MACROSEGREGATION
IN CONTINUOUS CASTING OF PHOSPHOR BRONZE -
IMPACT ON PROPERTIES AND MODELING OF FORMATION

M. Gruber-Pretzler, F. Mayer, M. Wu, A. Ludwig
University of Leoben, Department of Metallurgy,
Christian-Doppler Laboratory for Multiphase Simulation of Metallurgical Processes
Chair of Simulation and Modelling of Metallurgical Processes
Franz-Josef-Str. 18
A-8700 Leoben
monika.gruber-prentzler@mu-leoben.at

J. Riedle, U. Hofmann
Wieland-Werke AG
Central Laboratory, Research & Development
Graf-Arco Str. 36
D-89079 Ulm
Germany

ABSTRACT

Technical Sn-bronzes tend to form both macrosegregations and microsegregations during DC-casting due to the particular thermodynamic properties and kinetics of phase transformation. As a result a heterogeneous cast microstructure forms that is sometimes a reason for a decrease in workability. The extent of macrosegregations in DC-casting can effectively be influenced by casting parameters like casting velocity, primary cooling or inlet geometry which in fact change the relative flow between the melt and the forming solid. In order to understand the influence and interaction of the related phenomena, simulation methods are applied. The solidification of the strand as well as the formation of macrosegregation are simulated with a two phase volume averaging model. The velocity field of the melt flow is explicitly calculated by solving the corresponding momentum conservation equations. Within the mushy zone the local formation of microsegregations in the presence of feeding flow is estimated. The thermodynamics of the Cu-Sn system is accounted for and it is distinguished explicitly between interface and average concentrations. To investigate the influence of feeding flow on the formation of macrosegregations, a study has been performed. Based on this result, the phenomena of macrosegregations are described in a detailed discussion.
INTRODUCTION

Phosphor bronzes (tin bronze with a phosphorus content between 0.0125 wt% and 0.25 wt%) are among the oldest engineering materials. In Europe they were intensively used from the 3rd to the 1st millennium B.C. for manufacturing almost all articles for daily life such as bowls, sculptures, jewellery, weapons etc. [1]. This period is called the bronze age because this metal played a dominant role for the people in Europe, Asia and North Africa. In America, the oldest archaeological findings were dated back to 600 A.D. Nowadays many different parts are still made from phosphor bronzes, for example electrical connectors, contact springs, plain bearings, sleeve wires, musical instruments etc. The main reasons for the widespread popularity of phosphor bronzes are their high mechanical strength, corrosion resistance, and good electrical conductivity.

The most economical way to produce phosphor bronze alloy is continuous casting. But one of the critical problems in this process is the inhomogeneous distribution of the solute elements in the solidified strand, known as macrosegregation [2]. Usually, positive macrosegregations at the billet surface and negative segregations in the billet centre are apparent. In the last decades, great efforts have been done to understand the formation of this kind of solute inhomogeneity during solidification. Therefore, as a general conclusion [3, 4, 5, 6, 7], it can be stated that macrosegregations originate from many zones processes, caused by the relative motion between the solid and the liquid phase with mechanisms such as thermal-segregation convection, forced convection, feeding flow due to solidification shrinkage, grain sedimentation, etc. Earlier work on modelling was carried out in continuous (or direct chill) castings, but mostly on Al alloys [8, 9, 10, 11]. Moreover, due to the nature of the complexity of the multiphase phenomenon, only partial success was achieved. In the later 1990's the idea to treat the mushy zone by two separated phases, i.e. the solidified dendrites and the interdendritic melt, was born [12, 13, 14, 15, 16]. Recently it was possible to develop a 3-phase model for mixed columnar-equiaxed solidification based on the previous global-equiaxed solidification approach [4, 6, 7, 18, 19, 20]. In this solidification model the morphologies of the columnar and equiaxed phases are simplified as cylinders or spheres and the competitive growth of both columnar and equiaxed phases, melt convection, equiaxed grain sedimentation, and their influence on the species transport and macrosegregation are taken into account. In previous publications [21, 22], results of different case studies, in which the individual convection mechanism are separated and combined with a study on the influence of parameters on the macrosegregation, were reported.

For the further development of the continuous casting process of bronze two strategies are necessary. It is important to improve the knowledge about the properties and workability of the alloy. On the other hand, simulation and modelling work improves the understanding of the invisible physical processes taking place during solidification. The connection between these two strategies is kept by the comparison of experimental and simulation results.

