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Mechanisms of Macro-Segregation in Direct-Chill Casting of Aluminum Alloys

Dmitry Eskin
Materials innovation institute; Delft University of Technology, Mekelweg 2, 2628CD Delft, The Netherlands

This paper gives an overview on different mechanisms of macro-segregation upon direct-chill (DC) casting of aluminum alloys. With the advances in computer simulations and in experimental techniques it became possible to look at the impact of individual mechanisms in relation to the macroscopic parameters of the transition region of a DC cast billet and to the microscopic parameters of the billet structure. It is demonstrated that natural thermo-solutal convection in the liquid and slurry (semi-liquid) parts of the billet facilitates positive centerline segregation. Solidification shrinkage in the mushy (semi-solid) zone deflects the liquid flow towards the periphery of the billet and induces the negative centerline segregation, which magnitude depends on the steepness of the solidification front. The effects of thermo-solutal convection and shrinkage-induced flow depend on the structure of the billet to the extent that this structure influences the coherency and permeability of the transition region. The size of the billet, the casting speed and the presence of forced convection can change the ratio between the convective and shrinkage contributions and dramatically alter the segregation pattern. Free-floating crystals make negative contribution to the segregation in the regions of the billet where they concentrate, usually in the central portion of the billet. This is experimentally demonstrated by direct measurement of the composition of such grains and of the areas of their concentration. Their presence, however, does not necessarily mean that the segregation in the centre of the billet is negative. Other mechanisms of macro-segregation, e.g. convective flow, may compensate for the effect of free-floating grains especially in grain refined billets. Paper is illustrated by own experimental and computer-simulation results.

Keywords: *direct-chill casting; macro-segregation; convection; shrinkage; floating grains.*

1. Introduction

The fact that large-scale castings and ingots are not homogeneous with respect to their chemical composition has been known for centuries. It is widely cited that Italian metallurgist and foundryman V. Biringuccio described segregation in bronze gun barrels in his book "De la Pirotechnia" as early as in 1540. In 1574 Austro-Hungarian chemist L. Ercker published his observations of liquation in precious alloys. Most observations and studies of macro-segregation during the 19-th century has been done on precious metals, including works by W.C. Roberts-Austin (1875) and E. Matthey (1890) in Great Britain. It is acclaimed that Russian metallurgists A.S. Lavrov and N.V. Kalakutsky in 1866–1867 observed macro-segregation in steel ingots and noted that its degree depended on the size of the ingot. Lavrov wrote that the cause of macro-segregation was in the precipitation of carbon during steel solidification and accumulation of low-melting components in the center of the ingot. It was not until the beginning of the XX-th century, however, that the macro-segregation attracted real scientific interest, first as related to steel and bronze ingots and, later – to aluminum billets and ingots. We can mention the pioneering works of T. Turner, M.T. Murray, E.A. Smith, O. Bauer, H. Arndt, R.C. Reader, R. Kühnel, and F.W. Rowe in copper alloys and those of G. Masing, W. Claus, S.M. Voronov, and W. Roth in aluminum alloys (citation information is available in Ref. [1]).

During the first half of the XX-th century quite a number of theories have been suggested for the explanation of inverse segregation. These theories attempted to explain the numerous observations, some of which are summarized here. It was experimentally found that the inverse segregation occurred in alloys with a considerable freezing range and the extent of the segregation increased with the freezing range, e.g. works by Claus and Goederitz in 1928 and Voronov in 1927 and 1929. The presence of hydrogen was shown to promote exudations, while melt overheating increased the degree of segregation. Generally it was concluded by Masing and Dahl as early as in 1926 that hydrogen in aluminum alloys would adversely affect macro-segregation if it were trapped in the mushy zone. Therefore this influence was only typical of moderate cooling rates, when hydrogen was neither quenched in solid aluminum nor escaped the solidifying metal. The cooling rate was noted to be a determining factor in segregation already in early accounts, e.g. J.T. Smith in 1875. Bauer and Arndt (1921) emphasized a steep temperature gradient in the ingot as an essential condition for macro-segregation. While Voronov (1929) showed that any change in casting conditions which increased the cooling rate, i.e. reduced casting temperature, colder mold, lower pouring rate, increased mold conductivity, would increase the degree of inverse segregation in duralumin ingots.

