Equi-axed growth and related segregations in cast metallic alloys

G. Lesoult\textsuperscript{a,*}, V. Albert\textsuperscript{a}, B. Appolaine\textsuperscript{a}, H. Combeau\textsuperscript{a}, D. Daloz\textsuperscript{a}, A. Joly\textsuperscript{a}, C. Stomp\textsuperscript{a}, G.U. Grün\textsuperscript{b}, P. Jarry\textsuperscript{c}

\textsuperscript{a}Laboratoire de Science et Génie des Matériaux Métalliques, UMR-CNRS 7584, École des Mines, Parc de Sauret, F-54042 Nancy Cédex, France
\textsuperscript{b}VAW Aluminium AG, R&D, Georg-von-Boeselagen Street 25, D-53117 Bonn, Germany
\textsuperscript{c}Péchiney-Centre de Recherches de Voreppe, BP27, F-38340 Voreppe, France

Abstract

Full-scale trials of DC ingots and laboratory scale directional solidification experiments have been performed to study the effect of grain structure on macro-segregation in industrial cast products. An Al alloy sheet ingot was cast with constant casting conditions (speed, superheat, cooling rate) except for the grain refiner: the first half of the ingot was non-inoculated, while the second half was inoculated. The results indicate that the extent and intensity of the centreline segregation is modified via the grain-refinement treatment; the finer the grains are, the more intense is the macro-segregation.

Numerical simulations of directional solidification of binary Al–Cu alloys have been carried out with the help of a 2D finite volume software which takes account of the movement of the liquid with respect to the solid in the mushy zone. It is possible to account for the segregation pattern of the directionally solidified ingots that exhibit columnar or coarse equi-axed grain structures. Contrarily, the intense segregation of the fine-grained ingots is not yet understood. © 2001 Published by Elsevier Science Ltd.

Keywords: DC casting; Directional solidification; Al alloys; Grain structure; Macro-segregation

1. Introduction

The number of forms in which segregation manifests itself on the scale of the product reveals the variety of the basic phenomena that are involved and the complexity of their interactions:

(a) unsteady phenomena and end effects with a plane solid/liquid interface [1];
(b) violent stirring in the bulk liquid with a plane solid/liquid interface [2];
(c) washing out of the columnar, dendritic mushy zone due to moderate stirring [3,4];
(d) sedimentation of equi-axed crystals [5];
(e) in-depth circulation of inter-dendritic liquid in the mushy zone [6];
(f) deformation of the dendritic skeleton in the mushy zone [7–11].

Many times, in fact, several elementary phenomena compete to build the final overall segregation pattern in as-cast products: this is the case during the DC casting of aluminium-based alloys.

In 1984, Yu and Granger [12] described macro-segregation patterns obtained with the DC casting process. As an example, Fig. 1 shows a copper macro-segregation profile across the thickness of a DC-cast Al–Cu alloy sheet ingot. Surface exudation, subsurface enrichment and a near depleted zone can be accounted for by the developed macro-segregation theory, involving the movement of inter-dendritic liquid in the mushy zone. Contrarily, the centreline negative segregation observed cannot be explained easily, even though it seems to be associated with the observed duplex microstructure in the centre of the ingot, which comprises a mixture of fine dendrites and coarse cells. According to previous authors, the observed negative centreline segregation might be due to the transport of isothermal dendrites. These are supposed to form early in the solidification process, to be detached and carried by the strong convection current into the molten metal pool, then to grow isothermally at a temperature close to the liquidus temperature of the alloy within the thermal boundary layer. Finally, these dendrites would settle and become entrapped in the solidifying ingot at the bottom of the pool. Dorward and Beernet sen [13], Gariepy and Caron [14], and Chu and Jacoby [15], agreed with the view of Yu and Granger [12] that the
isothermal dendrites formed the coarse cells observed at the centre of the final product.