In the following experimental observations on macrosegregations in bronze continuous casting are reported. Further a detailed discussion on the development of macrosegregations during solidification is presented. The applied model is a generalization of the one-dimensional solution published by Flemings [23, 24, 25]. Therefore, we present here Flemings simple model can be used to understand the more complex case of industrial continuous casting. At the end a comparison of experimental measurements and numerical results is shown.

EXPERIMENTAL FACTS

Phosphor bronzes are alloys composed of copper (Cu), tin (Sn) and Phosphorus (P). According to European Standards the Tin content is limited to 9 wt% in wrought alloys and to 13 wt% in cast alloys. In equilibrium Tin and Copper form substitutional solid solutions up to approximately 15 wt% Sn [26]. Correspondingly, the strength of CuSn-alloys rises by increasing Tin content. This is shown in Figure 1 for the as-cast state [27] as well as for strips which were finally heat treated at 700 °C for 1 hour after several cold-work-anneal cycles. In addition, Tin ensures excellent corrosion resistance in casting processes.

The production of almost any product of bronze starts with casting. Pronounced segregation takes place in Phosphor bronzes because of the slow diffusion of Tin and the wide freezing range which extends up to approximately 200 °C [28]. The two types of segregations can be distinguished in solidified structures, namely microsegregation and macrosegregation. As it is shown in Figure 2, microsegregation can be made visible by metallurgical specimen preparation and optical microscopic methods. In the as-cast state the microstructure of CuSn8 consists of a- and β-phase which is present in the form of interdendritic precipitates. Microhardness measurements give 25.5.

Figure 1 - Ultimate tensile strength $\sigma_u$ of chill cast (line) [27] and annealed (squares) tin bronzes.
higher values for the eutectoid [23]. The wavelength A of the concentration fluctuations is in the order of 20 μm. Figure 4 displays macroscopic concentration profiles in castings of different size and shape. The Tin content measured by X-ray fluorescence spectroscopy changes over distances comparable to the dimension d of the casting. Generally, the

Figure 3 – Segregation curves across the bronze ingots of cylindrical or rectangular shape (d = dimension, x = position of chemical analysis measured from the surface, Bene = mean Tin content of the ingot, xtrue = actual Tin content at position x.)

NUMERICAL MODELING

Since a detailed description of the applied model is published in [22] the reader is referred to this paper. The main assumptions of the model can be summed up as follows:

- The thermodynamic for the binary Cu-Sn5 system is approximated by using a constant redistribution coefficient, K, and a constant liquidus slope, m. The solid fraction at the peritectic temperature reaches about 95-98 vol.%. Therefore, because the model for the peritectic reaction is still under development, it is assumed that the remaining liquid solidifies over a small temperature interval. The influence of the phosphorus is ignored up to now.
- Nucleation and growth of equiaxed grains are ignored.
- Columnar dendrites are thought to start growing at the mold wall as soon as the temperature drops below the liquidus temperature.
- Growing cylinders are used to approximate the columnar dendrites.
- A shell-like growth driven by diffusion around the cylinder is assumed.
- Corresponding source terms to account for feeding flow and thermo-solutal buoyancy driven flow are included.
- Mechanical interaction between the mesh and the flow is calculated via Darcy’s law. To model the mesh permeability the Blake-Kozeny permeability approach [17, 30] is applied.
In order to study the macrosegregation quantitatively, a mixture concentration, $c_m$, is defined according to

$$c_m = \frac{c_l \cdot \phi_l + c_s \cdot \phi_s}{\rho_l \cdot \phi_l + \rho_s \cdot \phi_s}.$$  

Here $c_l$ is the (averaged) liquid concentration, $c_s$ the (averaged) solute concentration, $\phi_l$ the volume fraction of liquid, $\phi_s$ the volume fraction of columnar dendrites, $\rho_l$ the liquid density and $\rho_s$ the solid density.

**Definition of the Benchmark**

The present study on the formation of macrosegregation is based on a calculation which takes into account feeding flow and forced convection. For the process simulation a casting velocity of $u_{cast} = 1.92 \text{ mm/s}$ and a casting temperature of $T_0 = 1389 \text{ K}$ are applied. Since the mold is of cylindrical shape, an axis symmetrical simulation has been chosen. Figure 4a shows a schematic picture of the mold where (Q) indicates the position of the nozzle, (G) shows the surface on the top, (Q) shows the upper part of the mold, (H) shows the lower part of the mold and which is assumed to be insulating, (B) shows the lower part of the graphite mold which is assumed to be insulating, (B) shows the lower part of the graphite mold which is assumed to be insulating. Figure 4b is a sketch of the considered DC casting process: (O) nozzle; (G) gas flow; (Q) graphite mold with insulation; (G) graphite and copper mold; (O) steel mold with water cooling.

