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### Numerical Models of Crystallization and Its Direction for Metal and Ceramic Materials in Technical Application

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#### 1. