar1

1Department of Materials Science and Engineering, Engineering Faculty, Ferdowsi University of, Mashhad- Iran.
2Department of Materials Science and Engineering, Iran University of Science and Technology Tehran- Iran.

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Abstract

Depending on the casting conditions and alloy composition, microstructure and properties of the aluminium alloys will be different. There are many techniques available for investigating the solidification of metals and alloys. In recent years computer-aided cooling curve analysis (CA-CCA) has been used to determine thermo-physical properties of alloys, latent heat and solid fraction. The aim of this study was to investigate the effect of cooling rate on the structural features of Al-4.8 wt.%Cu alloy by thermal analysis of cooling curves. To do this, Al-4.8 wt.%Cu alloy was melted and solidified applying 0.04, 0.42, and 1.08 °C/sec cooling rates. The temperature of the samples was recorded using a K thermocouple and a data acquisition system connected to a PC. It was found that the formation temperatures of various thermal parameters such as (liquidus, solidus and eutectic temperatures) are shifting by increasing of cooling rate from 0.04 °C/sec to 1.08 °C/sec. The structural results show that grain size and secondary dendrite arm spacing decreased by increasing of cooling rate.

Keywords: Cooling rate, Thermal analysis, α-Al-Cu Eutectic, Microsegregation

Introduction

The Al-Cu alloys have been widely used in aerospace, automobile, and airplane applications. Depending on the casting conditions and alloy composition, microstructure, properties and characteristics of the aluminum alloys will be different[1]. All industrial casting processes operate in a certain range of cooling rates. This range can be as low as 0.01 °C/sec for a massive sand casting, but also can be as high as 10³ °C/sec upon rapid solidification of granules and flakes. Majority of casting processes, however, operate in the range of cooling rates between 0.1 and 20 °C/sec.

* Corresponding author: M. Dehnavi, Mehdi_6664@yahoo.com
The cooling rate affects the structure of as-cast alloys in a well-established manner, i.e. the grain size, the dendrite arm spacing (DAS) and the size of structure constituents (both primary and eutectic) decrease with increasing the cooling rate. It should be specifically noted that the cooling rate (°C/sec) is not a synonym of the solidification rate (m/s). The latter is the magnitude of the velocity of the solidification front (in progressive solidification) or that of the tip of a dendrite (in consideration of a single-grain growth). Cooling rate is a less stringent parameter and can be represented as: (1) the solidification temperature range divided by the time required for an alloy to pass the (non-equilibrium) solidification range, or (2) a slope of the cooling curve at a specific temperature (usually at the liquidus), or (3) the rate of heat extraction from the solidifying volume. In general, the cooling rate reflects the heat transfer conditions of solidification [1,2]. There are many techniques available for investigating the solidification of metals and alloys. There are standardized techniques such Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). These techniques, although well documented and very accurate, prove to be inadequate for investigating solidification of metal alloys. They also require the use of extremely small samples, are expensive, need technical expertise, and are not appropriate for foundries [3,4]. The other way for investigating solidification of metals and alloys is the cooling curve analysis method. This technique is based on recording and analysis of the temperature versus time data collected during the solidification of the sample. In recent years computer-aided cooling curve analysis (CA-CCA) has been used to determine thermo-physical properties of alloys, latent heat and solid fraction. Because it’s very simple to setup it can be widely used, especially in industries. It just needs to place a thermocouple in the melt and allow the melt to solidify while the temperature is recorded as a function of time [5-8]. The cooling curve does not always clearly indicate all the reactions occurring during solidification of a casting clearly, due to the small amounts of heat evolved by certain phase transformations, so more sensitive techniques should be developed. It has been found that the first derivative of the cooling curve can be employed to emphasize small heat effects not resolved on the cooling curve itself [9,10]. The use of first derivatives improves the accuracy of determination of the characteristic features of the cooling curve [10].