The properties and grain structure of an alloy were also under scrutiny in relation to macro-segregation. First of all it was shown that the segregation developed during solidification and not in the liquid state as has been thought until the 1920s. The transition from the normal to inverse segregation was experimentally observed on increasing the thickness of the solidified shell of an ingot, e.g. by Fraenkel and Gödecke in 1929. The inverse segregation was often less in finer equiaxed structures than in columnar or coarse dendritic structures. This was related to the different mechanisms of feeding the solidification contraction, i.e. liquid feeding in columnar structures and mass feeding in equiaxed structure. As early as in 1925, Masing et al. correlated inverse segregation to volume contraction during solidification of metallic alloys. This theory was further developed by Phelps (1926) and Verö (1936) and formed a basis for the modern views on macro-segregation.

As applied to direct-chill casting the macro-segregation theory was developed in Russia based on the experimental studies by V.I. Dobatkin (1948), N.F. Anoshkin (1976) and V.A. Livanov (1977). The role of the formation of the macroscopically continuous and microscopically discontinuous solidification front was emphasized in the works of Dobatkin (1948). In modern terms it would be the ratio between coherency and permeability of the mushy zone. It was experimentally and analytically shown that the degree of macro-segregation is related to the shape of the billet sump and, therefore to the casting speed and the billet size. The transition between positive and negative centerline segregation was shown to be possible in dependence on the shrinkage ratio and the convection development.

The modern theory of macro-segregation was formulated in formalized in the works of M.C. Flemings in the 1960–1970s. This is essentially the modern macro-segregation theory as we know it now. Since that time a lot of efforts was devoted to the development of models for computer simulation of macro-segregation and much less – to the experimental studies.

Our work over the last 5 years was focused on finding the interaction between different macro-segregation mechanisms and on looking on the individual contributions of specific macro-segregation mechanisms.

The basics of all macro-segregation mechanisms can be formulated as the relative movement of liquid and solid phases during solidification [1, 2, 3]. This relative movement translates the partitioning of solute elements between liquid and solid phases (micro-segregation) to the difference of chemical composition on the macroscopic scale (macro-segregation). There are, however, different types of such a relative movement that are characteristic of different parts of the transition region of a casting, e.g. in the sump of a billet during direct-chill casting:

- thermo-solutal convection caused by temperature and concentration gradients, and the penetration of this convective flow into the slurry and mushy zones of a billet (see Fig. 1);
- transport of solid grains within the slurry zone by gravity and buoyancy forces, convective or forced flows;

- melt flow in the mushy zone that feeds solidification shrinkage and thermal contraction during solidification;
- melt flow in the mushy zone caused by metallostatic pressure;
- melt flow in the mushy zone caused by deformation (thermal contraction) of the solid network;
- forced melt flow caused by pouring, gas evolution, stirring, vibration, cavitation, rotation etc., which penetrates into the slurry and mushy zones of a billet or changes the direction of convective flows.

We know that commercial alloys usually solidify as dendrites, forming overall equiaxed structure in a billet. In the slurry zone (between the liquidus and the coherency isotherm in the transition region) the equiaxed grains are free to move and can travel short or long distances, depending on their size and direction of melt flow (see Fig. 1). In the mushy zone (between the coherency isotherm and the nonequilibrium solidus) however, these dendrites form a continuous solid network and have a fixed position in the billet. It can be considered that they move only in the direction of billet withdrawal and with the casting speed. Liquid flow within the mushy zone is limited to distances comparable to several grain sizes.

