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

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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.

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INTRODUCTION

Phosphor bronzes (tin bronze with a phosphor 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 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.C. Nowadays many different parts are still made from phosphor bronzes, for example electrical connectors, contact springs, plain bearings, sieve 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 macrosegregations [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 general conclusion [3, 4, 5, 6, 7], it can be stated that macrosegregations originate from mushy zone processes, caused by the relative motion between the solid and the liquid phase with mechanisms such as thermal-solutal convection, forced convection, feeding flow due to solidification shrinkage, grain sedimentation, etc. Earlier work on modeling 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 phenomena, only partial success was achieved. In the later 1980's the idea to treat the mushy zone by two separated phases, i.e. the solidified dendrite 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 globular-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 permeability 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 generalisation of the one dimensional solution published by Flemings [23, 24, 25]. Therefore, we present how 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 resistant properties. Phosphorus lowers the viscosity of the melt and improves the filling capability 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 [26]. The two types of segregations can be distinguished in solidified structures, namely microsegregation and macrosegregation. As it is shown in Figure 2 microsegregations can be made visible by metallographic specimen preparation and optical microscopic methods. In the as-cast state the microstructure of CuSn8 consists of α-phase and (α+δ)- eutectoid which is present in the form of interdendritic precipitates. Microhardness measurements give 2.5 times

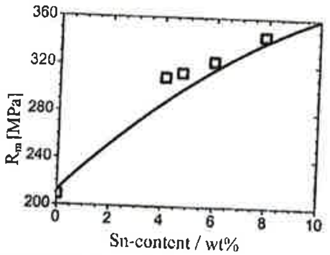

Figure 1 – Ultimate tensile strength R_m of chill cast (line) [27] and annealed (squares) tin bronzes

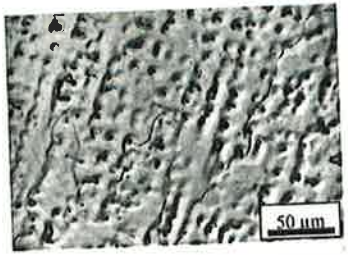

Figure 2 – Etched microstructure of as-cast CuSn8, viewed in optical interference microscope (magnification 500x)

higher values for the eutectoid [28]. The wave length λ 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

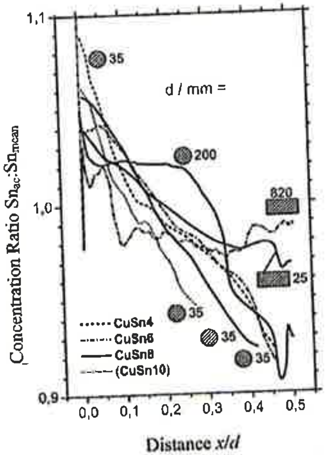

Figure 3 – Segregation curves across tin bronze ingots of cylindrical or rectangular shape (*d*: dimension, *x*: position of chemical analysis measured from the surface, Sn_{mean}: mean Tin content of the ingot, Sn_{ac}: actual Tin content at position *x*.)

Tin content in the outer parts of the ingot are significantly higher than in the centre. However, the so called inverse macrosegregation at the outer surface layer of the casting rots does not qualitatively depend on *d*.

In general segregations degrade mechanical properties. Using Figure 1 and 3, it can be estimated that the macrosegregation between the surface and the centre of the ingot lead to differences in the tensile strength R_m of at least 20 MPa. Furthermore by the enrichment of Tin towards the surface interdendritic precipitation of the δ-phase particles are pronounced. This uneven distribution of strength, hardness and brittleness of the δ-phase precipitations impedes the subsequent plastic deformation processes. Hence, undesirable segregations have to be removed. One possibility is to homogenize. The effect of homogenization heat treatment is characterised by the relaxation time $\tau = \lambda^2 / D(T)$. For example: At annealing temperature $T = 850$ °C the diffusion coefficient of Sn in Cu is given by $D = 3.9\ 10^{-9}$ cm²/s [29]. Correspondingly $\tau \approx 1000$ s for levelling microsegregation ($\lambda \approx 20$ µm) and $\tau > 30$ years for homogenisation macrosegregation in ingots ($\lambda > 20$ mm) are necessary. This example shows that the diffusion in the solid ingot is too slow to remove macrosegregation. During solidification it has to be avoided by choosing appropriate casting parameters. Therefore numerical calculations provide not only the possibility to check the influence of casting parameters on the macrosegregation distribution before doing experimental work but also provide the possibility to study the physics behind the process especially in important like the mushy zone, where measurement results are very difficult or not to obtain. The experiments then are used to evaluate the accuracy of the numerical model.