Materials and Methods
Binary Al–Cu alloy with the compositions given in Table.1 was prepared in an electrical resistance furnace from 99.9% pure aluminium and an Al–48% Cu master alloy. The chemical composition of the alloy was determined by a spark spectrum analysis. To investigate the effect of cooling rate on the solidification processing, specimens with dimensions (D×H) 22×20 mm and ~10g weight were melted inside a DTA furnace in an alumina crucible (Figure.1). High purity argon gas (99.999%) was running throughout the test to reduce the risk of oxidation of the samples. In the all experiments, the samples were heated to 705±5°C and isothermally kept at this temperature for a period of 150 s in order to stabilize the melt conditions. To create of different cooling rates, three experiments were designed as follows: (a) in the first series of experiments the sample was cooled inside the furnace (slow cooling rate 0.04 °C/sec), (b) in the second series of experiments, in order to increase the cooling rate, the sample was cooled at outside the furnace to the room temperature (middle cooling rate 0.42 °C/sec), (c) in the third series of experiments increase of the cooling
rate was obtained by compressed air injection into the sample chamber. (fast cooling rate 1.08 °C/sec). The temperature of the samples was recorded by a K-type thermocouple with the wire diameter of 0.15 mm placed at the center of the sample and an Advantech 4718 data acquisition system connected to a personal computer. In order to assure the good contact between the thermocouple and the melt, a quartz shield with an external diameter of 2.5 mm was used. Each trial was repeated three times. The temperature vs. time and first derivative were calculated and plotted. The fraction of the solid was calculated by using the Scheil equation as below:

\[ f = 1 - \left( \frac{T_m - T}{T_m - T_0} \right)^{1/k_0} \]  

where \( f \), \( T_m \), \( T \), \( T_0 \), and \( k_0 \) are solid fraction, melting temperature of pure Al, temperature, liquidus temperature, and partition coefficient respectively. There are different ways to define the cooling rate. In the present research the cooling rate was calculated by dividing the total solidification range (\( T_L - T_S \)) to the local solidification time according to [11]. Samples for microstructural examination were taken from a location close to the thermocouple tip. Samples were ground, polished and etched with Keller’s (10ml HF, 20ml HNO\(_3\), 20ml HCl, and 50ml distilled water) and 0.5% HF reagents. The microstructure was examined by an Olympus BX60 optical and LEO 1450VP electron microscopy. Hardness was measured using the Brinell hardness tester with a load of 10 Kgf.

**Table 1. Chemical composition (wt%) of the Al-Cu alloy.**

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Si</th>
<th>Fe</th>
<th>Mg</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.8</td>
<td>0.05</td>
<td>0.06</td>
<td>0.019</td>
<td>Bal</td>
</tr>
</tbody>
</table>

**Fig. 1.** a: sample and quartz shield b: alumina crucible and sample after solidification.

**Results and Discussion**

**Microstructure**

The microstructure of Al-Cu alloys is controlled by chemical composition and cooling rate. Bäckerud [12], found that Al-Cu alloys start to solidify through the development of a dendritic network followed by a eutectic reaction in the interdendritic regions by means of which the eutectic Al\(_2\)Cu is formed in combination with the remaining aluminum. With further decrease in temperature, the Al\(_2\)Cu phase precipitates
from the α-phase. Figure 2 shows the dendritic microstructures of the samples solidified at different cooling rates. The structure configurations at different experimental cooling rates were similar which consisted of α-Al dendrites and the interdendritic (α-Al2Cu) eutectic. It is clearly seen that the microstructure becomes fine by increase of the cooling rate.

Grain size and secondary dendrite arm spacing (SDAS)

The changes of microstructure were caused mainly by the different cooling rates of the melt. It is well known that the cooling rate plays an important role in the refinement of metal structures. A high cooling rate and a short solidification time can lead to the formation of a more refined microstructure, an extended solute solubility and even metastable phases. Grain size strictly depends on the cooling rate [1,2]. SDAS decreases with increasing the cooling rate because of the following reasons: (1) increasing the cooling rate increases the constitutional undercooling. This condition causes the formation of more secondary dendrite arms; (2) increasing the cooling rate causes the interface of the liquid and solid to move faster Consequently, ratio of area to volume of dendrite arms should increase in order to facilitate the heat extraction; (3) increase of dendrite thickness is the consequence of ripening and coalescence which needs diffusion and time. However, when cooling rate increases there is not enough time for these phenomena [13]. For the sample cooled with lowest cooling rate, the grain size is approximately 3430±3μm. Increased cooling rate causes the decrease of the grain size to 1278±4μm. Figure 3 presents a variation of the SDAS values. It is seen that the values follow different behaviours depending on the cooling rate, larger SDAS (323.8μm) being observed on sample solidified at 0.04 °C/sec when smaller SDAS (53μm) was obtained at 1.08 °C/sec. This reflects the fact that SDAS depends on the cooling rate, and more specifically on the solidification time. Figure 4 presents a variation of the grain size and SDAS as a function of the cooling rate.
Non-equilibrium eutectic