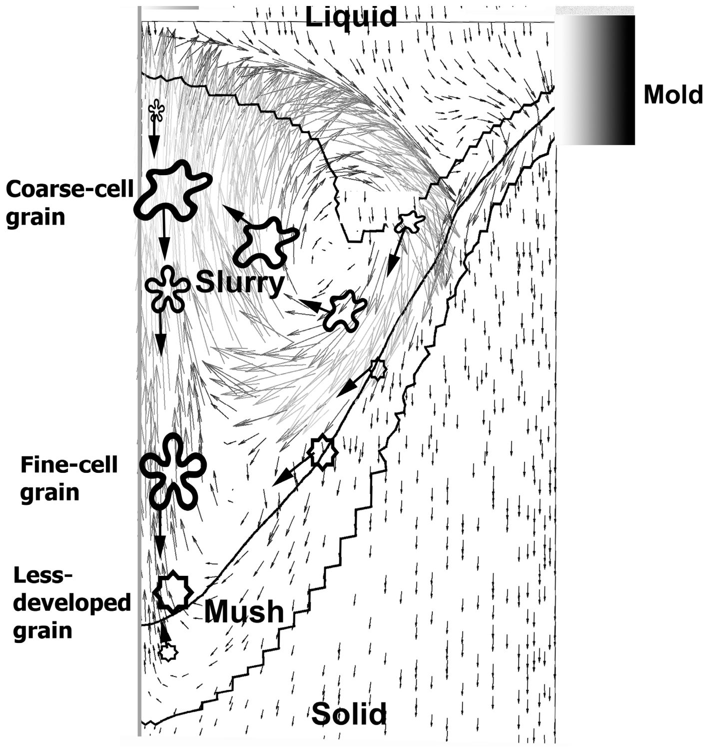
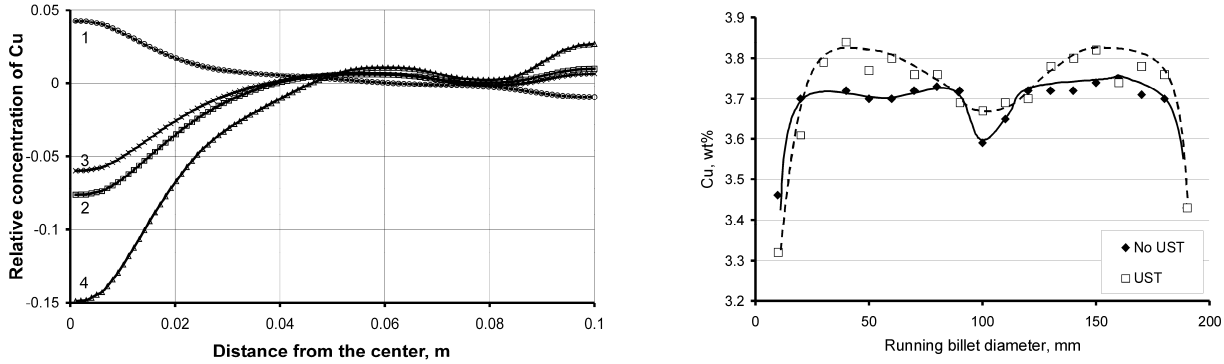


Figure 1. A scheme showing the typical melt flow pattern in the transition region of the sump of a DC cast round billet with liquidus, coherency and solidus isotherm separating liquid, slurry, mush and solid parts of the billet. Possible trajectories of free-floating crystals are shown. Only half of the billet is shown with the centerline on the left.

2. Convection-driven macro-segregation

One of the most recognized phenomena behind macro-segregation is thermo-solutal convection, or the melt flow driven by temperature and concentration gradients. These gradients exist in the liquid (or more correctly – fluid) part of a casting (billet) due to uneven cooling of the whole volume. The typical convective flow pattern in a DC cast billet is shown in Fig. 1. The main reason why this flow may affect the distribution of alloying elements in the billet cross-section is the penetration of this flow into the slurry zone and washing out of the liquid with the composition already changed by the solidification process. The interaction between the liquid pool and the transition zone of the billet was noted as the main reason for convection-driven segregation by Tageev in 1949 [4]. In addition, the thermo-solutal flow may assist in transporting the solid phase within the slurry region and to the liquid pool (see Fig. 1).



a b

Figure 2. (a) Results of computer simulation of macro-segregation with only thermo-solutal convection (1); with thermo-solutal convection and shrinkage-induced flow (2); same as 2 but with permeability of the mush increased two times (3); same as 2 but with the Scheil model of solidification (4) and (b) experimental results on macro-segregation upon DC casting of a 200-mm billet with forced centerline downward flow induced by ultrasonic horn in the hot top. Distance along diameter in (b) covers the entire billet diameter with 0 and 200 being at the surface. An Al–Cu alloy is used in all cases.

