The Influence of Mold Material on Cooling Curve, Solidification Parameters, and Micro-hardness of Al–6wt.%Si in Unidirectional Solidification

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Abstract. The influence of mold material on cooling curve, solidification parameters, and micro-hardness were investigated. Al–6wt.% Si in clay and stainless steel mold was directionally solidified using vertical Bridgman type furnace. The samples were heated up to 700°C at 1.9°C/s heat rate, held for 60 minutes, cooled, and withdrawn at 40 µm/s. The results show that the increasing of thermal conductivity by 72% affects cooling curve shape, solidification parameters, and micro-hardness. Furthermore, comparative evaluation of the exponent value of the function of micro-hardness to distance and micro-hardness to growth rate also have been made to proposed the range of exponent value for each mold material.

Keywords: unidirectional solidification, clay mold, cooling curve, micro-hardness

1. Introduction

Cooling curve is a plot of temperature dynamics and heat evolution during solidification processes related to phase transformation in the liquid. Temperature gradient, growth rate, and cooling rate are derived from the cooling curve. These parameters indicate the mechanism of microstructure evolution. The shape of cooling curve is affected by alloy type, compositions, and mold material.

Ceramics and metals were two types of mold materials, which were generally used in unidirectional solidification in a last decade. In metal type, there are carbon steel and stainless steel. Carbon steel mold was used by Araújo et. al and Barros et. al to investigate aluminum copper alloys [1,2]. Stainless steel was brought into practiced by Brito et. al and Verissimo et. al to study Al-Mg, Al-Mg-Si [3], and Mg-Zn [4] alloys. In the ceramic type, graphite [5–14] and alumina [15–20] were more common as mold material. Yet, there are no specific restrictions in mold materials type selection. Clay as mold material has been never been as an object of study. Clay has been widely applied in investment casting and it plays an important...
role as it can create a shell from a complicated pattern and therefore, providing an extensive information of clay as mold material will be a valuable thing.

Mold material influences the final structure of casting product by its ability to transfer heat. For instances, ceramic with 1.07 W/m.K heat transfer coefficient and stainless steel with 21.5 W/m.K heat transfer coefficient [21]. Stainless steel releases the amount of heat twenty one times bigger than the amount heat released by clay therefore this change affects the solidification behavior. However, there is still limited explanation on how much the change of heat transfer coefficient. By knowing this, ones can estimate the changes on the shape of cooling curve and solidification parameters.

Comparisons in several findings are made and dissimilarity of growth rate exponent value and microhardness values are found. Çadirli showed the relationship eutectic spacing and growth rate of Al–3wt.%Cu in ceramic mold and found the growth rate exponent value equals to 0.46 [11]. This is two-third of the growth rate exponent value obtained by Araujo et al. [1] in similar alloy composition with metal mold. Moreover, Araújo et al. compared their work to Kaya et al. and found the micro hardness values of Al–3wt.%Si in metal mold [1] are a higher than the microhardness values of Al–3wt.%Si in ceramic mold [22]. It is suspected these differences might be affected by mold material heat transfer ability.

Mold materials with its thermal conductivity is mentioned as one of major factors in determining microstructure however there have been limited explicit established explanations attributed to its effects on cooling curve and mechanical properties. Present work investigates experimentally the influences of clay and stainless steel as mold material on cooling curve, solidification parameters, microstructures, and hardness in unidirectional solidification.

2. Materials and Methods

Al–6wt.%Si samples were prepared by weighed amount of pure Al and Al–12wt.%Si in electrical furnace. Molten alloy was casted into a metal die (50 mm in length and 8 mm in diameter). The chemical compositions are presented in Table 1.

| Element | Si  | Cu  | Fe  | Mg  | Mn  | Cr  | Ni  | Zn  | Ti  | Ca  | P   | Pb  | Sb  | Sn  | Al  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| %       | 5.995 | 1.385 | 0.527 | 0.430 | 0.093 | 0.045 | 0.030 | 0.49 | 0.023 | 0.000 | 0.000 | 0.033 | 0.001 | 0.012 | 90.93 |