In summary, the most widely accepted explanation for the negative segregation in the centreline of Al alloys sheet ingots is the presence there of a definite fraction of coarse so-called isothermal grains. This description makes sense. However, the comparison between theoretical predictions and observations is indirect and qualitative, in connection with DC casting trials. Therefore, a research programme was carried out to re-assess experimentally, more precisely and quantitatively the effects of different variables, including grain structure, on the segregation patterns obtained in ingots.

At the laboratory scale, the authors studied the effects of the grain structure and of the settling of equi-axed grains on the longitudinal segregation in directionally solidified mini-ingots. At the plant scale, the authors studied the effect of inoculation on the grain structure and on the macro-segregation in DC cast sheet ingots. From a theoretical point of view, the experimental results on macro-segregation in directionally solidified mini-ingots were compared with the predictions of available models.

The aim of this work is to summarise the present achievements of this programme and suggest directions for further theoretical work to fully understand the main experimental results. It is divided into three main parts: directional solidification of simple Al–Cu and Al–Mg alloys; DC casting of Al–Mg based alloys; and general discussion.

2. Directional solidification of binary Al–Cu and Al–Mg alloys

Before summarising the results of the present experiments, the authors return to the phenomena that can lead to macro-segregation in the case of the directional solidification of Al–Cu ingots. A previous paper dealt with segregation patterns in mini-ingots due to some of the phenomena listed above, i.e., phenomena (a), (b) or (e), when the solid/liquid interface was either plane or columnar/dendritic [16]. The discussion was based on theoretical and numerical analyses, which include solidification shrinkage, porosity formation, and natural convection in the mushy zone, to predict macro-segregation [17,18].

Through a quick survey of some classical experimental results on the segregation pattern in directionally solidified small ingots, it can be noted that this segregation depends first on the morphology of the solid/liquid interface. Therefore, depends on the value of the ratio $G/l$.

For high $G/l$ values, the solid/liquid interface is plane, and the solidification results in a higher solute content at the end of the ingot if the partition coefficient is smaller than unity: it is referred to as normal segregation.

For moderate values of $G/l$, the solidification front is dendritic and the grain structure is columnar. Two different cases can occur depending on the solutal expansion coefficient of the liquid $\beta_w$:

$$
\beta_w = \frac{1}{\rho} \frac{\partial \rho}{\partial w}.
$$

When the solute is heavier than the base metal in the liquid, the copper in aluminium for instance, the solidification shrinkage is the only driving force for fluid flow during ideal directional solidification from the bottom. The solute profile is quite the opposite of the solute profile that is expected in the case of a directional solidification with a plane interface. Therefore, the related phenomenon is named inverse segregation: the first solid, which formed against the chill, has a solute content higher than the nominal content, then follows a central zone, which presents a copper content, slightly higher than the nominal one, and finally, the last solidified part presents a negative macro-segregation [19–22].

On the contrary, when the solute is lighter than the base metal in the liquid, the aluminium in nickel or the magnesium in aluminium for instance, some natural convection can appear, driven by thermosolutal forces. In this case, a positive segregation may appear at the top end when channels can form during solidification, i.e. when $G$ and $\nu$ are small enough.

The situation can be different and even more complex when the grain structure is equi-axed. Kato and Cahoon [19] compared the segregation along mini-ingots cast with inoculated and non-inoculated Al–4% Cu alloys and vertically solidified in the upward direction. They observed that the longitudinal segregation was more severe in the inoculated mini-ingots: positive near the chill, and negative at the end. The same conclusions were drawn by Murakami et al. [23] from experiments made with an Al–4.5% Cu alloy and by Rousset et al. [17] from observations made on Al–3.4%
Cu mini-ingots. The effect of macro-structure on macro-segregation has also been observed in mini-ingots that were vertically solidified in the downward direction. In this case, McCartney and Ahmadi [24] and Motegi and Ohno [25] observed that the solute content at the low end of the ingot (far from the chill) is lower for equi-axed than for columnar grain structure.

The effect of the structure on the macro-segregation profiles cannot be explained with the classical theory. As a matter of fact, it is unlikely that the grain structure can change the fluid flow, which is induced by the solidification shrinkage and which results in inverse segregation near the chill. Thermosolutal convection cannot explain it either as thermal solidification conditions for the different structures are roughly the same. Different hypotheses were proposed to explain the observed differences. It is interesting to note that authors who carried out upward solidification proposed to relate segregation and porosity. On the contrary, those who performed downward solidification suggested to relate segregation and sedimentation of equi-axed grains.

As no complete agreement was found on the origin of the correlation between the grain structure and the macro-segregation, a new series of experiments was carried out. The aim was to assess the effect of the following variables: solidification direction (upward or downward); grain structure; ingot length; and chill kind [26,27].

The ingots were cut longitudinally so that the central metal slices containing the thermocouples were removed, and two equal parts were left. The first one was polished and etched to observe the macro-structure (see the example in Fig. 2) and to measure the grain diameter of the equi-axed crystals as a function of distance from the chill.

A clear difference between the Cu macro-segregation profiles obtained for the columnar/equi-axed and the totally equi-axed structures is observed. Fig. 3 compares the results obtained for ingots 1 (fine equi-axed) and 6 (coarse columnar/equi-axed), both 55 mm in height, solidified on a copper chill. Ingot 1 is totally equi-axed, whereas ingot 6 exhibits a columnar/equi-axed transition. There are nearly zero Cu gradients along ingot 6. Contrarily, the equi-axed ingot has a decreasing copper segregation (except at the top end, where an increase can be observed).

Porosity measurements were performed using image analysis along ingot 1 (upward, equi-axed, copper chill, 55 mm), and ingot 6 upward, columnar/equi-axed, copper chill, 55 mm). The volume fraction of porosity increases regularly from the chill to the upper end in the case of the

Fig. 2. Grain structure: copper chill, upward solidification, $h = 55$ mm. Ingot 1: inoculated, fine-grained, equi-axed structure; Ingot 6: non-inoculated, coarse-grained, columnar/equi-axed.

Fig. 3. Longitudinal segregation, 55 mm height, copper chill, upward. Ingot 1 (equi-axed; ingot 6 (columnar/equi-axed)).
equi-axed structure, but it is always lower than 0.5%. It remains very low in the case of the columnar/equi-axed structure (lower than 0.1%) (Fig. 4). In this case, the difference in porosity between the two mini-ingots seems too small to be the main cause of the difference in macro-segregation according to the theoretical works available in the literature.

Downward solidification experiments were carried out with the same alloy. Fig. 5 presents the results obtained for ingot 1’ that was solidified in the same conditions as ingot 1 except for the direction. Comparison of the results related to ingot 1 and those related to ingot 1’ shows that the profiles in the first half of the ingots (near the chill) are quite similar, even though the profile for ingot 1 seems slightly steeper. Contrarily, they differ farther from the chill: at the end of ingot 1’, segregation is definitely negative (about −0.7%), whereas it is nearly zero for ingot 1.

A set of macro-segregation measurements, involving Al–4.75% Mg–0.35% Mn alloy ingots, similar to the measurements involving the Al–4.5% Cu ingots, were performed [28]. The same trends were observed for the Al–Mg alloys as for the Al–Cu ones when the grain structure was equi-axed and fine. This similarity is noticeable since the effect of the Mg content on the liquid density is the opposite of that of the Cu content. The segregation might be less sensitive to the liquid density in the case of the equi-axed solidification than in the case of the columnar one.

It is noteworthy that the most important difference in longitudinal segregation related to the grain structure depend neither on the porosity level nor on the direction of solidification. It is concluded that neither the porosity nor the settling of equi-axed crystals can explain the main difference between the profiles observed in the half part of the ingots that is adjacent to the chill, where the segregation is higher in the case of the totally equi-axed structure.

3. DC casting of Al–Mg based alloys

Plant-scale trials were designed to examine the effect of grain structure on macro-segregation in DC sheet ingots by varying the grain-refining practice with a Al–Mg based alloy. The dimensions of the mould and the casting conditions are given in a previous paper [29].

One sheet ingot was cast with two different conditions: the first half is non-grain refined (NGR) and the second half is grain refined (GR). In the ingot, several slices were cut in order to study the macro-segregation. In the following, only the results concerning two horizontal slices will be presented: one horizontal slice in the GR part and one in the NGR part.

In order to check the three-dimensional character of the phenomena that occur in the ingot, full maps of concentration were realised for each slice. These maps were achieved by optical emission spectrometry (OES) analyses following a fine regular mesh (mesh size: 2.5 cm). Results are reported in terms of relative segregation. The nominal composition of the ingot has been calculated as the average of all the chemical analyses realised on all of the slices (8000 points).

The schematic macro-segregation maps corresponding to the two parts of the ingot are shown in Fig. 6. In order to obtain a complete view of slices, each map has been built by symmetry from the data relative to the quarter that has been analysed.

When both sections show the same trend, i.e. centreline negative segregation, one can observe that it is more intense in the GR part of the ingot. Macro-segregation profiles of Mg along the thickness at a quarter of the width are shown in Fig. 7 (the locations of the profiles are indicated by the arrow in Fig. 6). They show two symmetric positive segregation lines. The segregation, both negative and positive, is more intense in the GR part: the total difference between the maximum and the minimum values of the relative deviation is about 14% for the GR part and 9% for the NGR part.

Concerning the macro-structure, the respective macro-etchings for the GR and NGR parts of the ingot are presented on the right-hand side of Fig. 6. It was noted that the darker zone (meaning smaller grain size) corresponds to the centreline segregation. A non-monotonic evolution of the grain size was observed over the thickness (brightness contrast) that was not resolved at this scale.

No columnar zone appears in the so-called NGR part due to the presence of residual Ti: the average Ti content is 0.0018 wt% in the NGR part, and 0.0040 wt% in the GR part.

Fig. 4. Surface fraction of porosity: Ingots 1 and 6.

Fig. 5. Longitudinal segregation, 55 mm height, copper chill, fine equi-axed. Ingots 1: upward; 1’: downward.
Parallel to the study of macro-segregation and macrostructure, some representative micro-photographs of the grain structure were taken. Typical photographs are presented in Fig. 8. The two sections show several common characters. The grain size increases from 50 to 200 mm from the skin; then, it decreases abruptly at the centreline. The main differences are the following:

(i) the grain size is obviously smaller in the GR part;
(ii) the shape of the grains is more dendritic in the NGR part and more globular in the GR part;
(iii) a mixed grain structure (coarse/very small) is present at the centre of the NGR part, but not in the GR part.

When comparing the structural features and the segregation data, one can make the following statements:

1. In the frame of the present industrial trials, the maximum negative segregation at the centreline of DC cast sheet ingots is not associated specifically with the presence of a duplex micro-structure (fine dendrites + coarse cells) at
the centre of the ingots. As a matter of fact, the duplex micro-structure was observed only in the NGR part, where the segregation is even slightly less severe, whereas negative centreline segregation exists in both the GR and NGR parts.

2. The most relevant structural feature to be correlated with the quantitative difference in segregation intensity between the GR and NGR parts is the morphology of the grains: more dendritic in the NGR part and more globular in the GR part. Contrarily, the obvious difference in grain size is likely not pertinent in itself.

3. The presence of finer grains at the centre of the ingots, which corresponds to a non-monotonic evolution of the grain size across the thickness of the cast products, results from the transport of grains by convection in the bulk liquid and in the mush.

4. General discussion

The first results of the research programme that have been reported here are useful to describe more precisely the phenomena that are responsible for the segregation in DC cast Al sheet ingots.

These results confirm some observations that were made by previous authors:

1. The negative centreline segregation that is observed in DC cast Al alloy sheet ingots is more severe when the cast metal is GR.

2. In the present case, the most intense segregation is observed for the casting conditions that result in grains with a morphology that is more globular than dendritic. In this respect, it is also interesting to note the fact that the effect of the addition of a grain refiner on the centreline segregation in DC cast ingots can depend on the symmetry of the product. Finn et al. [30] showed that adding grain refiner when casting an axi-symmetric DC ingot of Al–Cu alloy can result in a qualitative change of the centreline segregation from negative to positive. Contrarily, the present work does not confirm that the strong negative centreline segregation is associated with a mixed micro-structure (coarse/very small grains).

From all of these observations, it is concluded that the centreline segregation in Al alloy DC ingots is a consequence of two different factors: the movement of equi-axed grains due to forced convection, the pattern of which depends on the symmetry of the casting process; and the morphology of the grains, which depends on their nucleation and growth processes and which can therefore be correlated with their size.

At this stage of the programme, the unidirectional solidification experiments that were carried out at the laboratory scale were useful to begin to compare quantitatively some experimental results and theoretical predictions. Numerical simulations were performed in order to predict the 2D solute concentration patterns in axi-symmetric mini-ingots under the assumption that the segregation is due to solute transport by thermostal convection of the liquid through the mush and in the bulk. The calculated patterns fitted well the experimental ones that were obtained in non-inoculated ingots with coarse columnar and equi-axed grains. In general, the concentration gradients are small [31]. It was thus concluded that segregation in directionally solidified columnar ingots is actually due to the transport of solute by the liquid that flows through the solid skeleton of the mushy zone.

The ingots that were solidified under the same thermal conditions with the same alloy, but that had a fine equi-axed grain structure due to a grain refining treatment, exhibited a definite longitudinal concentration gradient, quite uniform from positive segregation near to the chill to negative segregation at the opposite extremity. These segregation profiles cannot be understood only in terms of liquid flow through the porous and fixed mushy zone. It is thought that the segregation is related to the movement of equi-axed grains in the fluid region of the mushy zone for the directional solidification of mini-ingsots as for the DC casting of industrial ingots. In the case of directional solidification, one might expect a large contribution of the settling of grains in the gravity field, therefore a large difference in segregation depending on the orientation of the solidification with respect to the gravity field. In fact, a limited difference in longitudinal segregation between upward and downward solidification of directionally solidified mini-ingsots was observed. This difference was localised at the final extremity of the ingots and could be explained semi-quantitatively in terms of settling of grains [28]. However, the segregation pattern in the main part of the equi-axed ingots is unaffected by the direction of the solidification conclusions although it is very different from the segregation pattern of columnar ingots.

5. Conclusions

In conclusion, it is accepted widely that considerable quantitative progress has become possible since Flemings and coworkers published their classical papers on the subject of macro-segregation in as-cast metal that exhibits columnar grain structure [6]. The present work has afforded new evidence of the success of the theory of macro-segregation due to fluid flow in directionally solidified columnar mini-ingots.

Contrarily, from the present results related to equi-axed structures, it is concluded that the segregation in ingots that exhibit a fine equi-axed grain structure is still an open field for future research. More work, both experimental and theoretical, is needed to understand fully the effects of the movement of the equi-axed grains, their morphology, and the permeability of the mushy zone in its different regions, on the segregation.
Acknowledgements

Part of this work was financially supported by the European Community within the program: Brite Euram EMPACT contract no. BRPR-CT95-0112.