Copper content for alloy is less than the maximum solubility of copper at eutectic temperature (5.65 wt.%) so it is expected that alloy should be solidified with a single phase structure (αAl). However, due to the microsegregation during solidification caused by incomplete diffusion processes and therefore incomplete mixing and redistribution of alloying components in solid and liquid phases, the liquid phase is enriched in the solute while the solid phase remains diluted. As a result, when the alloy reaches its equilibrium solidus during solidification, some liquid rich in the solute remains in the system. Giving a sufficient degree of microsegregation, the last liquid will solidify at the eutectic temperature thus producing non-equilibrium eutectics. This phenomenon can be observed even at very slow cooling rates of less than 0.1 °C/sec [1,2,5]. The eutectic structure of alloy at cooling rate 0.42 °C/sec with higher magnification is presented in Figure 5. It is obvious that alloy contains some eutectic phases which imply that the solidification process was non-equilibrium (NEq). The content of the NEq eutectic is usually considered as criteria for quantification of microsegregation level. As the NEq eutectic content increases the microsegregation level also increases [14,2].
Figure 6. shows the SEM backscattered electron images (BSE), of the samples solidified at different cooling rates. The microstructure consists of primary α-Al, (dark phase) and Al<sub>2</sub>Cu phase (white phase) precipitated from the α-phase and NEq eutectic microstructure. With increase of the cooling rate, the microsegregation increases, resulting in higher amount of white phase and Cu. The results of the volume fraction of α-Al<sub>2</sub>Cu eutectic in the structure completely solidified under different cooling rates obtained by image analysis, are given in Table 2. It is found that the volume fraction of α-Al<sub>2</sub>Cu eutectic increases with increasing cooling rate. The fractions of the α-Al<sub>2</sub>Cu eutectic at various cooling rates were calculated using the Scheil model, are about 20-40 % higher than the experimentally measured values in the present work. The Scheil equation predicts generally higher microsegregation than that found experimentally. The discrepancy between predicted and actual microsegregation measured experimentally arises from back diffusion in the solid and coarsening [15].

Table 2. Comparison of experimental and calculated fractions of the α-Al<sub>2</sub>Cu eutectic phase at different cooling rates.

<table>
<thead>
<tr>
<th>A</th>
<th>Alloy Name</th>
<th>Cooling rate (°C/sec)</th>
<th>(wt.%) Fraction Eutectic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Image Analysis</td>
</tr>
<tr>
<td>4.8 %Cu</td>
<td>0.04</td>
<td>5.1</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>0.42</td>
<td>5.7</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>1.08</td>
<td>7.4</td>
<td>9.1</td>
</tr>
</tbody>
</table>
Cooling curve

Figure 7 shows a typical cooling curve and its first derivative obtained for alloy at a cooling rate of 0.42 °C/sec. Two visible temperature arrests were noted on the cooling curve. More detailed information pertaining to the alloy’s thermal characteristics such as non-equilibrium liquidus, nucleation of the (α-Al2Cu) eutectic, etc. were determined using the first derivative curve. The temperatures of reactions denoted by numbers and the corresponding numerical values are presented in Table 3.

![Cooling and first derivative curves for alloy solidified at 0.42 °C/sec, the numbers correspond to the various reactions as presented in Table 3.](image)