The cast products were machined by lathe to reduce its diameter to 6 mm. Clay and stainless steel were mold materials in this experiment. The sample was inserted in 10 mm of outer diameter, 6 mm inside diameter, and 50 mm length cylinder molds. There are two types of mold, clay with 12.75 W/m.K thermal conductivity (laboratory tested) and stainless steel with 22 W/m.K respectively [23]. Four thermocouples were attached in the mold and their location were 10 (T1), 20 (T2), 30 mm (T3) from base/the cooling pad, and another (T4) was at the top surface of the sample. Each position had 120° angle differences respect to another (Figure 1a).

These thermocouples are connected to a data logger interface with computer. The lower part of the mold was put on a stainless steel withdrawal bar and upper part was held by stainless steel holder in which was connected to a 25 mm of diameter ceramic pipe. Figure 1b illustrated schematically the apparatus arrangement and the initial position of specimen. Each sample was heated up to 700°C at 1.9°C/s heat rate in a vertical Bridgman type furnace and was kept for 60 minutes. Then, it was withdrawn downward at 0.04 mm/s and was cooled at the bottom with water-cooled system inside the stainless steel withdrawal bar simultaneously. The furnace
temperature was maintained at 700°C. A data logger recorded the temperatures data and stroke positions during the process. The recording was stopped when the position of a cylinder was out of the furnace.

![Image of thermocouple positions in a mold](image1)

![Image of scheme of equipment](image2)

Figure 1 a. Thermocouple positions in a mold, b. Scheme of equipment.

The temperatures data were plotted as a function of time along with the stroke position. The cooling rates for each thermocouple position were determined by calculating the gradient of cooling curve line between liquidus and solidus temperature [24]. The temperature gradient for each thermocouple was calculated using the measured value of ΔT and the known value of ΔX. The growth rate of each sample was determined by dividing the distance of two thermocouples with the time taken by solid liquid interface to reach the second thermocouple. The calculating method of temperature gradient and growth rate refer to Kaya et al [11] and Çadirli [6].

Each sample was sectioned along its longitudinal direction then it was cold mounted with epoxy-resin. The longitudinal section was flattened with 800, 1000, 1200, and 2000 grit abrasive paper and subsequently polished. The samples were etched with NaOH 5 pct. for microstructural analysis. Microstructures and dendrite arms spacing observation was conducted using metallurgy microscope. Image J software was used to find the percentage of eutectic silicon. Micro-hardness values were evaluated with Boehler micro-hardness using 50g load and 10s dwelling time [11] [25]. The micro-hardness value was measured at 10, 20, 30, and 40 mm from heat extraction and 3 indentations was taken in each position.

3. Results and Discussion

3.1 Cooling curve, Solidification Parameters, and Microstructure

The liquidus and solidus temperature of Al–6wt.%Si is determined by drawing a vertical line at selected composition until it intersects with liquidus and solidus temperature line at Al-Si phase diagram [26]. The liquidus and solidus temperature are 628°C and 577°C accordingly.

Experimental cooling curve of Al–6wt.%Si in clay mold shows there are two types of slopes (Figure 2a). Steep slope at the beginning of solidification indicates a rapid solidification (high cooling rate) where a great amount of heat is released while shallow slope indicates slow
cooling (low cooling rate). The cooling rate is maximum at the beginning of solidification and gradually decreases as the distance from heat extraction increases. T1 curve has the highest cooling rate by 14.569°C/s in Al–6wt.%Si cooling curve then it falls to 2.509 (T2), 2.256 (T3), and 2.287 (T4) °C/s accordingly (Figure 2b). The initial solidification time is at 9.969s as liquidus temperature (T_L) was at T1 and finished as the solidus temperature (T_S) is at 69.746s (T4).