References

[1] V.G. Smith, W.A. Tiller, J.W. Rutter, Can. J. Phys. 33 (1955) 428.
[2] J.A. Burton, R.C. Prim, W.P. Slichter, J. Chem. Phys. 21 (1953) 1987.
[3] T. Takahashi, K. Ichikawa, M. Kudou, K. Shimahara, Trans. ISIJ 16 (1976) 283.
[4] Z. Zhong, H. Dörr, F. Oeters, Steel Res. 56 (6) (1985) 305.
[5] H.K. Chuang, K. Schwerdtfeger, Arch. Eisenhüttenwes. 46 (1975) 303.
[6] M.C. Flemings, R. Mehrabian, Solidification, ASM, New York, 1971 (chap. 10).
[7] G. Engström, H. Fredriksson, B. Rogberg, Scand. J. Metall. 12 (1983) 3.
[8] K. Miyazawa, K. Schwerdtfeger, Arch Eisenhüttenwes. 52 (11) (1981) 415.
[9] G. Lesoul, S. Sella, in: G. Martin, L.P. Kubin (Eds.), Non Linear Phenomena in Materials Science, Trans Tech, Germany, 1988, p. 167.
[10] G. Lesoul, S. Sella, Proceedings of the 6th International Iron and Steel Congress, vol. 1, Nagoya, Japan, 1990, p. 673.
[11] I. Ohnaka, T. Shimazu, Proceedings of the 6th International Iron and Steel Congress, vol. 1, Nagoya, Japan, 1990, p. 681.
[12] H. Yu, D.A. Granger, NASA Conference Publication, Cleveland, vol. 2337, 1984, p. 157.
[13] R.C. Dorward, D.J. Beerness, Light Metals 90, 919.
[14] B. Gariépy, Y. Caron, Light Metals, 1991.
[15] M.G. Chu, J.E. Jacoby, Light Metals (1990) 925.
[16] G. Lesoul, H. Combeau, in: I. Ohnaka, D.M. Stefanescu (Eds.), The Minerals, Metals and Materials Society, 1996, p. 43.
[17] Ph. Rousset, M. Rappaz, B. Hammart, Metall. Trans. A 26 (1995) 2349.
[18] V.R. Voller, S. Sundarraj, Int. J. Heat Mass Transfer 38 (6) (1995) 1009.
[19] H. Kato, J.R. Cahoon, Metall. Trans. A 16 (1985) 279.
[20] E. Scheil, Z. Metall. 38 (1947) 69.
[21] D.E. Adams, J. Inst. Metals 75 (1949) 809.
[22] J.S. Kirkaldy, W.V. Youdelis, Trans. AIME 212 (1958) 833.
[23] K. Murakami, C.Y. Liu, T. Okamoto, Solidification Processing, The Institute of Metals, London, 1987, p. 287.
[24] D.G. McCartney, S.M. Ahmadi, Metall. Trans. A 25 (1994) 1097.
[25] T. Moteki, A. Ohno, Trans. Jpn. Inst. Metals 25 (1984) 122.
[26] V. Albert, Ph. Jarry, H. Combeau, G. Lesoul, Materials, Functionality and Design, Proceedings of the 5th European Conference on Advanced Materials, Processes and Applications, Euromat 97 Maas- tricht April 1997.
[27] V. Albert, Ph. Jarry, H. Combeau, G. Lesoul, Solidification Processing 1997, in: J. Beech, H. Jones (Eds.), Proceedings of the 4th Decennial International Conference on Solidification Processing, Sheffield, July 1997, p. 341.
[28] V. Albert, Ph.D. Thesis INPL, Nancy, 1998.
[29] A. Joly, et al., 3rd International Conference on Solidification and Gravity, SCG, vol. 99, 1999, pp. 26–29
[30] T.L. Finn, M.G. Chu, W.D. Bennon, Micro/Macro Scale Phenomena in Solidification, ASME, HTD-vol. 218/AMD-vol. 139, 1992, pp. 17–26.
[31] C. Stomp et al., private communication, 1999 (in press).