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 CuSn6 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 Phosphor 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 mush and the flow is calculated via Darcy's law. To model the mush permeability the Blake-Kozeny permeability approach [17, 30] is applied.

- In order to study the macrosegregation quantitatively, a mixture concentration, c_{mix}, is defined according to

$$c_{mix} = \frac{c_l \cdot \rho_l \cdot f_l + c_c \cdot \rho_c \cdot f_c}{\rho_l \cdot f_l + \rho_c \cdot f_c}. \tag{1}$$

Here c_l is the (averaged) liquid concentration, c_0 the (averaged) columnar concentration, f_l the volume fraction of liquid, f_c the volume fraction of columnar dendrites, ρ_l the liquid density and ρ_c 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 mm/s and a casting temperature of T_0 = 1389 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 (①) indicates the position of the nozzle, (②) shows the surface on the top, (③) shows the upper part of the mold which is assumed to be insulating, (④) shows the lower part of the graphite mold which is surrounded by a copper–steel mold including a water cooling system (⑤). Figure 4b gives an overview over the boundary conditions used. Here (①) gives the position of the inlet, where a pressure inlet is taken. A heat transfer coefficient (HTC) of h = 50 W/m²K and a nozzle temperature of T_{SEN} = 1292 K are considered for the submerged entry nozzle (SEN) region. For (②) the HTC and the temperature have a value of h = 50 W/m²K and $T_{surface}$ = 325 K. For (③) almost ideal insulation is assumed with h = 10 W/m²K and T_{mold} = 1292 K. For (④) h = 3000 W/m²K and T_{mold} = 550 K and for (⑤) h = 1000 W/m²K and T_{water} = 300 K. The constant velocity u_{cast} = 1.92 mm/s is taken for the outlet (⑥). For the nozzle and for the free surface a slip condition is used. The mold wall is assumed to move with the casting velocity. Therefore, a slip condition for the liquid phase and a non-slip condition for the columnar phase are applied. The grid has a size of 9016 cells. For initial conditions, the simulation is started with hot melt (Tin_{ll} = 1292 K) at rest (u_{cast} = 0 m/s). The presented results are taken after reaching a steady state. The conservation equations are numerically solved by using the control-volume based finite difference CFD software FLUENT, version 6.2 [31]. Additional source terms are calculated via UDF (user defined functions).

Numerical Results

The studied continuous casting process of a CuSn6 alloy starts with the melt preheated to the casting temperature of T_0 = 1389 K. The hot melt enters the mold through one nozzle in the centre 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 graphite mold. Figure 5 shows the calculated steady state temperature field. Solidification starts at the liquidus temperature of CuSn6, namely at T_{liquid} =1289 K ((①), Figure 5) and

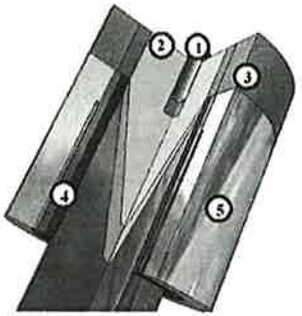

Figure 4a - Sketch of the considered DC casting process: ① nozzle; ② free surface; ③ graphite mold with isolation; ④ graphite and copper mold; ⑤ steel mold with water cooling

