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Increasing the Liquidus Temperature by Employing the Controlled Diffusion Solidification (CDS) Process: A Potential Route to Improved Castings

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Abstract. Recent theories suggest the existence of an incubation time, over which a liquid alloy prepares for nucleation by decomposing into compositional fluctuations. Accordingly, in a recent work by the present authors, the solidification path of a Controlled Diffusion Solidification (CDS) mixture was calculated. The calculated CDS path begins at a higher liquidus temperature comparing to conventional solidification and the fraction solid values are achieved at a relatively higher temperature. To provide information on the CDS mechanism and physical structure of the CDS mixture in the mushy zone, Al-7.8Zn-2.6Mg-2Cu alloy was solidified, in this study, via conventional and CDS process in the presence and absence of recalescence. Typical grain structures obtained via the two solidification conditions is characterized using Electron Back Scattered Diffraction. Results showed that the nucleation continues to occur in the presence of recalescence, while it is suppressed in its absence. According to the two step nucleation theory, the increase in the nucleation temperature causes sufficient recalescence in the mixture, allowing the un-nucleated liquid phase to decompose into chemical fluctuations and prepares for further nucleation. As a result, in the presence of recalescence, nucleation in a CDS mixture is not as readily halted as during the conventional solidification, which is in contradiction with the recent theories developed based on the classical theory of nucleation.

1. Introduction

Controlled Diffusion Solidification (CDS) process is a relatively novel casting method to be used for near net shape casting of wrought aluminum alloys ^[1,2]. Wrought aluminum alloys are single phase alloys, the low fraction of non-equilibrium liquid during the later solidification stages, leave them very brittle and prone to hot tearing, thereby non-castable ^[3]. By taking the advantages of mixing two precursor melts with different thermal mass at a definite mass ratio, which are held nearly above their respective liquidus temperatures, the CDS process results in a microstructure mostly composed of globular equiaxed grains ^[4]. The facilitated feeding associated with the globular structure is claimed as the main reason of reduction in the hot tearing susceptibility of the alloys by CDS processing which enables shape casting with wrought aluminum alloy ^[4-6].

The intrinsic difficulty associated with experimental and numerical study of the dynamic events occurring in the liquid state and during the course of mixing led researchers to follow some hypothetical



mechanisms based on the phenomenology of the process, and to focus pragmatically on the improvement of properties in the cast parts produced via CDS process. Therefore, the main mechanism of reduction in hot tear susceptibility by CDS, which is probably dependent on some special nucleation and growth phenomena in the process, remains to be revealed.

A recent attempt by the authors showed that the early stage of solidification path follows the Scheil solidification curve of the high thermal-mass (HTM) alloy ^[7]. Using this approach and assuming the concept of continuity of the solidification path, the absolute value of fraction solids was determined. From this work it was possible to determine the onset temperature of solidification (zero fraction solid) of the CDS mixture which is the same as that of the HTM alloy. It is noteworthy that the major problem with assessing the solidification path (nucleation and growth) of a CDS mixture is the impossibility of detecting the onset of solidification. As such, the complete solidification path of a CDS mixture cannot be experimentally extracted but it can be calculated in some way ^[7]. Regarding the physical structure of the alloy within the semi-solid region, however, no information can be deduced from the solidification path obtained by the phenomenological method of Computer Aided Thermal Analysis (CATA). That is, whether solidification proceeds by non-stop nucleation or growth of some already nucleated ones remains to be understood more thoroughly.

To investigate more deeply and provide information concerning the physics of the alloy during the CDS processing, it seems necessary to make a distinction between the isothermal and non-isothermal solidification. This can help to integrate the CDS process with the conventional casting methods. The effect of recalescence becomes considerable with approaching from solidification at high cooling rates towards isothermal solidification ^[8]. Even though the isothermal solidification is not something hypothetical and occurs in some cases including the center of DC-cast ingots ^[9,10].

The recalescence has been reported as the main nucleation suppression mechanism ^[8]. When recalescence is absent, i.e. in real casting conditions of industrial cooling rates, however, nucleation is also stopped after a given solid fraction value. This has been related to formation of a “solute suppression nucleation” (SSN) zone ^[11] or “nucleation-free” zone (NFZ) ^[12] caused by the segregation of solute elements. As a result, more time is required for nucleation events to occur, over which the liquid must cool further to fulfill the undercooling required for nucleation. From another point of view, solute segregation reduces potency of nucleants deactivating them when surrounded by the segregated liquid ^[9].

