CONTROLLED DIFFUSION SOLIDIFICATION

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Abstract

Wrought aluminum-based alloys exhibit superior physical and mechanical properties compared to conventional shape casting alloys. However, wrought alloys cannot be cast into near net shapes because they develop hot tears and hot cracks during solidification. For this reason, these alloys are typically cast into ingots and are subsequently brought to final shape by mechanical processes such as rolling, extrusion, drawing and forging. These processes significantly increase the cost of the manufactured component. **Controlled Diffusion Solidification** (CDS) is a novel process that allows casting of wrought alloys directly into final shapes that are free of hot tears, thus CDS eliminates the added cost of machining. The process follows a different route from conventional casting methods. In CDS two liquid alloys of predetermined composition and temperature are mixed together so that upon solidification the resultant alloy has a globular rather than a dendritic microstructure. The hot tearing tendency of wrought alloys originates from the inadequate permeability of their dendritic network, which obstructs the flow of interdendritic liquid and hinders compensation for shrinkage. The nondendritic microstructure made possible by CDS minimizes hot-tearing thus enabling wrought alloys to be cast directly.

Keywords: *wrought Al alloys, cast alloys, hot tearing, diffusion solidification*

Introduction

Controlled Diffusion solidification (CDS), a concept that was first introduced by Apelian and Langford in 1980 [1], and further developed by Shankhar et al [2] is a process that provides alloys with globular microstructure by mixing two liquid alloys. Previous work utilizing CDS has been shown to provide globular microstructures in various alloy systems [2] but the underlying principles that govern formation of the globular microstructure are yet to be understood. The present study is intended to quantify the effect of various process variables on the formation and the stability of the globular morphology and specifically to establish an operational window for the process. Work on the mechanism and the theoretical framework is ongoing at WPI.

In separate sets of experiments the effect of superheat of the liquid aluminum (which is mixed with a lower temperature liquid alloy), the effect of cooling rate, and the effect of adding grain refiner additions to the melt were investigated.

Background

The challenge we face in the CDS process is the mixing of two melts that are both near their respective liquidus temperatures. Experimentally, we have verified with various different Al based systems that through this reaction-mixing process we can obtain globular microstructures.

In most casting processes the master alloy is melted in the furnace and alloying elements are added subsequently. Upon stirring, either mechanically or through Lorentz forces the liquid melt becomes homogeneous and is then poured. In the CDS process we start with a relatively pure liquid metal near its melting point, and pour it into a second alloy melt, which is near its liquidus. Figure 1 illustrates the CDS process; in this case, commercial grade pure Al is mixed with Al-33%Cu.

The reason why this process is different from the traditional mixing of the alloying elements in a furnace is that in CDS solidification and liquid diffusion are coupled as soon as the two liquids come into contact. Specifically, le us explore what happens upon contact of the two liquid masses. Assuming a hypothetical binary phase diagram with a eutectic point as in Figure 2 C_e is the eutectic concentration and C_o is the target alloy composition. There are three ways by which the two liquid melts may mix depending on their temperature and relative weights.
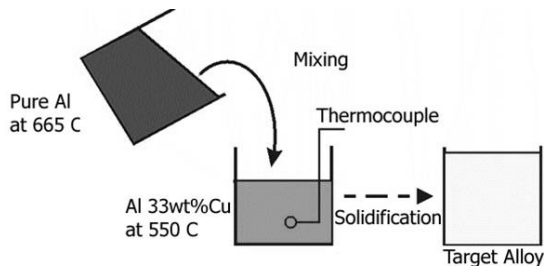
Figure 1: Schematic illustration of the CDS process applied. Pure Al is poured into a eutectic Al-33wt%Cu melt. The process temperature is monitored by means of a thermocouple that is submerged in the eutectic melt. Melting points: Al :659°C; Al-33wt%Cu: 545 ^{o}C.
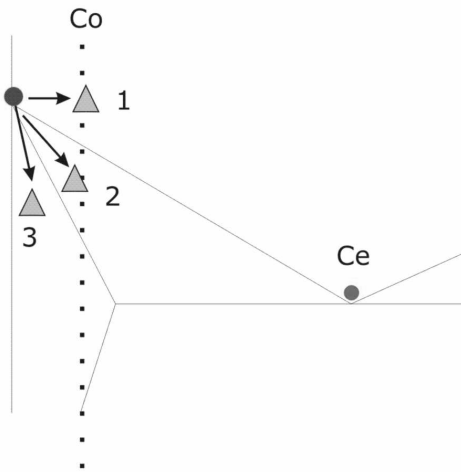

Figure 2: Hypothetical phase diagram with initial two compositions pure element (i.e., Al) and Ce (eutectic composition) showing three possible mixing paths; namely, (1) alloying , (2) reaction mixing, and (3) quenching.

