Controlled diffusion solidification: application to metal casting

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ABSTRACT
Wrought aluminum-based alloys exhibit superior physical and mechanical properties compared to conventional cast alloys. However, wrought alloys cannot be cast 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. Controlled Diffusion Solidification (CDS) is a novel process that allows casting of wrought alloys directly into final shapes that are free of hot tears. 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. In the initial application of Diffusion Solidification, introduced by Apelian and Langford [1], two phases - a solute enriched liquid phase and a solute poor solid phase (held at the same temperature on the isothermal line) are brought into intimate contact, and solute diffusion from the liquid to the solid phase takes place. As the liquid loses solute, solidification.

KEYWORDS
Al-Cu alloy, solidification, globular microstructure, mixing.
proceeds via mass flow. In contrast, during conventional casting methods the alloy solidifies by extraction of heat from the melt and temperature is reduced as one moves down an iso-concentration line. Partitioning takes place and two phases are formed: primary alpha phase and enriched liquid phase. Moreover, the heat released by the liquid phase flows in the direction opposite to the motion of the liquid/solid interface and it is the heat flow that governs the solidification time. In CDS, solidification times are independent of the size of the casting since solidification is controlled by diffusion rather than heat flow.

BACKGROUND:
SOLID – LIQUID SYSTEM

The first application of CDS was the development of a rapid-cycle casting process for steel [1]. Solidification takes place by carbon redistribution between iron-saturated high-carbon liquid iron and low carbon solid iron pre-existing in a refractory mold. Liquid iron, having high carbon content is brought into contact with a low carbon solid iron isothermally, and the liquid solidifies by rejecting carbon to the surrounding solid iron. The mold is first filled with uniform-sized low carbon steel shot, then heated and subsequently infiltrated with liquid cast iron (2 to 4%) under moderate pressure. Since no heat need be rejected to the surroundings during this process, the solidification time is shorter and the economic scaling law is less dependent on the size of the casting than in conventional casting processes. By utilizing CDS, metallic systems may be cast at still lower temperatures than rheocasting.

Considering the simple binary diagram in Figure 1, conventional, rheocasting and CDS paths are directly compared. In the rheocasting process solidification occurs by manipulation of temperature on an iso-composition line, whereas the diffusion solidification process, is carried out isothermally by manipulation of composition, i.e. by solute rejection from the liquid phase. In steels, carbon diffuses into the preheated spherical low carbon steel particles out of the high carbon liquid (eutectic cast iron) under isothermal conditions. The average carbon content of the mixture is within the austenite portion of the iron carbon phase diagram so complete solidification can take place. The process has practical utility because the large solubility of carbon in face-centered cubic austenite permits the pure iron solid particles to be a sink for the carbon atoms contained in the liquid phase, which is high in carbon (cast iron).

PROCESS ADVANTAGES

In conventional casting, solidification occurs via heat transport over a temperature range and the final structure is dendritic; in CDS castings solidification occurs via mass transport, the process is isothermal and the liquid-solid front is planar. Other advantages of the CDS process are that casting takes place at a lower temperature and that the process can be carried out isothermally to cause 100% solidification and to obtain complete homogenization of the resulting casting, all without rejecting any heat to the mold. Solidification time in conventional casting processes is dependent on casting dimensions and mold characteristics. In CDS castings, the solidification time is essentially independent of casting dimensions and is controlled by the infiltrable shot size. Furthermore, the mold characteristics do not control the solidification time in CDS castings. In brief solidification time and mold filling time are shorter when compared to conventional castings.

- In conventional (sand) castings, \( t_c \) time for solidification is proportional to \( \ell^2 \) the dimensional term, length. (Chorinov’s Rule [2])
- In CDS casting on the other hand, \( t_{cds} \) is proportional to \( \ell_{molds}^2 \); where \( p \) is the infiltration pressure available [3].

The weaker dependence of solidification time on workpiece dimension can be advantageous when considering the CDS process for automation. Cycle times comparable to die casting ought to be achievable with the CDS process for die casting of steels. There is much less of a problem of thermal shock to the “die” (mold), and the microstructure of the
resultant casting is homogeneous with respect to carbon because of its rapid diffusion over these short distances. In CDS, the preheated solid particles occupy approximately 5/8 of the final volume of the casting prior to infiltration of the liquid phase; therefore, solidification shrinkage and heat of solidification to be accommodated are at least proportionately reduced. Although in conventional castings a riser is needed and the solidification shrinkage is concentrated in the last liquid to freeze, no riser is needed in diffusionally solidified castings and the solidification shrinkage is isolated, uniformly distributed and smaller in amount [4].