These theories assume Classic Nucleation Theory (CNT) as the mechanism responsible for nucleation during every stages of solidification ^[8]. The CNT approach behaves alloy liquid like a pure one and considers simultaneous occurrence of the chemical and structural fluctuations in the liquid at some supercooling. This last is the heart of the CNT approach. A supercooled condition in the liquid is favorable to make structural fluctuations, which is an athermal transition. At the same time, however, it disfavors chemical fluctuations which is a diffusion controlled process dependent on the temperature. Moreover, due to the presence of heterogeneous nucleation sites or intentionally added grain refiners, there requires only negligible amount of supercooling. It should be noted here that only 1% of the total added inoculants take part in the nucleation process ^[13]. Hence, the suppression effect by inoculant deactivation caused by solute segregation which necessitates only a marginally higher constitutional supercooling may not be significant.

In contrast to the CNT, Two-Step Nucleation (TSN), or Homophase Fluctuation Mediated (HFM), theory ^[14,15] believes in the formation of a metastable phase (homophase), wherein the stable solid nuclei will be formed subsequently. More accurate understanding of the nucleation suppression phenomenon is required to be considered under the TSN concept to improve the prediction models for grain size.

The main purpose of this study is to provide information regarding the physical structure of the mush of an AA 7xxx alloy during the CDS process. The recently obtained solidification path for the CDS processed alloy ^[7] is used in this study to describe the nucleation suppression mechanism according to the TSN approach.

2. Experimental procedure

Precursor melts used in this investigation as the high thermal-mass (HTM) and the low thermal-mass (LTM) alloys were respectively Al-Mg_{3.5} and Al-Zn_{31.2}-Cu₈, which were mixed at the mass ratio (ratio between the mass of the HTM melt and that of the LTM melt) of 3 to result in the target alloy composition, Al-Zn_{7.8}-Mg_{2.6}-Cu₂, during the CDS process.

The temperature of the melts before mixing were set to be marginally above the corresponding liquidus temperatures (5 °C). It should be noted that the successful response of this precursor couple to CDS process has been previously reported in Ref. ^[16].

The CDS mixture was immediately cast into a metallic mould which was used for cooling curve measurement and thermal analysis. This mould was a steel cup having a uniform thickness of 1 mm, coated by BN and preheated at 500 °C. The aim was to investigate isothermal solidification of CDS mixture. Another die with a cylindrical shape, and an inner diameter of 15 mm and a height of 100 mm was used to investigate the solidification behaviour of the CDS mixture under a low recalescence condition. The cooling rate of metal in the solidification range was 3 °C/s in the die and 0.17 °C/s in the steel cup.

The cross section of the castings was examined using a field emission scanning electron microscope (FE-SEM) equipped with an electron back-scattered diffraction (EBSD) probe to study the grain structure of the specimens. For EBSD characterization, the samples, preliminary prepared according to standard metallography procedure, were etched in 1 M NaOH solution at 60 °C for 90 s and rinsed in HNO₃ for 30 s in order to remove Beilby layer on the specimens ^[17].

3. Results and discussion

The nucleation suppression phenomenon in the alloys has been described so far based on the CNT approach, which cannot provide information concerning the pathway of atoms leading towards nucleation. A better realization of the phenomenon is needed keeping in mind the theory of Ostwald's rule of stages ^[18] or a TSN approach being able to provide information regarding pre-nucleation events occurring in the liquid state.

The calculated CDS path evidences that the first nuclei form at higher temperature, and the solidification proceeds to its end at a relatively higher temperature comparing to conventional solidification. At any given temperature, the value of fraction solid is higher in the CDS case comparing to conventional solidification ^[7]. Whether the increase in solid fraction is by nucleation or growth of the present nuclei can be realized through post-mortem examination of the grain structure and grain size distribution.

Fig. 1 shows the quaternion misorientation (QM) maps of a relatively large area of the samples solidified in the absence (die) and presence (steel cup) of recalescence, respectively shown in Figs. 1a and 1b. The different colours in the QM maps refer to different orientations, and therefore individual grains. The grain structure of both the specimens is equiaxed, even though it seems the number of large grains is greater in absence of recalescence. This can be better addressed through the statistical distributions of the grain size, which are shown in Fig. 2. As observed the log-normal distribution fits well with both the graphs, showing that nucleation suppression occurs to some extent in both the solidification conditions. The first inflection point can be interpreted as the onset of nucleation suppression or the size at which the growth begins to dominate the process of solidification ^[19]. Accordingly, nucleation is suppressed at a grain size of 38 µm in the absence of recalescence. The corresponding size in the recalescence condition is 63 µm. This comparatively larger value of the grain size at the onset of nucleation suppression can be directly related to the coarsening of grains.

