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Study on non-equilibrium solidification microstructure of Al–Cu3–Si–Mg alloy by MMDF

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Abstract

Al–Cu3–Si–Mg wheel hubs were prepared by molten metals die forging (MMDF). The as-cast microstructure morphology of the alloy formed under pressure was observed by optical microscope and scanning electron microscope. The granular phases $\theta$ (Al$_3$Cu) were distributed in the $\alpha$–Al grains, and the cross phases $\beta$ (Mg$_2$Si) grew near the grain boundary in the $\alpha$–Al grains. Polygonal compounds $\varphi$ (Al$_5$Ti$_3$La$_2$Ce$_4$Cu) and irregular eutectic structures mainly formed by $\alpha + Al_3Cu$ eutectic formed under non-equilibrium solidification were found at the grain boundaries. $Q(Al_3CuMg_5Si_4)$ phases were found at the intersection of grain boundaries. With the increase of pressure, the proportion of irregular eutectic structures ($\alpha + Al_3Cu$) decreased from 7.3% to 5.2%. Combined with microstructure analysis and thermodynamic software analysis, the non-equilibrium solidification path was determined as follows: $L \rightarrow L + \varphi \rightarrow L + \alpha + \varphi \rightarrow L + (\alpha + e) + \alpha + \varphi \rightarrow (\alpha + e) + Q + [\alpha + \varphi] \rightarrow (\alpha + e) + Q + [\alpha + \varphi + \beta] \rightarrow (\alpha + e) + Q + [\alpha + \varphi + \beta]$

1. Introduction

As a near net molding process, molten metals die forging (MMDF) is to inject a certain amount of molten metal into the metal mold cavity and apply constant static pressure, make the molten metal solidified under the pressure. The process changes the melting point, heat transfer coefficient, solidification rate and other parameters of the material, which has the advantages of eliminating shrinkage porosity, refining grain and so on. Compared with traditional gravity casting, dense castings with high mechanical properties such as high strength and creep resistance can be obtained by MMDF [1–3]. The cooling rate of molten metal is faster and non-equilibrium solidification occurs in the MMDF process. Hence, traditional equilibrium solidification theory is no longer applicable. The non-equilibrium solidification and the solid-state phase transformation in the subsequent heat treatment process are two closely related physical processes, which together determine the final properties. In other words, the effective control of non-equilibrium solidification structures is one of the keys to the control of material properties [4–6].

Different from typical Al–Si casting aluminum alloys such as A356 (AA standard), Al–Cu3–Si–Mg wrought aluminum alloy has wider range of crystallization temperature, higher tendency of segregation and hot cracking, and worse fluidity due to its alloy element characteristics. The defects such as shrinkage porosity, intergranular segregation and hot cracking are easily to occur during the casting process of the Al–Cu3–Si–Mg wrought aluminum alloy, which reduced the forming quality and mechanical properties [7]. From the point of view of the final properties of the material, the mechanical properties of this wrought aluminum alloy prepared by MMDF are higher than those of casting aluminum alloy with similar composition. In order to realize the lightweight of military equipment, Al–Cu3–Si–Mg aluminum alloy with high strength and low density becomes the first choice [8–10]. At present, Al–Cu3–Si–Mg aluminum alloy special vehicle wheel hubs are usually produced by MMDF, which has the advantages of eliminating shrinkage porosity, accelerating cooling and refining grain, and can make up for the disadvantages of wide crystallization range and poor fluidity of Al–Cu3–Si–Mg aluminum alloy. However, those advantages are highly dependent on equipment and molds. Under certain premise during
MMDF process, the adjustment and optimization of pressure process parameters can also play a certain role [11, 12]. The importance of controlling the non-equilibrium solidification structures of Al–Cu3–Si–Mg alloy under pressure is highlighted.