**Numerical Results**

The studied continuous casting process of a CuSn alloy starts with the melt preheated to the casting temperature of $T_0 = 1389 \text{ K}$. The hot melt enters the mold through one nozzle in the center of the casting. Due to the fact that the upper part of the mold is thought to be insulating, cooling starts where the hot melt reaches the water cooled mold. Figure 5 shows the calculated steady state temperature field. Solidification starts at the liquidus temperature of CuSn, namely at $T_{liquidus} = 1292 \text{ K}$ (Q0), Figure 5 and is completed at the end temperature of $T_f = 1072 \text{ K}$ (Q9). This temperature represents the peritectic temperature of the binary CuSn system. The columnar mushy zone, extending from $T_{liquidus}$ to $T_f$, shows a volume fraction of columnar from 0 to 0.97. Based on the fact that the casting reaches a solid fraction of about 99% at $T_s$, and because the model for the peritectic reactions is still under development, it is assumed that the remaining liquid solidifies over a small temperature interval at $T_f$. Feeding flow and forced convection lead to a special flow pattern, namely in a way that besides a big
strong vortex at the inlet (I, Figure 5), a second higher velocity field appears in the mushy zone, right in the middle of the casting (II, Figure 5). Feeding flow is always directed from the dendrite tip towards its roots and thus carries segregated melt into the mush. Since the early work of Flemings in 1967 [23, 24, 25], this phenomenon is known to produce positive macrosegregation at the surface of a casting, the so-called inverse segregation. Figure 6 shows a schematically picture of growing dendrites where three different zones are considered: the liquid in front of the solidifying region, followed by

![Figure 5 - Temperature field of the casting (in K). @ T_{inlet} = 1289 K; @ T_0 = 1072 K; I: strong inlet jet; II: high velocity field in the casting centre](image)

the mushy zone with liquid and solid developing to a totally solidified zone. After Flemings [23, 24, 25] the concentration profile has negative $c_{ma}$ values in the mush whereas in the solidified casting no macrosegregation appears (black line, Figure 6). This expectation is based on a situation where the isotherms of $T_{melt}$ and $T_{solid}$ in a solidifying casting move parallel to each other due to the considered constant temperature gradient. Equ. 2 shows Flemings “Local Solute Redistribution Equation” (LSRE).

![Figure 6 - Expected one-dimensional $c_{ma}$ profile of solidifying zone after [23, 24, 25], dashed line: for increasing and dashed-dotted line for decreasing mushy zone width](image)

![Figure 7 - Macrosegregation: positive macrosegregations at the mold wall and negative ones in the centre of the casting](image)

Here $\delta$ is the solute redistribution coefficient, $v$ an independent melt velocity, $v_T$ the velocity of the isotherms, $G$ the temperature gradient and $T'$ the cooling rate. If the temperature gradient is not constant and therefore the two isotherms are not parallel, the width of the mushy zone may change. In the case of an increasing temperature gradient, the mushy zone width decreases and a negative macrosegregation forms (dashed-dotted line).
Figure 6). In the case of a decreasing temperature gradient, the mushy zone width increases and a positive macrosegregation forms (dashed line, Figure 6).

These results from Fleury's LSRE equation (Equation 2) can be understood as explained in the following: The melt enters a volume element with a concentration $c_0$ and leaves the volume element with a concentration $c_0^{*}$. During solidification, the melt becomes enriched in solute (microsegregation) and therefore $c_0^{*}$ is expected to be larger than $c_0$ (dilution). This in fact would lead to a negative macrosegregation in this volume element. However, due to solidification the volume flow of the liquid entering the volume element is larger than the volume flow of the liquid leaving the volume element. This may lead to accumulation of solute. For low solid fraction the dilution is dominant compared to the enrichment (decreasing $c_{\text{mac}}$), for large solid fraction it is the reverse (increasing $c_{\text{mac}}$).