![Figure 2 a. Al– 6wt.% Si in clay mold cooling curve and distance from heat extraction, b. Cooling rate of Al–6wt.%Si in clay mold at various thermocouple positions](image)

The slope of cooling curve of Al–6wt.%Si in stainless steel is 16 times higher in average than the slope of cooling curve of Al–6wt.%Si in clay mold. The solidification of Al–6wt.%Si in stainless steel mold occurs from 33.82s to 975.96s (Figure 3a). The major dropped of temperature is at T1 and the drop is slightly decrease as the thermocouple position away from heat extraction. The highest cooling rate is at T1 by 0.755°C/s and the lowest is at T4 by 0.105°C/s (Figure 3b).
The cooling rates are varies between each curve and it contributes to the different grain size and microstructure formation. High cooling rate at T1 in both cooling curve contribute to rapid solidification. Sudden drop of temperature does not provide allowable time for microstructures to grow and as a result fine microstructures are formed (Figure 4a, d). Coarse microstructures are found at lower cooling rate (T2, T3, and T4) (Figure 4b, c, e, f). Clay mold isolates the heat from furnace to the samples thus the heat is extracted only at the bottom and less time is needed to solidify all the liquid. While samples in stainless steel mold obtain additional heat from the furnace, therefore, the heat is maintained and slow cooling is occurred. Increasing to nearly twice-thermal conductivity of mold material decreases solidification time about 15 times, reduces about 16 times the cooling curve slope and moves the initial position of cooling curve by 23.85s to the right.

As cooling rate increases on the one hand, it increases solidification rate and triggers the formation of fine microstructure and non-equilibrium eutectics, on the other hand it decreases solidification time and dendrite arms spacing. When solidification rate exceed the interfacial diffusion coefficient over atomic distance value, solute trapping occurs [27]. However as the cooling rate decreased, more segregation occurred, it is indicated by coarse eutectic silicon in stainless steel sample (Figure 5d, e, f).

The gaps between cooling curves are related to the temperature gradient. The highest gradient in both curve is occurred adjacent to the heat extraction and it is lessening as the distance from heat extraction increases (Figure 4a). The highest gradient is at 10 mm from heat extraction point, 7.68°C/mm for clay mold and 5.6°C/mm for stainless steel mold curve. For clay mold, it gradually decreases and hits the lowest point at 20 mm and raises to 3.9°C/mm at 40 mm (end of solidification) and for stainless steel mold, it drops to 3.08 at 20 mm and finally falls to a minimum value 2.78°C/s at 40 mm. Although the details are different both curve is showing the same trends, the temperature gradient gradually is decreases as the distance is increases.

![Gradient temperature and growth rate](image-url)

**Figure 4 a.** Gradient temperature and b. growth rate of Al–6wt. %Si at 10, 20, 40 mm in two different mold materials

The temperature gradient depends on the heat released at the bottom and the side mold. Liquid metal starts to solidify at the bottom of cylinder and a great number of heat is released.
When the clay mold wall resists the additional heat, the existing heat flow is mainly on vertical direction. This causes a significant difference between two measured points in vertical direction. Unlike the condition in the clay mold, stainless steel mold wall transfers heat from the furnace to liquid thus less temperature gradient is gained. Temperature gradient data parallels with growth rate data where the growth rate of Al–6wt. %Si in clay is higher about 0.958 mm/°C in average than the growth rate of Al–6wt. %Si in stainless steel (Figure 4b). The growth rate of clay and stainless steel are as follows 1.0 to 0.868 mm/°C and 0.296 to 0.117 mm/°C. High growth rate is confirmed by the formation of microstructures, fine columnar microstructures are found in clay mold samples. This microstructure is found at 10 to 40 mm and it getting thicker as the distance increased.

Thermal conductivity of mold material affects the shape cooling curves and solidification parameters. Increasing thermal conductivity from 12.75 W/m.K to 22 W/m.K increases cooling curve time range by increasing the total solidification time about 15 times and reduces the curve slopes about 1/16 times. To solidification parameters, it increases the cooling rate about 16 times however it reduces the gradient temperature and the growth rate about 0.958 mm/°C and about 0.595 mm/s respectively.