The liquidus temperature of the alloy solidified at 0.42 °C/sec was found at 648.2 °C where the first crystallites nucleated from the melt. That point was characterized by the sudden change in the first derivative curve (point 1 in Figure 7). The change in slope of the cooling curve at temperature of liquidus arrest results from the heat of solidification of the α phase. Hence, point 1, where the derivative curve rises rapidly, shows the nucleation of α-Al, whereas point 2, shows growth and thickening of α-Al dendrites. Next change on the first derivative curve was characterized at 542.3°C and corresponded to the nucleation of the (α-Al2Cu) eutectic (point 3 in Figure 7) where solid fraction at this point was approximately 94%. The termination of the solidification, which corresponded to the non-equilibrium solidus temperature was observed at 532.3°C (point 4 in Figure 7) when solid fraction reaches the value of 100%. The cooling curves recorded for alloy at various cooling rates are shown in Figure 8. It is seen that formation temperatures of the various phases are changed when the cooling rate is increased. The shift magnitude increases with an increasing cooling rate. This shift changes the characteristic parameters of thermal analysis, particularly in the solidus region. The cooling rate is proportional to the heat extraction from the sample during solidification. Therefore, at a low cooling rate (0.04 °C/sec), the rate of heat extraction from the sample is slow and the slope of the cooling curve is small, creating a wide cooling curve. However, at a high cooling rate (1.08 °C/sec) the rate of heat extraction from the sample is fast, the slope of the cooling curve is steep and it makes a narrow cooling curve.
Fig. 8. Temperature vs. time cooling curves recorded for alloy at different cooling rates.

Table 3. Non-equilibrium thermal characteristics of alloy obtained during the solidification process.

<table>
<thead>
<tr>
<th>points</th>
<th>Thermal characteristics</th>
<th>(°C/sec) Average cooling rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.04</td>
</tr>
<tr>
<td>1</td>
<td>Nucleation of the primary dendrite α-Al</td>
<td>649.8</td>
</tr>
<tr>
<td>3</td>
<td>Formation of the α-Al2Cu eutectic</td>
<td>547</td>
</tr>
<tr>
<td>4</td>
<td>End of solidification</td>
<td>542</td>
</tr>
<tr>
<td></td>
<td>(°C) Solidification range</td>
<td>107.8</td>
</tr>
</tbody>
</table>

End solidification temperature changes in a more important rate than liquidus temperature, due to microsegregation effects during solidification [5]. Since the last liquid is rich of all solutes rejected by the primary solid phase, there are a lot of possibilities for secondary phase’s formation, which affects the decrease the expected solidus temperature [16]. Figure 9. represents a variation of the end solidification temperature and variation of the α-Al2Cu eutectic nucleation temperature as a function of cooling rate. As the cooling rate increases from 0.04 to 1.08 °C/sec, the α-Al2Cu eutectic nucleation temperature decrease from approximately 547°C to 540.2°C. The end solidification temperature is decreased from 542°C for the 0.04 °C/sec cooling rate to 528.8°C for 1.08 °C/sec cooling rate.
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Fig. 9. Variation of the end solidification temperature and variation of the $\alpha$-Al$_2$Cu eutectic nucleation temperature as a function of cooling rate.

**Solid Fraction**

The solid fraction at different cooling rates is calculated based on the Scheil equation (Eq. (1)) and plotted in Figure 10. As can be seen, the solidification rate ($\frac{df}{dT}$) is very high at the beginning of solidification and it will decrease at the end of solidification. In this way a large fraction of melt solidifies at the early stage of solidification and the solidification rate slows down by decreasing the temperature so that the solid fraction reaches to 93% at eutectic temperature. The curves are very consistent at the early stages of solidification (up to 80% solid) but at the end of solidification the deviation is increased especially due to more effective microsegregation.

Fig. 10. Solid fraction vs. temperature at various cooling rates.
Hardness

Figure 11. presents a variation of the hardness as a function of cooling rate. The hardness grows with increment of the cooling rate. The hardness increases from 42.8 HB for lowest cooling rate to 54.4 HB for highest cooling rate. The change of the cooling rate from 0.04 to 1.08 °C/sec causes an hardness increase of about ~19%.

Conclusions

The effect of the cooling rate on the structural features such as grain size, SDAS, eutectic fraction and thermal analysis characteristic parameters of Al-4.8 wt.%Cu alloy was examined. The conclusions drawn from this study are summarized as follows:

1. Solidification parameters are affected by the cooling rate. The formation temperatures of various phases are changed with an increasing cooling rate.
2. Increasing the cooling rate decreases significantly the Al nucleation temperature, α-Al_2Cu eutectic temperature and solidification temperature.
3. The grain size and secondary dendrite arm spacing of alloy determined by image analysis, show that the both of grain size and SDAS decrease with increasing cooling rate.
4. At different cooling rates the microstructure does not change fundamentally, but it can be noted that at lower cooling rate the quantity of trapped liquid in the interdendritic regions is lesser.

References