Path 1: Alloying in the liquid state

If the two melts have enough superheat, they will form a homogeneous liquid melt with the target composition Co. This liquid melt will solidify with a dendritic microstructure.

Path 2: Reaction Mixing – CDS

If the superheats are controlled, such that the resulting alloy is in the two-phase region and reaction mixing will occur giving rise to a globular microstructure.

Path 3: Quenching

If the eutectic liquid mass is substantially larger than the pure liquid mass, then the pure liquid mass will be partially quenched, resulting in segregation.

Experiments were conducted to establish processing conditions that lead to *Path 2*. In brief, it has been determined that the two respective superheats of two melts and the ratio of the thermal masses are key factors that provide the limiting values for globular microstructure formation.

In general, when two alloy melts of controlled composition and temperature are brought together, two events occur: (1) thermal equilibration by the redistribution of thermal energy in the resulting alloy *via* conduction and convection, and (2) chemical equilibration by mass diffusion across the liquid interfaces. Figure 3 illustrates that once the solid has nucleated from the liquid, the absence of constitutional undercooling during the early stages of growth and convection leads to the development of a planar interface, and thus a globular primary phase [3].

In Figure 4 micrographs are presented of samples, which were prepared following the three paths shown in Figure 2. The system is Al – Al-33wt%Cu; pure Al being one melt, and the eutectic composition being the other melt.

The first sample (far left in Figure 4) was mixed with high superheats for both melts and the mixture was left to solidify. Mixing the melts with high superheats leads to the creation of a homogeneous liquid alloy with target concentration Co. As shown in Figure 4, the microstructure is dendritic and some segregation is evident because the copper is heavier and settles.

The second sample (center of Figure 4) followed the reaction-mixing path and two areas can clearly be distinguished. On the top is the dendritic region and on the bottom the globular region. The dendritic zone is most likely due to settling of the globular grains. Similar results have been reported in the literature regarding grain settling but with a different grain refining method [4].

The third sample (far right, Figure 4) was produced by mixing a small quantity of liquid aluminum with a larger quantity of eutectic melt.

The result was immediate quenching of the Al as it entered the crucible and minimum mixing between the two liquids. Air entrapment is due to rapid solidification that occurred.

C_O

C_L

T_L

T
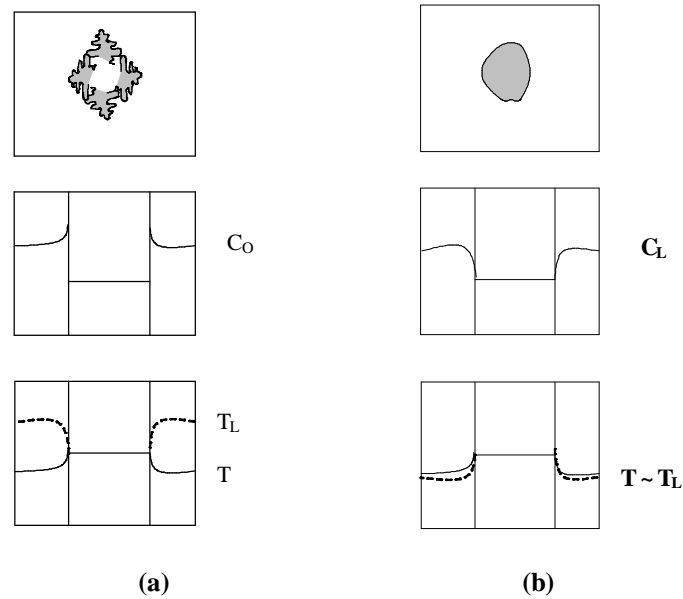
$T \sim T_L$

(a)　　　　　　　　**(b)**

Figure 3: a) Schematic showing constitutional undercooling in a free growing dendrite in an under-cooled melt. The alloy has an initial composition of C0, the solute is rejected across the interface, leading to a drop in the liquidus temperature (TL) ahead of the interface. The region between the actual temperature of the liquid (T) and TL leads to the breakdown of a planar interface into a dendritic structure; b) Schematic showing the condition when a liquid of composition CL (i.e., Al-33%Cu) is mixed with Pure Al. Clearly, growth of the structure follows the liquidus line, leading to minimal or no constitutional undercooling, and leading to a non-dendritic structure [3].
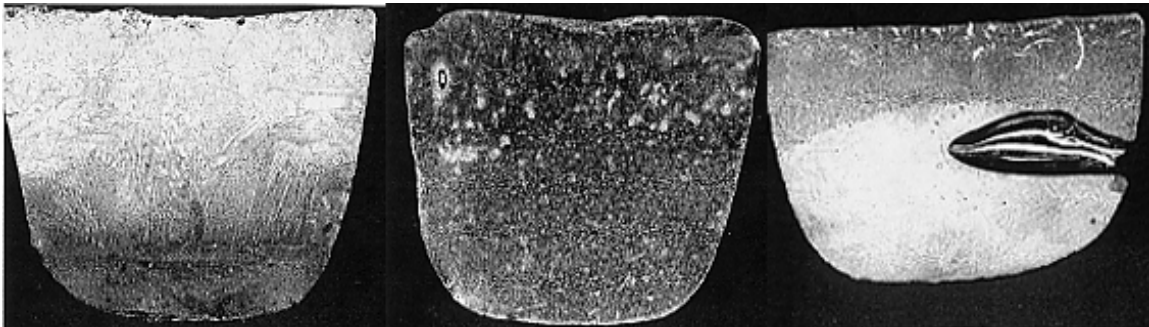

Figure 4: From left to right - 1) Homogeneous liquid solidifying, 2) Reaction mixing, and 3) Quenching.

As shown in Figure 5, 300g of pure Al liquid is kept at a controlled temperature in the resistance furnace. A thermocouple placed in the center of the melt monitors the melt temperature. In the Induction furnace, 50gr of Liquid Al-33wt%Cu is maintained at 650-700°C. The liquid Al-33wt%Cu is taken out of the furnace and placed on a refractory material. A thermocouple is inserted at the center of the melt and the temperature is monitored. When the Temperature drops to 550°C the pure Al is poured in the Al-33wt%Cu crucible (Figure 5). The alloy is left to solidify at room temperature or with forced convection. Thermal curves are recorded and

analyzed and micrographs are taken from various cross-sections.

Figure 5: Schematic diagram of mixing process.

Sample Preparation for Microstructure Evaluation

Samples were cut vertically in half with a SiC cutting wheel and one side was ground and polished with Struers SiC papers using water as a coolant. Subsequently, the samples were etched using Keller's Reagent (2.5 % HNO_3, 1.5 % HCl, 0.5 % HF, balance H_2O) for approximately 7-8 sec. Micrographs were taken from the bulk of the sample.

Sensitivity of Processing Variables

<u>*Effect of Superheat*</u>

The effect of superheat of the pure Al melt was investigated in these experiments. Three levels of superheat were evaluated, each differing by 10 ^{o}C – see Table I, below. The results show that at the higher superheat value of 682 ^{o}C the microstructure is composed of rosettes, while at lower superheats it is globular. The maximum superheat that provides globular microstructure defines the operational window. A large operational window is vital for the process, because tighter processing parameters mean reduced flexibility and increased cost in controlling the process.
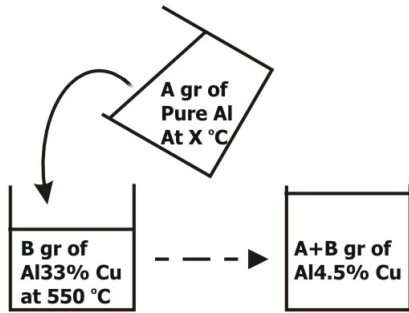
Table I: Mixing parameters and data from thermal curves.

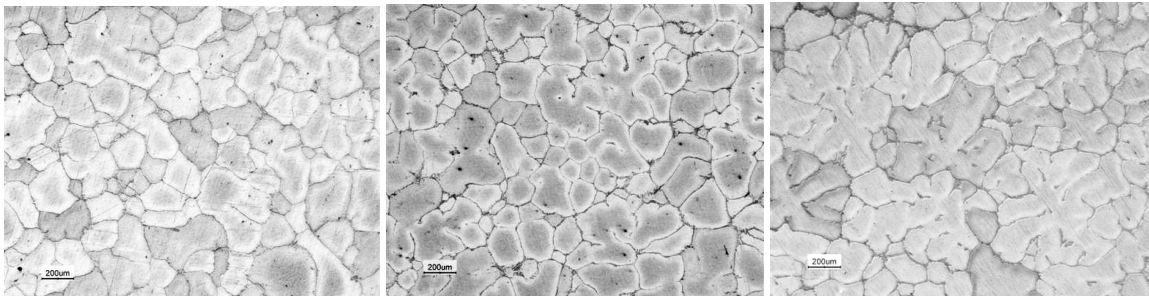| Al Pouring T (^{o}C)	Al-33wt%Cu T(^{o}C)
662	549
671	549
682	550

Figure 6: Representative microstructures from the center of the samples. Left: Al Superheat: 662 ^{o}C, middle: 671 ^{o}C, right: 682 ^{o}C.

<u>*Effect of Cooling Rate*</u>

In order to achieve globular microstructures a high nucleation rate should be followed by a slow cooling rate. At high cooling rates the evolving globular grains become unstable and become dendritic. No grain refiners were added to the system. The addition of a grain refiner would enhance the nucleation and globular stability could be attained at even higher cooling rates.