At present, the influence of pressure parameter by MMDF on the solidification microstructure of casting aluminum alloy was mature, but there were few studies on the non-equilibrium solidification microstructure of Al–Cu3–Si–Mg wrought aluminum alloy by MMDF. M. Zhang et al [13] studied the influence of varying pressure on the microstructure and mechanical properties of Al–Cu-based alloy under MMDF. The study showed that with the increase of pressure, the grain size of the alloy matrix and the number of secondary dendrite arms decreased significantly, and intermetallic compounds were found at grain boundary at tensile fracture. However, the composition of intermetallic compounds and the non-equilibrium solidified microstructure at grain boundary have not been studied in detail. Chen [14] et al studied the microstructures of Thixoforming Al–Cu–Si–Mg alloy castings at different positions under the condition of MMDF. The results showed that the microscopic pores and cracks were reduced in the higher-pressure position of the castings. With the increased of casting pressure, the reticular eutectic structure at grain boundary decreased. According to the lever law of equilibrium phase diagram, the quantity of eutectic structure is a constant value when the material compositions are constant. It became a problem to understand how pressure changes the number of eutectic structures. In this study, Al–Cu3–Si–Mg aluminum alloy wheel hubs were produced by MMDF. By adjusting the pressure parameters of hydraulic machine, the non-equilibrium solidification microstructure of Al–Cu3–Si–Mg aluminum alloy and its changing rule with pressure were studied. Meanwhile, the non-equilibrium solidification path of Al–Cu3–Si–Mg alloy was revealed with the help of thermodynamics software Pandat.

2. Experimental materials and method

The experimental material in this study was based on the 2A50 wrought aluminum alloy (YS standard), raised the copper content to the upper limit of the standard, and the content of other alloying elements was slightly adjusted. The adjusted 2A50 was melted in a continuous melting furnace (YN-R-500-1200T) at 760 °C. Then poured the molten metal into transfer ladle after all the alloy melted. Added 2% rod like Al-10 La/ Ce rare earth master alloy with diameter of 10 mm and length of 50 mm into the transfer ladle for modification. Stirred the molten metal with a graphite rod coated with ZnO for 10 min until it was completely melted. 0.1% Al5Ti1B refiner was put into the bell jar and pressed into the molten metal, then degassed by argon gas for 12 min. Stirred the molten metal evenly and removed the slag. The molten aluminum alloy after refining was poured into a quantitative pouring machine (W650 SVPC) to prepare for pouring at a temperature of 739 °C. A small amount of Al–Cu3–Si–Mg aluminum alloy molten metal was taken to detect the chemical composition, as shown in table 1. It could be obvious that the content ratio of Cu: Si: Mg is about 3:1:1.

Direct MMDF method was applied to pressure solidification test of wheel hubs. The wheel hub die was installed on the THP16-3000 MMDF hydraulic machine. The die adopted concave-convex structure, which the upper and lower mold cavities were sprayed with graphite lubricant to separate the casting from the mold cavities. Punches were divided into internal punch and external punch, which have the same stroke to ensure that the outer edge and bottom of the wheel hub were under pressure. The preheating temperature of the mold was 220 °C. Then molten metal was poured into the center of the mold cavity. The punches went down at the speed of 150 mm s⁻¹ until it contacted the molten metal, and extruded the molten metal to completely fill the cavity. Four different specific pressures of 80 MPa, 92.3 MPa, 102.6 MPa and 118 MPa were used for preparation, and the pressure holding time was 27 s to obtain the wheel hubs.

The as-cast samples at the bottom of the hub under each pressure were taken. All samples were taken at the center. Metallurgical samples under different pressures were prepared according to standard. The samples were grounded with SiC sandpaper and polished with 0.3 μm Al₂O₃. The polished samples were then washed in an alcohol solution in an ultrasonic cleaner for 120 s. Finally, keller reagent (2.5%HNO₃, 1.5%HCI, 1%HF, 95%H₂O) was used to corrode for 15 s. Optical microscope (OM, DM2000) and scanning electron microscope (SEM, S4800) were used to observe the solidification microstructures, 10 fields of view were selected for observation. The Image Analysis System 11.0 was used for quantitative metallographic analysis. The secondary dendrite arm spacing (SDAS) was measured by dendrite method, the equiaxed dendrite size was measured by intercept method, and the eutectic fraction at grain boundary was measured by cell counting method.

| Table 1. Composition of Al–Cu3–Si–Mg aluminum alloy (mass fraction, %). |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Cu  | Si  | Mg  | Mn  | Ti  | Fe  | La/Ce | Al  |
| 2.4 | 0.8 | 0.56| 0.5 | 0.073| 0.1 | 0.15 | Bal |


Based on thermodynamic calculation software Pandat, the thermodynamic behavior of Al–Cu3–Si–Mg alloy during solidification was studied. In solidification simulation, the proportion of Al, Cu, Si and Mg was set as 0.9624, 0.024, 0.008 and 0.0056, respectively. The solidification temperature range was set as 0–1000 K. The non-equilibrium solidification model based on Scheil Gulliver equation was used for calculation.

3. Experimental results

3.1. Non-equilibrium solidification microstructure of Al–Cu3–Si–Mg alloy

Figure 1 shows the low-magnification optical metallography of the as-cast microstructure of Al–Cu3–Si–Mg alloy at the bottom of the hub under the specific pressure of 118 MPa. It can be observed that the non-equilibrium solidification microstructure of the Al–Cu3–Si–Mg alloy had typical fine dendrite structure (region A), accompanied by coarse equiaxed dendrite morphology (region B). The secondary dendrite arm spacing of fine dendrite in region A was about 16 ~ 17 μm, and the average diameter of equiaxed dendrite in region B was about 143 ~ 147 μm.

Figures 2–4 show the high-magnification optical metallography, scanning electron microscopy and EDS analysis of the as-cast microstructure of the Al–Cu3–Si–Mg alloy at a specific pressure of 80 MPa. According to figures 2(a), (b), it can be found that there were dark spherical particles a in the primary α–Al grains, with an average diameter of 2 ~ 3 μm and scattered distribution, the average distance between adjacent particles is 30 ~ 50 μm. The EDS analysis results of spherical particle phases in figure 2(c) show that the phases mainly contained Al and Cu elements, with a small amount of Mg, Si elements. Based on the atomic ratio of Al and Cu, it was inferred that the spherical particles were θ (Al2Cu), which were the product of secondary precipitation.
Light white polygonal phases were found in figures 3(a), (b), which were the quadrilateral or hexagonal small plane structures with side length of 15 ~ 30 μm. Most of them are distributed at grain boundaries. The EDS analysis results of polygonal phases in figure 3(c) show that these phases mainly contained Al and Ti elements, and a small amount of rare earth La/CE and Cu elements. According to the atomic ratio, those phases were Al<sub>x</sub> Ti<sub>9</sub> La<sub>2</sub> Ce<sub>6</sub> Cu intermetallic compounds.

Figures 4(a), (b) show the high-magnification optical microscope images of the grain boundary. It can be seen that the bright white phases existed at the grain boundary and filled the whole grain boundary. EDS analysis results in figure 4(c) shows that the bright white phases at grain boundary mainly contained Al and Cu elements, and the Al: Cu atomic ratio is about 2: 1. It was speculated that the bright white phases at the grain boundary were the Al<sub>2</sub>Cu phases distributed separately in the divorced eutectic structures (α + Al<sub>2</sub>Cu). In this divorced eutectic structures, eutectics α were completely separated from eutectics Al<sub>2</sub>Cu. When eutectic reaction occurs, eutectics α grew firstly by attaching to primary α–Al, and then eutectics Al<sub>2</sub>Cu grew alone at the final solidification places such as grain boundary and interdendritic region. These eutectic structures had no typical lamellar or skeletal morphology.