Figure 1 shows that the penetration of the melt flow into the slurry zone occurs in the outer quarter of the billet cross-section. Thus the solute-enriched liquid from this part of the billet is mixed with the bulk liquid and the resultant mixture is brought to the centre of the billet. The result is centerline positive segregation as shown in Fig. 2a by curve 1. At the billet periphery the melt flow is directed towards the surface (Fig. 1). Here the liquid of the nominal composition penetrates the mushy zone and dilutes the melt that is enriched there by solidification. Hence, a negative segregation at the billet periphery is facilitated (curve 1 in Fig. 2a). Generally, we can conclude that the natural thermo-solutal convection in DC cast billets of aluminum alloys enhances the normal (direct) macro-segregation.

It has been clearly demonstrated experimentally that the macro-segregation pattern depends on the extent and direction of convection [5]. The downward centerline flow enhances the positive centerline segregation by forcing the enriched liquid to stay and solidify in the centre; whereas the upward centerline flow facilitates negative centerline segregation, extracting the enriched liquid from the transition region. This is illustrated in Fig. 3 where the results of experiments and computer simulations are given together. In this case a mechanical pump was placed in the liquid part of the sump of the billet. Other means of forced convection may lead to similar results. As an example, Fig. 2b shows the effect of the downward forced flow induced by the ultrasonic sonotrode (horn) placed in the hot top along the centerline of the billet. Macro-segregation pattern changes with the same trend as with the pump, i.e. the extent of negative centerline segregation becomes less.

3. Shrinkage-driven macro-segregation

Historical accounts summarized elsewhere [1, 3] show that the importance of shrinkage-driven flows for the formation of inverse segregation has been realized as early as in the 1930s. The inverse segregation is caused by the movement of the solute-rich liquid in the direction opposite to the movement of the solidification front. In the case of DC casting, that would be a melt flow directed from the centre to the periphery of a billet (ingot).