| Clay mold                                                                                                                                         |
| a. 10-20 mm at 7.67°C/mm gradient temperature.                                                                                                   |
| b. 20-30 mm at 2.7°C/mm gradient temperature.                                                                                                    |
| c. 30-40 mm at 3.96°C/mm gradient temperature.                                                                                                  |

| Stainless steel mold                                                                                                                          |
| d. 10-20 mm at 5.6°C/mm gradient temperature.                                                                                                  |
| e. 20-30 mm at 3.08°C/mm gradient temperature.                                                                                                 |
| f. 30-40 mm at 2.78°C/mm gradient temperature.                                                                                                 |

Figure 5 Temperature gradients of clay and stainless steel mold in various positions from heat extraction and its microstructure.
Primary Dendrite Arms Spacing (PDAS) data in both sample confirms well with solidification parameters data (Figure 6). The PDAS are reducing as the distance from heat extraction increases. It also can be observed that the PDAS of the sample in clay mold has less length than the sample in stainless steel mold, this result later will affect the hardness value.

3.2 Micro-hardness

Micro-hardness values of Al– 6wt.%Si in clay and stainless steel mold as a function of distance from heat extraction shows similar micro-hardness trend. The micro-hardness values decrease as the distance increase. Maximum values of micro-hardness are obtained from the position near to heat extraction point. This relationship agrees with the cooling rate, gradient temperature, and PDAS data. High cooling rate contributes to finer microstructures. As the position is further, finer branches disappear and thicker branches exist. However, the micro-hardness values of Al– 6wt.%Si in clay mold are lower than those in stainless steel mold. The micro-hardness values of Al– 6wt.%Si in clay mold and stainless steel are from 62.2 to 46.2 kgt/mm² and from 75.8 to 57.78 kg/mm² respectively. Complete segregation is occurred in stainless steel samples due to slow cooling and triggers the formation coarse silicon, while in the clay sample the alloying elements is trapped in α-Al. These coarse silicon microstructures have higher hardness value than α-Al hardness value and it is relatively in large amount in stainless steel samples. By applying power law method, the exponent values of clay and stainless steel mold are obtained, 0.113 and 0.037 respectively. Compared to the exponent values of similar mold material, stainless steel exponents value are lower than 0.069, the exponents value obtained by Araujo et al. [1].

Figure 8 shows the variation of micro-hardness as a function of growth rate for Al–6wt.%Si in clay and stainless mold. Both curves have similar trend, the values of micro-hardness increase as the growth rate increase. Micro-hardness and growth rate relationship are expressed in form of \(HV = kV^b\). The exponent values related to growth rate of Al–6wt.%Si in clay and stainless steel were 0.2478 and 0.1334 respectively (Figure 8). The exponent value of Al–6wt.% Si in clay are higher than 0.07, the exponent value by Engin et al. [28] for Al–Ni–Fe alloys with graphite mold moreover the value are slightly under the given ranged 0.12–0.14 by Kaya et al. [22] for different binary alloy system in similar solidification condition. The
exponent value of Al–6 wt.% Si in stainless steel mold is smaller than 0.71, the exponent value of Al–6 wt.% Si in carbon steel mold by Vasconcelos et al. [29].

Figure 7 Microhardness of Al–6 wt.% Si as a function of position

Figure 8 Microhardness of Al–6 wt.% Si as a function of growth rate

4. Conclusions

Experimental investigation of the influences of clay and stainless steel as mold material on cooling curve, solidification parameters, microstructures, and hardness in unidirectional is performed. As thermal conductivity increases by 72%:

1. The time range of the cooling curve increases about 15 times and the curve slope reduces about 1/16 times.
2. The cooling rate increases about 16 times and the gradient temperature and the growth rate reduce about 0.958 mm/°C and 0.595 mm/s respectively.
3. The PDAS reduces about 98.7 to 19.6%.
4. The micro-hardness value increases about 21.8-53.4%, the function of micro-hardness to distance exponent value reduces about 67.3%.
5. The exponent value of the micro-hardness to growth rate decreases about 46.2%.

5. Acknowledgements

This work is supported by Ministry of Research, Technology and Higher Education of the Republic of Indonesia and Indonesia Endowment Fund for Education (LPDP).

6. References

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