Figure 5 shows the SEM images and EDS analysis results of several grain boundaries. According to figures 5(a), (b), it can be seen that gray massive phases existed at some grain boundaries with side length of 3 ~ 5 μm. EDS analysis results showed that the alloying elements of the phases mainly include Si, Mn and Fe, the gray massive phases were speculated to be Fe-rich impurity phases (FeMnSi)Al<sub>6</sub>. The phases were enveloped by the eutectics Al<sub>2</sub>Cu in the divorced eutectic structures, some of their boundaries were close to the primary α–Al, while other boundaries had gaps with the eutectics Al<sub>2</sub>Cu. In figures 5(c), (d), black irregular phases e was found at some grain boundaries. EDS analysis results showed that the alloying elements of the phase were mainly composed of Cu, Mg and Si elements, and the atomic ratio of the phases was presumed to be Q (Al<sub>5</sub>Cu<sub>2</sub>Mg<sub>8</sub>Si<sub>6</sub>). These phases mainly existed at the intersection of two grain boundaries and grew at the end of eutectics Al<sub>2</sub>Cu of divorced eutectic structures. It can be seen from figures 6(a), (b) that there were some cross shaped phases f near the grain boundary in the grains, and the length of a single cross shaped phase was 1 ~ 3 μm. EDS analysis results at point F showed that the phase mainly contained Al, Mg and Si elements, and the Mg: Si atomic ratio was about 2:1. It was speculated that the cross shaped phases were Mg<sub>5</sub>Si. The spacing of single cross shaped phase was 1 ~ 2μm.
3.2. Effect of pressure on microstructure of Al–Cu3–Si–Mg alloy

Figure 7 shows the change of microstructures at the sampling center at the bottom of Al–Cu3–Si–Mg alloy hub with specific pressure. As shown in figures 7(a)–(d), it could be clearly seen that the primary $\alpha$–Al dendrites at the center of the bottom of the hubs kept refining with the increase of pressure. After the specific pressure of MMDF increased from 80 MPa to 118 MPa, the primary $\alpha$–Al secondary dendrite arm spacing decreased from 25 $\mu$m to 16.6 $\mu$m. The average diameter of equiaxed dendrite primary $\alpha$–Al decreased from 190 $\mu$m to 146 $\mu$m under increasing pressure. The variation of primary $\alpha$–Al dendrite size with pressure was shown in figure 8.

Figure 9 shows the change of eutectic structures at the grain boundaries under different pressures. It can be seen from figures 9(a), (b) that when the specific pressure of MMDF was increased from 80 MPa to 118 MPa, the Al$_2$Cu in the non-equilibrium divorced eutectic structures at the grain boundary were significantly reduced. Figure 9(c) shows the variation curve of eutectic fraction in non-equilibrium solidification at grain boundary measured by metallographic software Image Analysis System. It can be found that the non-equilibrium eutectic microstructure fraction at the grain boundary from the bottom of the hubs decreased with the increase of pressure. With the increase of pressure, the eutectic microstructure fraction at the bottom of the hubs decreased from 7.3% to 5.2%. Polygonal phases Al$_{x}$Ti$_{y}$La$_{z}$Ce$_{p}$Cu, granular phases $\theta$ (Al$_2$Cu) had no obvious change with the increase of specific pressure of MMDF.