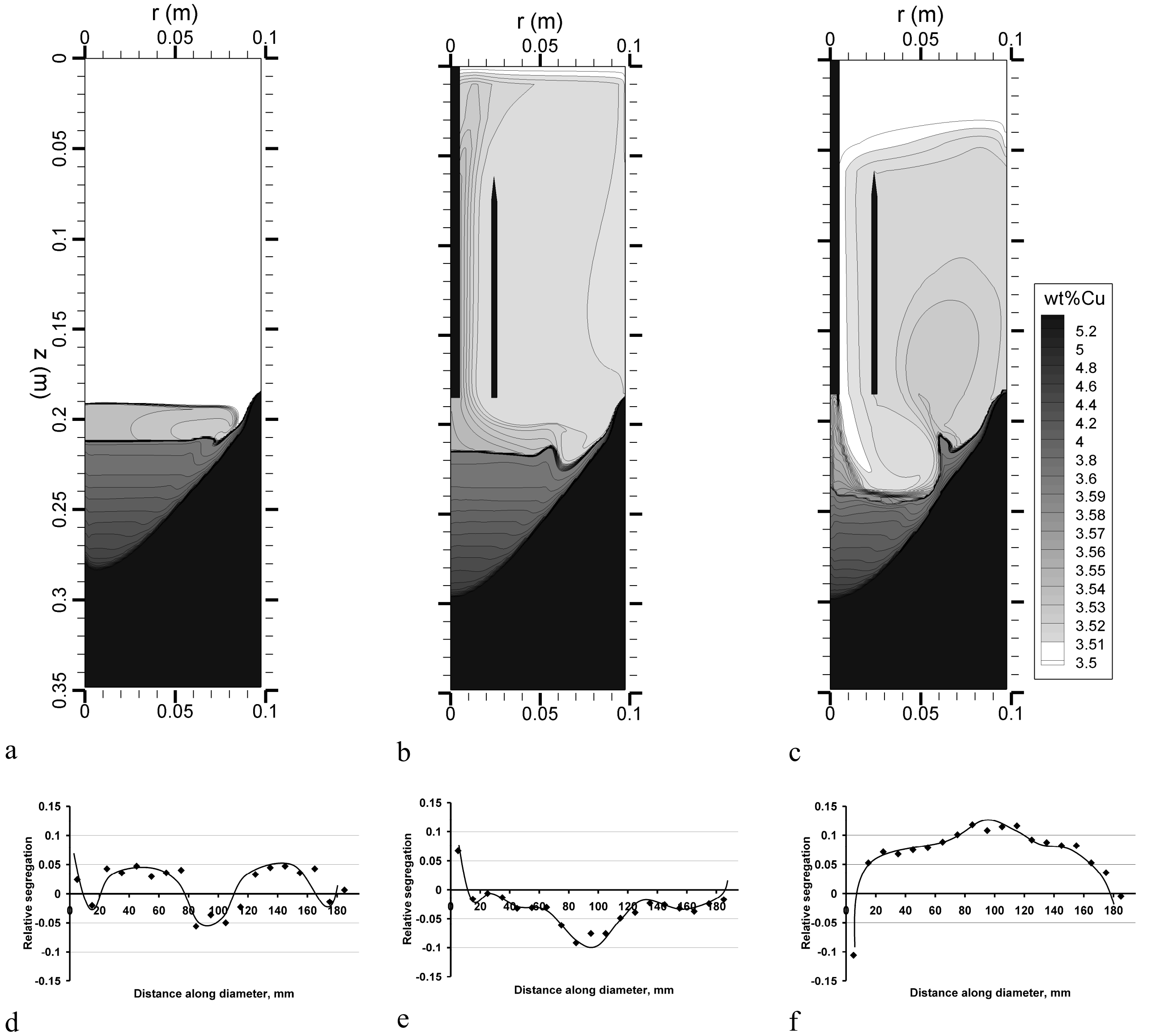


Figure 3. Effect of forced centerline convection induced by a mechanical pump on the extent and direction of macro-segregation upon DC casting of a binary Al–Cu alloy: (a, d) natural convection, idle pump; (b, e) upward forced flow; (c, f) downward forced flow. Results of computer simulation of convective patterns and copper concentration in the melt, right half of the round billet is shown (a–c) and experimentally measured relative segregation of copper across the billet diameter (d–f) [6].

Solidification shrinkage is a result of density change during solidification and occurs throughout the entire solidification range. In the slurry zone, however, the solidification shrinkage is easily compensated by the melt flow. There is no pressure difference that may result in the additional flows and the solidification shrinkage does not play any significant role in the relative movement of solid and liquid in the slurry zone, the main influence being exerted by thermo-solutal convection. Deeper into the mushy zone when the permeability is limited and the feeding of the solid phase is restricted, the solidification shrinkage (assisted closer to the solidus by thermal contraction of the solid phase) causes the pressure difference over the solidifying layer of the mushy zone that creates the driving force for the so-called “shrinkage-driven” flow. The flow in the mushy zone, in spite of its small magnitude, involves highly enriched liquid, which determines its significance for the macro-segregation. It is important that this flow is directed perpendicular to the solidification front.

The horizontal component of shrinkage-induced flow velocity vector takes the solute away from the centre to the surface, though this solute transport physically occurs very slowly. Step by step, however, an overall solute transfer occurs from the centre of the billet to its surface. The depletion in the centre cannot be compensated, as there is no horizontal inflow of the solute from more enriched regions. At the surface, there is a pile-up of the solute as there is no outflow. Because the magnitude of the shrinkage-induced flow is dependant on the shrinkage ratio, one may conclude that the corresponding macro-segregation should depend on the dimensions of the mushy zone and the degree of shrinkage. There is also a clear correlation between the shape of the solidification front and the degree of shrinkage-induced segregation, which has been noted already in the 1940s [7]. The deeper the sump, the more solute is taken from the centre of the billet to the periphery [8]. Hence, there is a direct link to the casting speed.

Computer simulations using a model that includes solidification shrinkage demonstrate the high potential of the shrinkage-driven flow in the formation of inverse segregation during DC casting [8]. Figure 2a (curves 2–4) gives a clear evidence of that. Note also the effect of permeability that is the function of structure. We can conclude that the shrinkage-induced flow is responsible for the occurrence of negative centerline segregation.