**METALLURGY OF CDS**

Diffusion solidification as a casting technique for steels produces unique properties and microstructures without resorting to extreme pressures, and it may therefore compete favorably with hot isostatic pressing as a way of consolidating atomized metal powder (shot). The atomized shot has the benefits of rapid solidification (because of the small size of individual particles) and of the controlled melting and solidification environments and the infiltrating liquid has the benefits of vacuum melting. Magnitude of shrinkage cavitation is controlled by particle size distribution of the shot and by the content of inclusions (such as aluminum oxide or silicates in steel). Steel castings have been made by CDS with more than 99% of theoretical density, for example [3]. Since solidification proceeds simultaneously throughout the casting during CDS, hot tearing and macrosegregation of impurities and alloying elements are decreased. The microstructure of diffusion-solidified steels is more like that of wrought steel than of cast steels - there is no columnar zone. The grain size and grain orientation of the diffusionally solidified casting is instead controlled by the grains in the initially solid portion of the charge. It is possible to produce completely homogeneous microstructures free of microsegregation by CDS since the particle size is chosen to minimize the freezing time by minimizing the diffusion distance consistent with successful forced infiltration under a reasonable external pressure. Most alloy systems to which SD can be applied are nearly completely homogenized soon after the completion of freezing. It has been discovered that it may even be possible to achieve relatively good homogenization with respect to third alloying elements (i.e. those not taking part in the basic SD mechanism, such as silicon and manganese in plain Fe-C-Mn-Si steel). Manganese, for example, can have positive microsegregation (more Mn in the last metal to freeze), and negative or even neutral microsegregation depending on whether the shot has low, high, or the same manganese concentration as the liquid. Apparently, the sharp carbon differential [3] at the solid-liquid interface and elastic interaction due to the difference in size of Fe and X atoms act to defeat the mechanism usually leading to microsegregation (slow diffusion in the solid, rapid mixing in the liquid). This is not necessarily a general phenomenon in CDS, it is only a possibility. Presumably, the liquid-state and solid-state concentrations of the third alloying elements can be made to be nearly identical at the solid-liquid interface, thus defeating the usual ternary distribution coefficient given by the ratio of the solid and liquid solubilities of that element in the alloy system. Bear in mind that CDS occurs isothermally and is a transient phenomenon between initially out-of-equilibrium components: the original solid and the infiltrant liquid. There are other advantages for CDS castings. Pieces with small surface to volume ratios or those with drastic changes in cross-section can easily be produced because the casting solidifies without rejecting heat to the surroundings. Also, the casting will be free of laps and cold shuts because the mold is heated prior to infiltration. Excellent ductility of CDS steel castings can be obtained if they are adequately infiltrated and if metallurgical bonding is achieved at the original solid-liquid interface. Surface and subsurface scales such as silicates are especially harmful and lead to doted-line fractures along the particles outlining the original shot surface. All that is necessary to correct this fault is to leave sufficient carbon in the original shot to reduce the silicates during heating to the process temperature [3]. It is even possible to reduce the shrinkage cavitation below the theoretical amount if the total number of remaining inclusions is substantially less than the number of intershot interstices [3].

**APPLICATION OF CDS TO LIQUID – LIQUID SYSTEMS**

At WPI we are investigating the application of CDS to liquid-liquid metallic systems, specifically to Al based alloys [5,6,7,8]. We have established that mixing of two liquid melts of controlled composition and temperature can yield a predominantly globular microstructure rather than a dendritic one. The formation of the globular microstructure is related to the degree of undercooling and the density of primary crystals. A model has been developed that can define the optimum process parameters in terms of degree of mixing in order to attain highly refined globular microstructures.

**CDS (LIQUID – LIQUID SYSTEM): PROCESS DESCRIPTION**

The process starts with a relatively pure liquid metal near its liquidus temperature, which is subsequently poured into a second alloy melt, which is also near its liquidus. 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 phenomena as soon as the two liquids come into contact. In Figure 2 a schematic diagram of the process is given when employed on the Al-Cu binary phase diagram. Pure Al near its liquidus is being poured in a eutectic Al-33%Cu alloy also near its liquidus. No external mixing is applied to the resulting alloy.
LIQUID-LIQUID MIXING CONSIDERATIONS

Let us explore what happens upon contact of the two liquid masses. Assume a hypothetical binary phase diagram with a eutectic point as shown in Figure 3. Ce is the eutectic concentration and Co is the target alloy composition. There are three ways by which the two liquid melts may mix depending on their temperature and relative weights.

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 3. 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 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 than the liquid 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 [9].

Fig. 2: Schematic diagram of the CDS [Liquid – Liquid system].

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

Fig. 4: From left to right - 1) Solidification of homogeneous liquid, 2) Reaction mixing, and 3) Quenching.
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.

**SENSITIVITY OF PROCESSING VARIABLES**

The objective of the following experiments was to quantify the effect of the various process variables. In this first set, we explored the effect of the superheat of the liquid-Al (which is mixed with the lower temperature liquid - the eutectic composition melt). It is important to establish this operational window because the amount of allowable Al superheat is a key factor for the development of a non-dendritic microstructure.

**EFFECT OF SUPERHEAT**

The effect of superheat of the pure Al melt was investigated in these experiments. Three levels of superheat were evaluated, each differing by 10 °C – see Table I, below. The results show that at the higher superheat value of 682 °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.

**EFFECT OF COOLING RATE**

In order to achieve globular microstructures a high nucleation rate of the solid 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 6. 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.
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 7, 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.

EFFECT OF EXPERIMENTAL VARIABLES - CONCLUSIONS

The following conclusions are drawn:
- A globular microstructure is attainable with Al superheat up to 10 °C.
- Lower cooling rates favor the stability of globular growth
- The presence of grain refiner (GR) eliminates the dendritic zone due to increased nucleation

- Nucleation rate and microstructure quality increase 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 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 temperature, 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.

APPLICATION OF CDS TO COMMERCIAL ALLOYS CASTING OF 2014 ALLOY USING CDS

In order to demonstrate the applicability of the CDS method to casting wrought alloys that belong to the 2xxx system, the CDS method was used to cast 2014 alloy having the following nominal composition,

<table>
<thead>
<tr>
<th>Cu (wt.%)</th>
<th>Minor elements</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4</td>
<td>2.0</td>
<td>Remainder</td>
</tr>
</tbody>
</table>

Precursor alloy #1 and precursor alloy #2 were poured in a crucible and allowed to mix naturally while they air-cooled – see Table III.

The measured chemistry of the resultant alloy was as follows:

<table>
<thead>
<tr>
<th>Cu (wt.%)</th>
<th>Minor elements</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.57</td>
<td>1.5</td>
<td>Balance</td>
</tr>
</tbody>
</table>

The globular microstructure is shown in Figure 8.

Table III: Chemical Analyses, Weight Fraction, and Temperature of the Precursor Alloys Used in Casting 2014 Alloy via CDS

<table>
<thead>
<tr>
<th>Chemical analysis:</th>
<th>Precursor Alloy #1</th>
<th>Precursor Alloy #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (wt.%)</td>
<td>33</td>
<td>-</td>
</tr>
<tr>
<td>Al (wt.%)</td>
<td>67</td>
<td>~98</td>
</tr>
<tr>
<td>Liquidus temperature (°C)</td>
<td>548</td>
<td>660</td>
</tr>
<tr>
<td>Weight fraction</td>
<td>~ 0.14</td>
<td>~ 0.86</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>550</td>
<td>665</td>
</tr>
<tr>
<td>Liquidus temperature of 2014 alloy (°C)</td>
<td>648</td>
<td></td>
</tr>
<tr>
<td>Maximum temperature of resultant alloy (°C)</td>
<td>646</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 8: Micrographs of a 2024 Al-Cu alloy cast by mixing Pure Al and Al-33%Cu, (a) optical image of the final solidified structure, (b) back scattered SEM image of the final solidified structure.
SUMMARY

A novel and easy to employ method has recently been devised to allow casting of wrought alloys. The method, which is referred to as Controlled Diffusion Solidification (CDS) relies on mixing two precursor liquid alloys of precisely controlled chemistry and temperature in order to produce a predetermined alloy composition. The final temperature of the resultant alloy is aimed at a temperature that is a few degrees below the alloy’s liquidus temperature, and therefore contains some fraction solid that allows fast, copious nucleation of the solid phase from the liquid phase. Consequently, the resultant alloy solidifies over a short temperature range and has a non-dendritic microstructure that minimizes its tendency towards hot tearing and makes it more amenable to casting operations, rather than the predominantly dendritic microstructure that is typical of conventionally cast alloys. In this publication, the process variables are explored and an operational window is established. In addition, the applicability of the CDS is demonstrated for commercial alloys.

REFERENCES

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