4. Discussion

4.1. Analysis of non-equilibrium solidification microstructure of Al–Cu3–Si–Mg alloy

Through optical microscope, scanning electron microscope and EDS analysis, it can be seen that the matrix of as-cast solidification microstructure of Al–Cu3–Si–Mg alloy was composed of primary $\alpha$–Al with a small...
amount of Cu, Mg and Si elements dissolving in it. In the solidification process, due to the addition of rare earth elements La/Ce and refiner Al₅T₁₂B, fine high melting point CE-rich rare earth phases Al₅Ce and Al₅Ti formed at the initial stage of solidification. These two phases served as non-uniform nucleating particles to increase the nucleation rate and refine the as-cast microstructures. Qin et al. studied the effect of the addition of rare earth element Sr/Ce on the in situ Mg₂Si/Al–Si–Cu composites, which shows that the addition of rare earth elements Ce has a refining effect on the size of both the aluminum alloy matrix and the in situ Mg₂Si. According to the analysis of the experimental results in this paper, the addition of rare earth element La/Ce and titanium reacted to form polygon intermetallic compounds AlₓT₇₆La₂Ce₆Cu at the initial solidification stage. Such intermetallic compounds containing rare earth generally has a higher melting point. These compounds formed in the early stage of metal solidification, most of them concentrated at the grain boundaries of primary α-Al. Similar to Al₅Ce and Al₅Ti, they hindered the growth of primary α-Al grains.

The most important alloying element in Al–Cu₃–Si–Mg alloy was Cu, which accounted for 2.4% of the total element content. It can be seen from the binary phase diagram of Al–Cu, under the condition of equilibrium solidification, when Cu content was less than 5.7%, eutectic reaction did not occur when the temperature dropped to 548 °C during solidification. After the molten metal was completely solidified and cooled to room temperature, the microstructure only contained primary α-Al and the second phases precipitated from α-Al solid solution. However, in the actual solidification behavior, as long as the external conditions to promote the solidification, it belonged to the non-equilibrium solidification, especially for the solidification process of MMDF under such pressure conditions. In the solidification process of molten metal, the undercooling was increased due to the effect of pressure, and the left end point of eutectic line moved to the left, resulting in the formation of non-equilibrium solidification eutectic structures with Cu content higher than 5.7% in the

![Figure 6. SEM and EDS analysis of cross phases: (a) Cross phases near the grain boundary; (b) the cross phase growing on θ(Al₅Cu) phase; (c) EDS analysis of f point.](image)
remaining unsolidified liquid phase at the end of solidification. The content of Primary $\alpha$–Al was much higher than that of eutectic structure because the content of Cu was still low, which is much lower than that of eutectic point 33.2%. At this time, the eutectics $\alpha$, which were similar to the primary $\alpha$–Al, were dependent on the primary $\alpha$–Al to grow, while the other eutectics Al$_2$Cu were dependent on the eutectics $\alpha$ to grow at the final solidification place such as grain boundary, forming divorced eutectic structure. These irregular eutectics were the product of non-equilibrium solidification, there was no common growth interface between the two eutectic phases, and the two eutectic phases grew separately at different rates, the alternating features of the two phases completely disappeared. The Q($Al_5Cu_2Mg_8Si_6$) phases appeared at the intersection of several grain boundaries and existed at the end of irregular eutectics Al$_2$Cu, indicating that Q($Al_5Cu_2Mg_8Si_6$) phases might be formed at the last stage of solidification. At the end of solidification, Mg and Si elements were discharged due to the growth of eutectic Al$_2$Cu at grain boundary. The content of alloying elements Mg and Si in the remaining

**Figure 7.** Change of microstructure morphology at the bottom of wheel hubs with specific pressure: (a) 80 MPa; (b) 92.3 MPa; (c) 102.6 MPa; (d) 118 MPa.

**Figure 8.** Primary $\alpha$–Al dendrite size curve as a function of pressure.
unsolidified liquid phase increased, and the $\text{Q(Al}_5\text{Cu}_2\text{Mg}_6\text{Si}_6)$ phases were formed by reaction at the intersection of grain boundaries.

The dark spherical particles $\theta$ ($\text{Al}_2\text{Cu}$) were the secondary phases precipitated from primary $\alpha$–$\text{Al}$ solid solution when the temperature dropped below the eutectic line. The size of 2 ~ 3 $\mu\text{m}$ can not strengthen the matrix, it needs to be followed by solution treatment and aging to precipitate the dispersed strengthening phase to strengthen the matrix.  

### 4.2. Variation of as-cast microstructure of Al–Cu3–Si–Mg alloy with pressure

With the increase of hydraulic press pressure, the grain size of $\alpha$–$\text{Al}$ matrix at the bottom of Al–Cu3–Si–Mg alloy wheel hubs was obviously refined. On the one hand, according to the Clausius–Clapeyron relation, with the increase of pressure, the undercooling degree and the initial cooling rate of aluminum alloy melt increased, the critical nucleation size and the nucleation work decreased greatly, and the nucleation rate of primary $\alpha$–$\text{Al}$ increased. At the same time, the potential heat release of the alloy was faster, which caused the atomic diffusion in the molten metal to be blocked, thus refined the primary $\alpha$–$\text{Al}$ matrix. Therefore, the arm spacing and equiaxed size of primary $\alpha$–$\text{Al}$ dendrite decreased with increasing pressure. On the other hand, in the process of MMDF, the molten metal firstly solidified on the inner wall of the die cavity to form a metal shell. Plastic deformation occurred in the metal shell under pressure, the non-solidified molten metal was strongly fed and filled the void, caused $\alpha$–$\text{Al}$ grains at the front of the solidification interface to break and formed new crystal nuclei, which also plays a role of grain refinement. Therefore, it was easier to obtain fine and uniform structures by solidification under pressure.

At the same time, the pressure reduced the gap between the molten metal and the die, increasing the effective contact area between them, the cooling rate of solidification was also improved. Lower solidification temperature and faster cooling rate limited the movement of solute atoms in the molten metal, resulting in the decrease of diffusion coefficient of alloying elements in the liquid phase, the distribution of alloying elements in the precipitated solid phase tended to be homogenized. Alloying elements in primary $\alpha$–$\text{Al}$ solid solutions were...
higher than the equilibrium value, and the supersaturated solid solutions were formed. With the increase of specific pressure, the supersaturation of solid solution formed by solidification increased and more alloying elements were dissolved, which reduced the enrichment of alloying element atoms at the front of solidification interface, resulting in a significant reduction in the precipitation of non-equilibrium eutectic structures.

Polygonal compounds Al\textsubscript{x}Ti\textsubscript{9}La\textsubscript{2}Ce\textsubscript{6}Cu and particle phases \( \theta \) (Al\textsubscript{2}Cu) did not change significantly with pressure, due to the small content of constituent elements, and the change of pressure was not enough to change its size and morphology.

### 4.3. Non-equilibrium solidification path of Al–Cu3–Si–Mg alloy

Based on the analysis of as-cast microstructure of Al–Cu3–Si–Mg alloy, directing against the main phases such as Al\textsubscript{x}Ti\textsubscript{9}La\textsubscript{2}Ce\textsubscript{6}Cu, \( \theta \) (Al\textsubscript{2}Cu), Q (Al\textsubscript{5}Cu\textsubscript{2}Mg\textsubscript{8}Si\textsubscript{6}) and Mg\textsubscript{2}Si in the as-cast microstructure, combined with Al–Cu, Al–Ce and Al–Mg\textsubscript{2}Si phase diagrams. It was speculated that the non-equilibrium solidification path of Al–Cu3–Si–Mg alloy:

\[
L \rightarrow L + \varphi \rightarrow L + \alpha + \varphi \rightarrow L + (\alpha + e) + \alpha \\
+ \varphi \rightarrow (\alpha + e) + Q + \alpha + \varphi \rightarrow (\alpha + e) + Q \\
+[\alpha + \theta] + \varphi \rightarrow (\alpha + e) + Q + [\alpha + \theta + \beta] + \varphi
\]

Where \( L \) is the liquid phase; \( \varphi \) are the polygonal compounds Al\textsubscript{x}Ti\textsubscript{9}La\textsubscript{2}Ce\textsubscript{6}Cu; \( \alpha \) is the primary \( \alpha \)–Al; \( \alpha + e \) are the non-equilibrium solidification eutectic structures at grain boundary; \( \theta \) are the secondary precipitation Al\textsubscript{2}Cu phases; Q are the Q (Al\textsubscript{5}Cu\textsubscript{2}Mg\textsubscript{8}Si\textsubscript{6}) phases; \( \beta \) are the cross shaped Mg\textsubscript{2}Si phases.