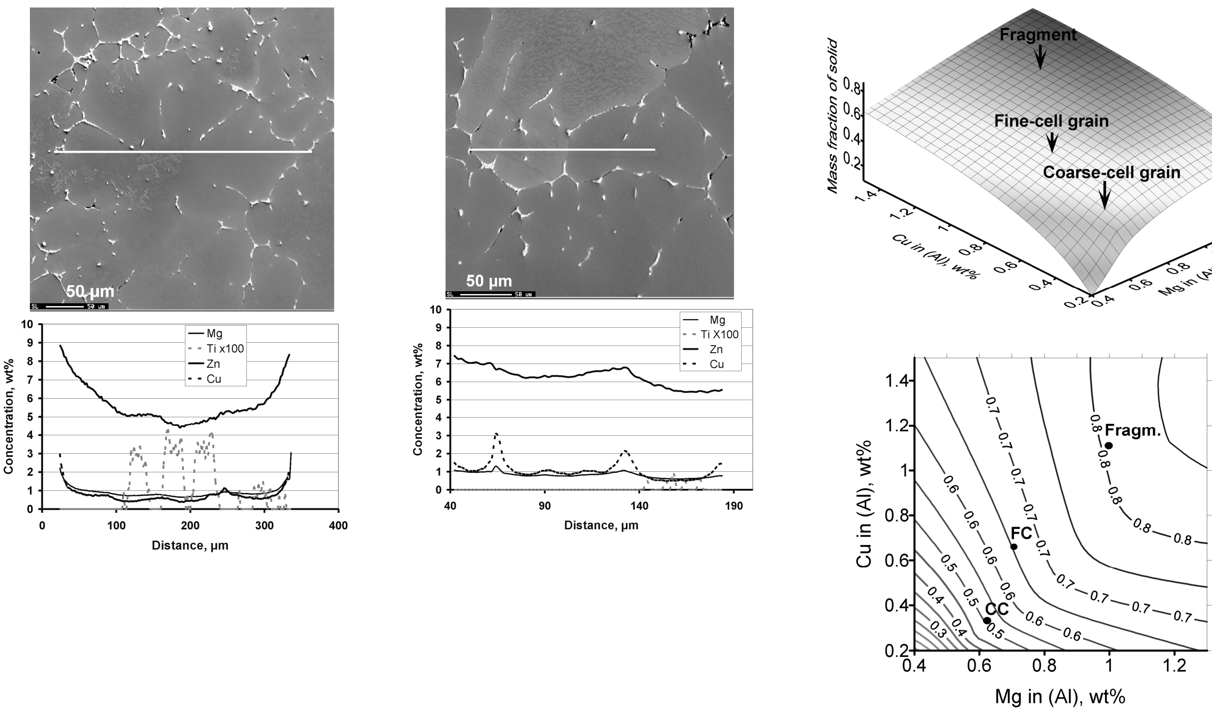
4. Free-floating grains and macro-segregation

Movement and sedimentation/growth of solid grains in the slurry zone is sometimes considered as the main mechanism of centerline segregation in DC cast billets and ingots [9, 10]. At the same time, as we discussed in the previous section, the negative centerline segregation can be explained by the action of the shrinkage-induced flow. Frequent occurrence of duplex grain structures in the center of a billet (grains with coarse and fine internal structure) is taken as an evidence of solid-phase transport (floating) within the transition region (see Fig. 1), which might effect the extent of the centerline segregation. The mainstream concept assumes that if the *coarse-cell dendrites* are solute-poor, fine dendrites (the last to solidify) are rich in solute [9, 11].

If we assume that floating grains arrive from other part of the billet and settle in its centre, then they effectively bring there more solid phase than it should be at this point at time and space. As the primary solid in hypoeutectic aluminum alloys is always depleted of the solute, the accumulation of the floating grains has to contribute to the negative segregation.

We performed electron-probe microanalysis (EPMA) measurements on several coarse and fine cells in the duplex structures found in the centre of 195-mm billets from 2024 and 7075 alloys [12, 13]. Both grain-refined (GR) and non-grain refined (NGR) alloys were tested. Line scans of Cu, Mg, and Zn concentrations in both NGR and GR DC cast samples clearly demonstrate that coarser cells are more solute-depleted as compared to the ‘regular’ finer cells. In the case of grain refining, the difference in minimum concentrations is less, probably due to a more efficient back diffusion in the finer structure. The areas occupied by fine-cell grains are close by composition to the average alloy composition or are enriched in solutes, especially in GR alloys cast at a low speed. From these measurements, the minimum Cu, Mg, and Zn concentrations in the centre of dendrite cells were tabulated. These values were then compared with the composition of the aluminum solid solution in equilibrium with the liquid during solidification and the corresponding volume fraction of solid was derived based on the Scheil solidification model using Thermocalc. The results shown in Fig. 4 clearly demonstrate that coarse-cell grains, fine-cell grains and less developed dendrites (found in grain refined 7075 alloy) have been formed in different parts of the sump as depicted in Fig. 1.