According to the grain size distributions and the QM maps, it seems the grains are uniformly graded in the presence of recalescence as compared with those in the recalescence-free condition, where they are well-graded. That is, recalescence caused the grains to be all about the same size. Moreover, the coarse tail of the fit curve (Fig. 2b) approaches to a non-zero value showing that the coarse grains are

formed as a result of a re-nucleation phenomenon leading to this higher-kinetics nucleation. It should be noted that the total number of grains in the constant area of the QM maps shown in Fig. 1, is higher in the recalescence condition.

Recalescence and solute segregation are well-known as the main nucleation suppression mechanisms during conventional solidification of alloys. It seems, however, they cannot suppress nucleation events in the isothermally solidifying CDS mixture. Moreover, athermal nucleation is believed as the mechanism by which nucleation keeps continuing during the non-isothermal solidification; i.e. higher cooling rates. As discussed, in the absence of recalescence, nucleation get ceased at a relatively smaller grain size or solid fraction. The athermal nucleation is therefore not effective to promote nucleation rate in a CDS mixture. This clearly demonstrates that CNT fails to predict the nucleation rate for CDS process.

This non-conventional behaviour can be explained by assuming the TSN theory which in contrast with the CNT requires some chemical fluctuations to precede the formation of stable solid nuclei. According to the TSN mechanism, the nucleation of stable crystalline nuclei occurs in two steps: formation of a metastable (intermediate) phase followed by appearance of the crystalline nuclei inside it. In contrast to the later step which is a diffusionless transformation, the former is diffusion-controlled and its kinetics depends upon the temperature.

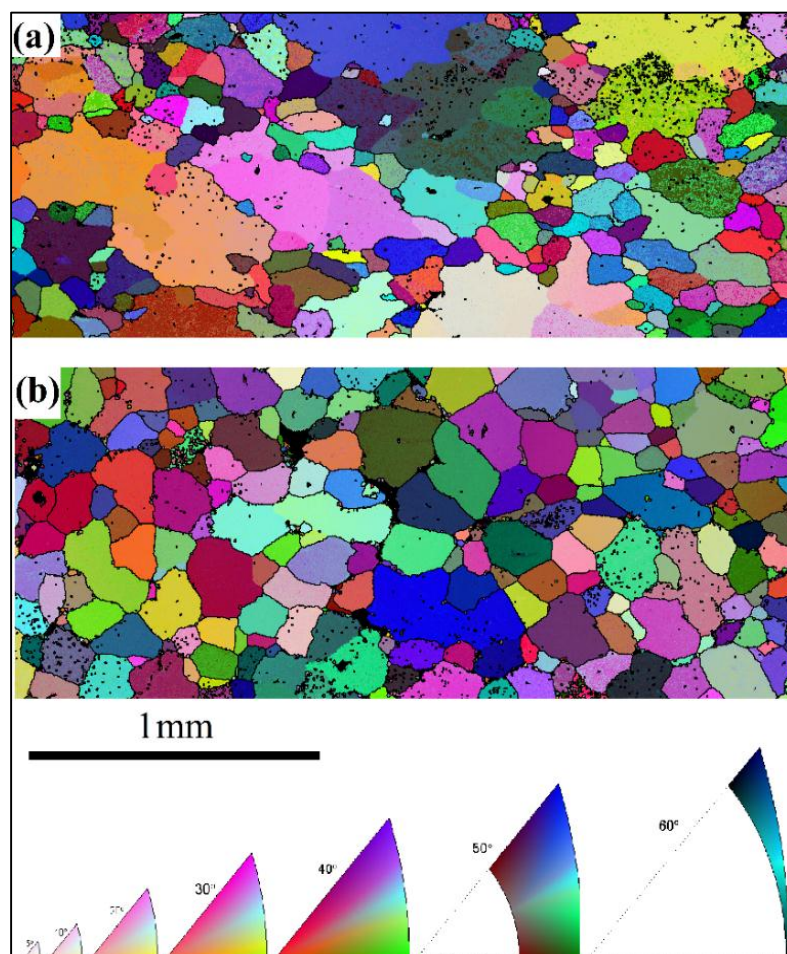


Figure 1. Quaternion maps of the typical grain structure of the specimens solidified in the (a) absence and (b) presence of recalescence.