The non-equilibrium solidification process can be expressed as: At the beginning of the solidification, when the temperature was reduced to 660 °C, due to the addition of La/Ce and Ti, the fine and high melting point rare earth phases Al\textsubscript{4}Ce and Al\textsubscript{3}Ti were first precipitated in the liquid phase, which served as non-uniform nucleation particles to increase the nucleation rate and refined the as-cast microstructure. Then the remaining Ti and Ce reacted with Al and Cu to form polygonal compounds Al\textsubscript{x}Ti\textsubscript{9}La\textsubscript{2}Ce\textsubscript{6}Cu which melting point is slightly lower than 660 °C. When the temperature decreased to about 600 °C, primary phases \( \alpha \)–Al precipitated out from the liquid phase. At this time, Al\textsubscript{4}Ce, Al\textsubscript{3}Ti and part of Al\textsubscript{x}Ti\textsubscript{9}La\textsubscript{2}Ce\textsubscript{6}Cu were enriched at the growth interface of primary \( \alpha \)–Al grains, which hindered the growth of \( \alpha \)–Al grains. With the decrease of temperature, the primary phases grew until the residual liquid phase reached eutectic composition, and \( L \rightarrow (\alpha + e) \) eutectic reaction took place at 548 °C, the divorced eutectic structures were mainly manifested in the eutectic Al\textsubscript{2}Cu formed at the grain boundaries. At the last stage of eutectic reaction, Q (Al\textsubscript{5}Cu\textsubscript{2}Mg\textsubscript{8}Si\textsubscript{6}) phases were formed at the intersection of grain boundaries due to the high content of Mg and Si in the last remaining liquid phase until the liquid phase disappeared completely. When the temperature dropped below the eutectic temperature, granular Al\textsubscript{2}Cu phases precipitated in primary solid solution \( \alpha \)–Al. When the solidification temperature was reduced to room temperature, the micro segregation of primary \( \alpha \)–Al was caused by the dragging of solute under non-equilibrium solidification condition. The closer the grain interior was to the grain boundary, the higher the alloy element content was. It led to a small amount of cross-shaped Mg\textsubscript{2}Si phases grew close to \( \alpha \)–Al grain boundaries in the grains. The non-equilibrium solidification path of Al–Cu3–Si–Mg is shown in figure 10.
4.4. Thermodynamic analysis of Solidification process of Al–Cu3–Si–Mg alloy

Figure 11 shows the curve of solid phase fraction changing with temperature during the solidification process of Al–Cu3–Si–Mg alloy. It can be found that the alloy precipitated solid phases at 912 K, the precipitation rate was fast at the beginning and then slow. The solid phases fraction increased in a parabolic form with the decrease of temperature. When the temperature reached 792 K, the residual liquid fraction was about 10%, temperature decreased slowly, and the eutectic reaction occurred at this time. At 782 K, the liquid phase disappeared completely and the liquid-solid phase transition ended. When the temperature dropped below 782 K, solid phase transition occurred.