The obtained results and their analysis allow us to make the following conclusions. There are two mechanisms contributing to the negative centerline segregation: shrinkage-induced flow and free-floating grains. It is important to realize that the shrinkage-induced flow is a physical phenomenon that is always present in the transition region of a solidifying billet, whereas the transport of solute-lean solid with its accumulation in a certain part of a casting is a conditional incident, the occurrence of which depends on a number of factors such as the structure evolution, temperature regime, and the direction of strong flows.



a b c

Figure 4: Distribution of alloying elements in (a) coarse-cell and (b) fine-cell grains in the center of a grain refined 7075 alloy billet and (c) the dependence of mass fraction of solid on the composition of solid aluminum at the liquid/solid interface during solidification of a 7075 alloy. Arrows and dots show the minimum concentrations found in different grain types found in billets cast at 80 mm/min (CC–coarse-cell grain; FC–fine-cell grain; Fragm.–fragment).

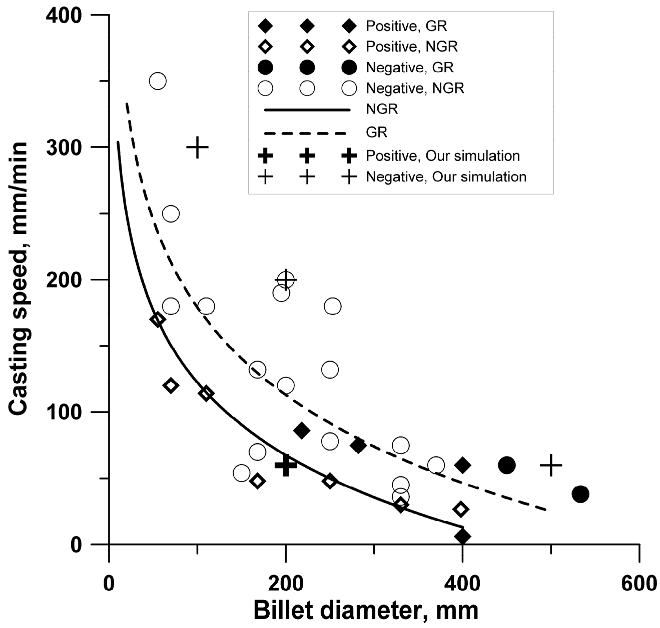


Figure 5. Effect of billet diameter and casting speed on the sign of centerline segregation upon DC casting of various aluminum alloys. Dashed line is for grain refined and solid line – for not grain-refined alloys [1].

5. Conclusions

Experimental studies together with computer simulations enable one to study the contributions of different mechanisms into the overall macro-segregation picture observed during DC casting of aluminum alloys. Computer simulation gives a unique opportunity to inspect the separate contributions of different mechanisms that are practically inseparable in experiment. On the other hand carefully designed experiments can shed a light on the mechanisms that are yet to be reliably modeled. Convection affects the segregation pattern in dependence on the flow direction. Natural convection in the sump of a DC cast billet enhances the positive centerline segregation. Shrinkage flow facilitates the negative centerline segregation. There is a direct correlation between the geometry of the billet sump (affected by the process parameters) and the degree of macro-segregation. The transport of solid grains in the sump of a DC cast billet contributes to the negative centerline inverse segregation. The overall macro-segregation pattern observed in real billets and ingots is a result of complex combination of different mechanisms, which is affected by the structure and process parameters. In principle it is possible to obtain positive or negative centerline segregation for a wide range of billet sizes by the control of the casing speed, which determines the shape of the sump and, therefore the extent of shrinkage and convection flows, and the formation and transport of floating grains. This is illustrated in Fig. 5.

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