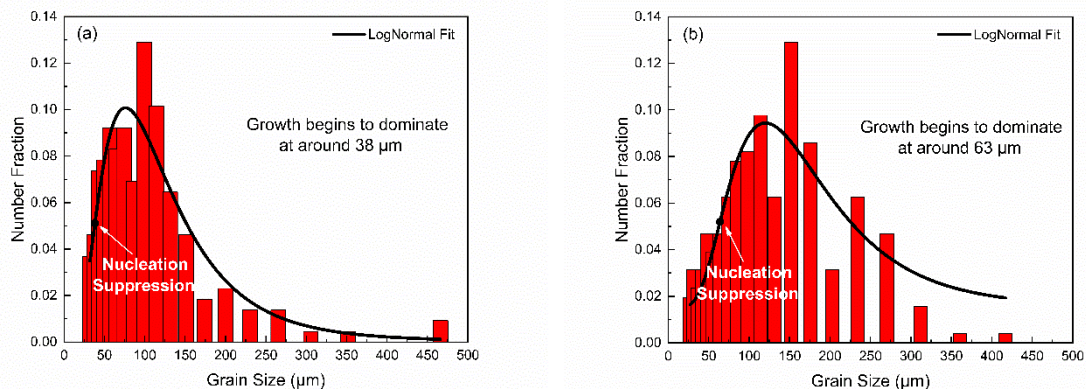


Figure 2. Distributions of the grain size referred to quaternion maps shown in Figure 1 at (a) absence and (b) presence of recalescence. The log-normal distribution fits on the data and the growth begins to dominate respectively at around size of 38 and 63 μm .

The SSN and NFZ theories are developed based on the assumption of the CNT approach. Accordingly, the retardance or suppression of nucleation is because of the insufficient constitutional supercooling in the liquid caused by decreasing either the liquidus temperature or nucleant's potency. Based on TSN, for non-stop nucleation in the liquid alloy, the formation of a metastable phase (chemical fluctuations) is mandatory. Suppression of nucleation in the CDS mixture in the absence of recalescence means that, it is this step which retards further nucleation. As the liquid is not prepared for nucleation, the atoms prefer to add to the already formed nuclei through atom-by-atom absorption ^[20] (a manner which is completely different from the concept of wetting which is required according to the CNT) and continue the solidification process in this way. Similarly, the latent heat of solidification leading to the recalescence in the case of very low cooling rate or isothermal solidification accelerate the first step by increasing the atomic mobility. As a result, nucleation in the CDS mixture is not ceased in the presence of recalescence. This, however, may raise a new question: why does recalescence cease nucleation in the case of conventional solidification? The answer would be the as-decomposed state of the liquid at the time when recalescence become significant in a CDS mixture. During conventional solidification, the recalescence and solute segregation are concurrent. In other words, the liquid is heating while it is enriching by segregating atoms. The un-nucleated liquid in the CDS mixture, is reached in the supercooled state where it is spontaneously decomposed to chemical fluctuations. This decomposition become accelerated by latent heat induced due to solidification of already formed grains. As a result, the un-nucleated liquid prepares for formation of stable nuclei.

Conclusions

Two-step nucleation theories are demanded to be used instead of the somehow ill-defined classical nucleation theory to justify the nucleation suppression phenomenon in metallic alloys. The results of the current study show that, in contrast to the understanding based on the classical nucleation theory (CNT) approach, recalescence can help avoiding nucleation suppression in a controlled diffusion solidification (CDS) mixture.

The solute suppression nucleation (SSN) and nucleation free zone (NFZ) theories developed based on the CNT approach should be revised, considering Ostwald's rule of stages, in order to provide better prediction of nucleation rate and as-solidified grain size. Here, it was proposed that the recalescence induced by latent heat of solidification in the high thermal-mass melt, during the mechanical mixing

stage, helps the un-nucleated liquid to decompose into chemical fluctuations and through this, further nucleation becomes possible in the newly formed solute-poor fluctuations.

Dealing with shape casting with wrought aluminum alloys, the CDS process can result in a higher nucleation rate in the relatively thicker sections, where solidification proceeds at the presence of recalescence, and a lower nucleation rate in the thinner sections. As this is the shrinkage of the hotspot which imposes stress on a hot tear-sensitive region of a casting, this higher nucleation rate in the hotspot could postpone coherency point and thereby onset of shrinkage-force buildup, which would be the main mechanism of reduction in hot tearing susceptibility by the CDS process.

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