The same experimental setup is employed as above; after the melts have been mixed, three different cooling rates were imposed. The experimental results confirm the hypothesis – see Figure 7. Increased cooling rate leads to instability of the globular phase and the resulting microstructure becomes dendritic. The lower the cooling rate the more uniform and globular the microstructure is as more time is allowed for diffusion.

This result may seem to constrain the CDS process only to casting processes with a slow cooling rate. However the above results are without the presence of any alloying elements. With the presence of a grain refiner higher cooling rates should be achievable.

Table 2: Cooling rates and mixing temperatures.

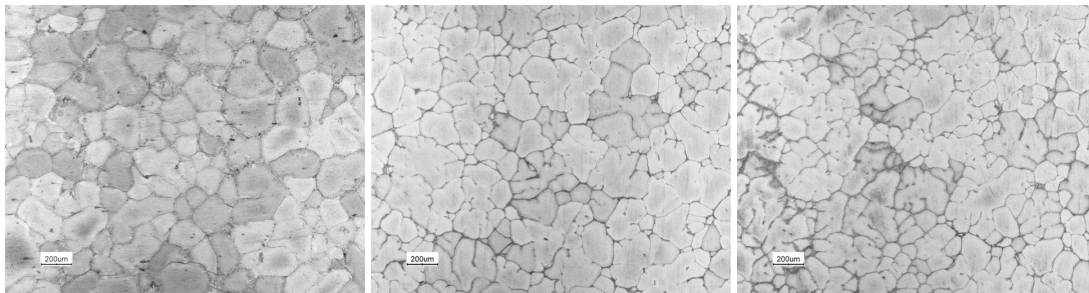| Cooling Rate ^{o}C/sec	Al Temp (^{o}C)	Al-33wt% Cu Temp (^{o}C)
0.25	660	547
0.4	660	552
1.3	660	548

Figure 7: Representative microstructures from the center of the samples. Cooling rates: left: 0.25 ^{o}C/sec, middle: 0.4 ^{o}C/sec, right 1.3 ^{o}C/sec. Lower cooling rates favor globular microstructure.

Effect of Grain Refiner Addition

When the liquid Al comes into contact with the eutectic melt it cools rapidly and nucleation commences. To investigate the effect of grain refiners added to the melt (additional nuclei), two experiments were carried out. In the first, the grain refiner Al-5wt%Ti-1wt%B was added to the pure Al prior to mixing. In the second, the GR was added to the eutectic Al-33wt%Cu prior to mixing. Finally an alloy with the target composition with grain refiner was conventionally cast.

As can be seen in Figure 8, the degree of grain refinement is much higher when the grain refiner is added in the pure Al. Grain size is smaller and the grains are uniform throughout the sample. In the other two cases there does not appear to be significant difference in grain size.
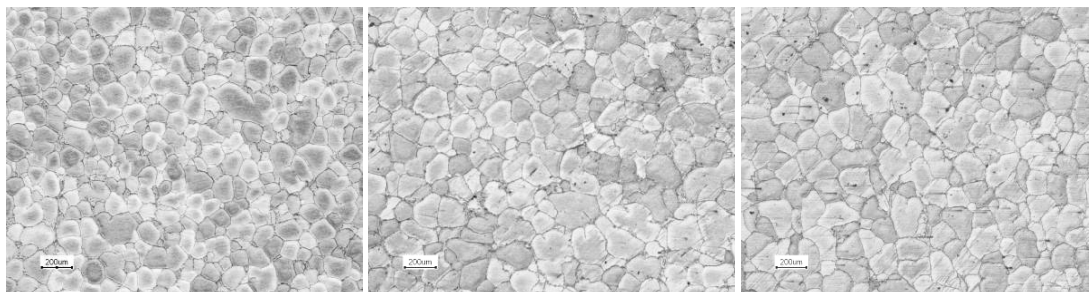

Figure 8: Representative microstructures from the center of the samples. Left: Grain refiner Al-5wt%Ti-1wt%B added to the pure Al; middle: Grain refiner added to the eutectic melt; right: Al-4.5wt%Cu grain refined and traditionally cast.

Conclusions

Following conclusions are drawn:

- Globular microstructure is attainable with Al superheat up to 10 ^{o}C.

- Lower cooling rates favor the stability of globular growth

- Presence of grain refiner (GR) eliminates the dendritic zone due to increased nucleation

- Nucleation rate and microstructure quality increases significantly when the GR is added to the pure Al melt.

- Processing variables are such that the operating window for CDS is commercially viable.

Globular microstructures and reduced grain size should minimize hot-tearing tendency of difficult to cast alloys. The binary alloy systems that should be more flexible and more efficient in obtaining globular microstructure are the ones with higher eutectic points, and the ones that have a large temperature difference between the eutectic and the pure phase. The high composition difference ensures higher diffusion rates, and the temperature difference provides a larger operational window.

References

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