As shown in Table 2. With the decrease of temperature, the concentration, existing phases and reactions of each alloying element in the unsolidified molten metal of Al–Cu3–Si–Mg alloy at different temperatures changed. Several important nodes were selected to demonstrate. According to the phases and reaction formula, the primary \( \alpha \)-Al with a centrocubic structure began to precipitate at 912 K as the matrix, and the primary \( \alpha \)-Al was completely precipitated at 791 K. The concentration of alloying elements in the remaining unsolidified metal increased. At 791 K, part of the face-centered cubic \( \alpha \)-Al was attached to the primary \( \alpha \)-Al, and irregular eutectics \( \text{AlCu}_\Theta \) were formed at the grain boundary of the primary \( \alpha \)-Al. The structure of the irregular eutectics \( \text{AlCu}_\Theta \) were the same as that of the secondary-precipitated phases \( \theta \) (Al\( _2 \)Cu) from the subsequent solid phase transition, which was caused by the separated eutectic reaction. Due to the non-equilibrium solidification, the temperature dropped slightly during the eutectic reaction. Before the end of the eutectic reaction at 784 K, there is still an uncured liquid phase, at which time the content of alloying elements in the liquid phase reached the highest. At 784 K, the last remaining liquid phase formed \( \text{Al}_3 \text{Cu}_2 \text{Mg}_8 \text{Si}_6 \) at the intersection of grain boundaries. At 782 K, the reaction was complete and the liquid phase disappeared. It can be found that the reaction sequence of liquid-solid phase transition calculated by thermodynamics was consistent with the predicted solidification path of Al–Cu3–Si–Mg. In addition, there was no reaction related to the cross Mg\( _2 \)Si phases and the secondary-precipitated phases \( \theta \) (Al\( _2 \)Cu) during the liquid-solid phase transition. It can be confirmed that those two phases were generated during the solid phase transition, which was also consistent with the predicted results.
5. Conclusions

In this study, Al–Cu3–Si–Mg wheel hubs were prepared by MMDF method. The as-cast microstructure of the bottom of the wheel hubs under the condition of non-equilibrium solidification and the influence of pressure on it was studied. Combined with thermodynamic calculation, the non-equilibrium solidification path of Al–Cu3–Mg–Si was predicted. The main conclusions were obtained as follows:

(1) The as-cast microstructures of Al–Cu3–Si–Mg alloy were composed of fine dendrite and coarse equiaxed dendrite α-Al. Polygon compounds Al7Ti3La2Ce6Cu and divorced eutectic structures (α + Al12Cu) were mainly found at the primary α-Al grain boundary, and the irregular bright white eutectics Al12Cu were distributed separately, while the eutectics α had no obvious characteristics. Black W (Cu9Mg7Si3Al) phases were found at the intersection of α-Al grain boundaries. Spherical granular phases (Al12Cu) were found in primary α-Al. The cross-shaped phases Mg2Si grew near the grain boundaries inside the α-Al grain.

(2) Under the condition of MMDF, the dendrites and equiaxed grains of α-Al matrix at the bottom of wheel hubs were refined with the increase of pressure. When the pressure increased from 80 MPa to 118 MPa, the secondary dendrite arm spacing and equiaxed grain average diameter of α-Al matrix decreased by 33.6% and 23.2%, respectively. The irregular eutectic fraction at grain boundary decreased from 7.3% to 5.2% with increasing pressure. Polygonal phase Al7Ti3La2Ce6Cu, spherical granular phase (Al12Cu) had no obvious change with pressure.

(3) Combining with the as-cast microstructure, phase diagram analysis and thermodynamic calculation, the non-equilibrium solidification path of Al–Cu3–Si–Mg alloy was predicted:

At the initial stage of solidification, fine rare earth phases Al4Ce and Al7Ti with high melting point first precipitate in liquid phase, then polygonal compounds Al7Ti3La2Ce6Cu were formed with a lower melting point. With the decrease of temperature, the liquid phase precipitated the primary phases α-Al, the primary phases grew until the remaining liquid phase reached the eutectic point of Al–Cu phase diagram and the eutectic reaction occurred. After the completion of Al–Cu eutectic reaction, the content of Mg and Si elements in the remaining liquid phase were highest, and Cu9Mg7Si3Al phases were formed at the intersection of grain boundary until the liquid phase disappeared completely. When the temperature was lower than eutectic temperature, granular Al12Cu phases were precipitated in primary α-Al. When the alloy was cooled to room temperature, a small amount of cross-shaped Mg2Si grew in the primary α-Al grain near the grain boundaries.

(4) For the liquid-solid phase transition, the thermodynamic analysis results agreed well with the predicted solidification path.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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