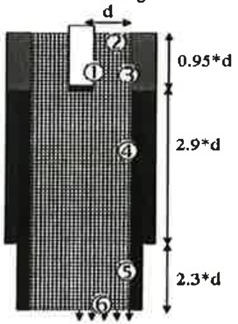

Figure 4b - Grid and interfaces for boundary conditions (details given in the text)

is completed at the end temperature of T_E =1072 K ((②), Figure 5). This temperature represents the peritectic temperature of the binary CuSn system. The columnar mushy zone, extending from T_{liquid} to T_E, shows a volume fraction of columnar from 0 to 0.97. Based on the fact that the casting reaches a solid fraction of about 97% at T_E, 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_E. 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 the mushy zone with liquid and solid developing to a totally solidified zone. After Flemings [23, 24, 25] the concentration profile has negative c_{mix} 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_{liquid} and T_{solidus} in a solidifying casting move parallel to each other due to the considered constant temperature gradient. Equ. 2 shows Flemmings "Local Solute Redistribution Equation" (LSRE).

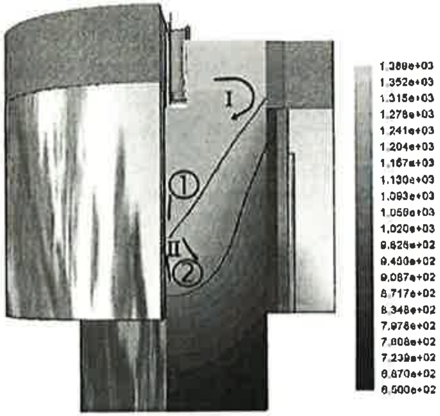

Figure 5 - Temperature field of the casting (in K). ① T_{liquid}=1289 K; ② T_{E}=1072 K, I: strong inlet jet; II: high velocity field in the casting centre

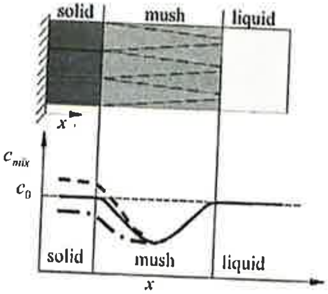

Figure 6 – Expected one dimensional c_{mix} profile of solidifying zone after [23, 24, 25], dashed line: for increasing and dashed-dotted line for decreasing mushy zone width

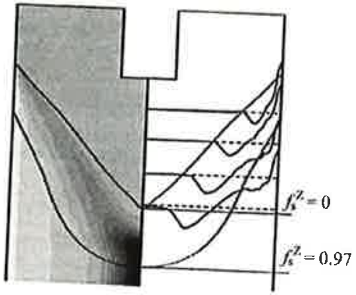

Figure 7 – Macrosegregation: positive macrosegregations at the mold wall and negative ones in the centre of the casting

$$\frac{\partial f_l}{\partial c_l} = -\left(\frac{1-\beta}{1-k}\right)\cdot\left(1+\frac{v}{v_T}\right)\cdot\frac{f_l}{c_l} \quad \text{with } \beta = \frac{\rho_c - \rho_l}{\rho_c} \quad \text{and } v_T = -\frac{\dot{T}}{G} \qquad (2)$$

Here k is the solute redistribution coefficient, v an independent melt velocity, v_T the velocity of the isotherms, G the temperature gradient and $\dot{T}$ 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 Flemings LSRE equation (Equation 2) can be understood as explained in the following: The melt enters a volume element with a concentration c_l^{in} and leaves the volume element with a concentration c_l^{out}. During solidification, the melt becomes enriched in solute (microsegregation) and therefore c_l^{out} is expected to be larger than c_l^{in} (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 (enrichment). This may lead to accumulation of solute. For low solid fraction the dilution is dominant compared to the enrichment (decreasing c_{mix}), for large solid fraction it is the reverse (increasing c_{mix}).

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_{mix}). On the right hand side several horizontal profiles are presented which were taken at 0.15, 020, 0.25 and 0.30 m depth of the cast- ing. The last concentration profile is taken before the isotherm of T_{liquid} reaches the centre of the casting. The horizontal slashed 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 $f_s^Z = 0$ (volume fraction solid in the centre of the casting) and $f_s^Z = 0{,}97$ 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_{mix} versus distance x form the centre of the billet. When reaching T_{liquid} ($f_s^Z = 0$) in 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 val- ues 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_{mix}^Z is in- creasing 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_{mix}^Z reaches a minimum at 0.375 m. Following the description of Figure 6, the zone below this depth is fed by al- ready segregated melt and therefore c_{mix}^Z increases again till the depth of 0.405 m where the fully solid zone is reached.