Figure 7 shows on the left hand side a contour plot of the calculated macrosegregation pattern. The gray color shows no macrosegregation whereas the white and almost white areas (at the wall of the casting) show positive and the black areas (in the centre of the casting) negative macrosegregations ($c_{\text{mac}}$). On the right hand side several horizontal profiles are presented which were taken at 0.315, 0.405, 0.375, 0.355 and 0.305 m depth of the casting. The three concentration profiles are taken before the isotherm of $723 K$ reaches the centre of the casting. The horizontal dashed lines in the profiles show the position of the original alloy concentration (6 wt% Sn). The specific negative mixture concentration profile in the mushy zone is developed (similar as the curves shown in Figure 6). The high positive macrosegregation at the mold wall forms because of the inverse segregation. Additionally, a plateau of positive segregated solid forms attached to the inverse segregation. This positive macrosegregation is induced by the increasing mushy zone width in this area due to a decreasing temperature gradient.

Figure 8 gives a more detailed view on the macrosegregation pattern between $\beta = 0$ (volume fraction solid in the centre of the casting) and $\beta = 0.97$ at a depth of 0.315, 0.330, 0.345, 0.360, 0.375, 0.390 and 0.405 m. On the right hand side, in addition, a vertical profile along the centre of the casting is shown. Where Figure 9 shows all the profiles overlaid in a plot of $c_{\text{mac}}$ versus distance $x$ forming the centre of the billet. When reaching $\beta = 0$ (0 m) at the centre of the casting the two developed minima (left side and right side) in the mushy zone touch each other and in the following the negative values of macrosegregation in the centre increase, in our case, to a depth of 0.375 m (Figure 8 and 9).

Looking at the profiles between 0.375 m and 0.405 m it can be seen that $c_{\text{mac}}$ is increasing again to a smaller value below $c_0$. The reason for this is the fact that the centre of the casting is fed by almost fresh, less segregated melt until $c_{\text{mac}}$ reaches a minimum at 0.375 m. Following the description of Figure 6, the zone below this depth is fed by already segregated melt and therefore $c_{\text{mac}}$ increases again till the depth of 0.405 m where the fully solid zone is reached.

Figure 8 - left: Development of macrosegregations (white: positive; black: negative), between 0 and 0.97% volume fraction solid phase in the centre of the casting, right: vertical macrosegregation profile in the centre of the casting.

Figure 9 - Development of $c_{\text{mac}}$ over the casting length and the casting radius. Black dotted lines show the $c_{\text{mac}}$ profiles indicated by the gray arrows at 0.315 m, 0.375 m and 0.405 m depth, gray lines show the $c_{\text{mac}}$ profiles between 0.315 m and 0.375 m depth, black lines show the $c_{\text{mac}}$ profiles between 0.375 m and 0.405 m depth.
COMPARISON OF EXPERIMENTAL AND NUMERICAL RESULTS

By comparing an experimentally measured (Figure 10) with a calculated (Figure 11) Sn-concentration profile through the solidified casting we obtain a good qualitative agreement. By having a closer look there are especially two points that have to be discussed: First, in the experimental results higher positive macrosegregations are obtained at the wall than in the simulation result. Second, in the experiment a special W-form in the centre of the casting is observed. These two effects are not reflected in the simulation results. One reason for that could be that nucleation and sedimentation of the equiaxed grains are not taken into account yet. Another reason could be the fact that solidification does not stop at 100% solid fraction but 0.97 vol% and that the effect of Phosphor is not included. These features will be addressed in future work.

Figure 10 - Typical surface-to-surface Sn distribution in a CuSn7.6 cylindrical billet

Figure 11 - Calculated profile of Sn distribution in a CuSn6 cylindrical billet

CONCLUSIONS

The presented paper shows that macrosegregations in tin-bronzes lead to a decrease in the workability of the continuous casting product. Since macrosegregations can only be influenced economically by a special treatment during the casting process, simulation work is meaningful in order to predict the localization and strength of macrosegregations based on the process conditions. The first steps towards these predictions are done by studying the different physical phenomena occurring during solidification. It is shown that the macrosegregation pattern in the solidified strand strongly depends on the intensification of flow patterns and mushy zone development. Roughly speaking, positive macrosegregations appear in areas where the mushy zone is increasing due to a decreasing temperature gradient, while negative macrosegregations appear in areas where the mushy zone is decreasing in thickness. The simulation work qualitatively reproduces the experimental macrosegregation profiles.

Further studies are planned to investigate the influence of the casting conditions, like casting temperature, casting velocity and geometry, especially for the inlet nozzle. These studies will include the impact of the equiaxed phase and the small, but maybe not neglectable, Phosphor-content by a ternary thermodynamic model.

REFERENCES