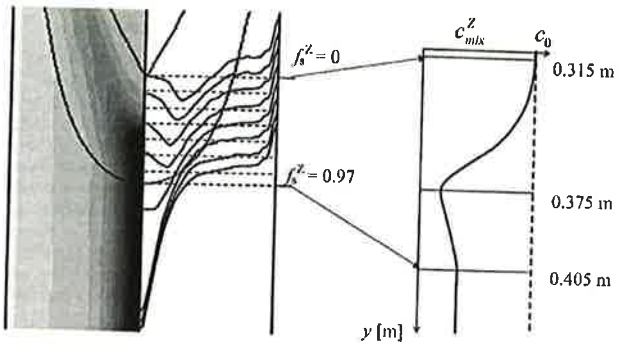

Figure 8 – left: Development of macrosegregations (white: positive; black: negative), between 0 and 0.97% volume fraction solid phase in the centre of the casting, right: vertical macrosegregation profile in the centre of the casting

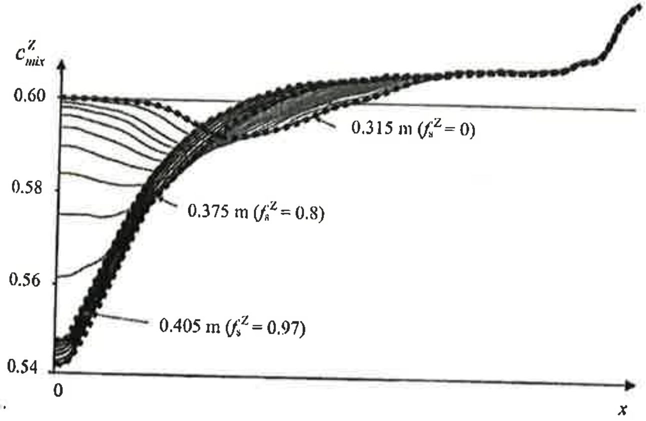

Figure 9 – Development of c_{mix} over the casting length and the casting radius x. Black dotted lines show the c_{mix} profiles indicated by the gray arrows at 0.315 m, 0.375 m and 0.405 m depth, gray lines show the c_{mix} profiles between 0.315 m and 0.375 m depth, black lines show the c_{mix} profiles 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.

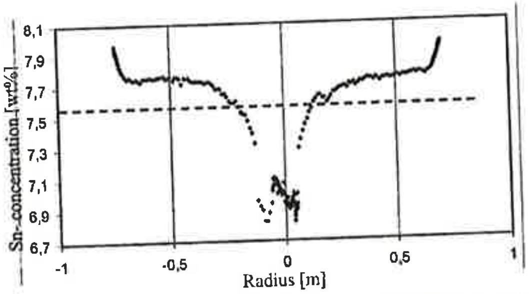

Figure 10 - Typical surface-to-surface Sn distribution in a CuSn7,6 cylindrical billet

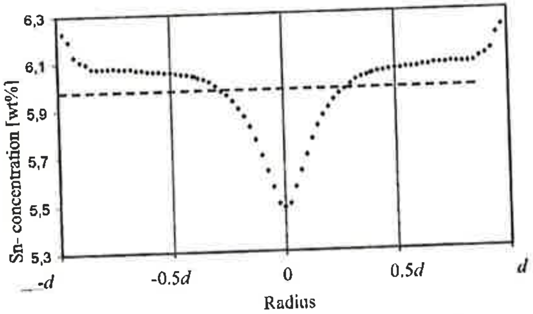

Figure 11 - Calculated profile of Sn distribution in a CuSn6 cylindrical billet

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 localisation 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 interaction of flow pattern 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 planed 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.

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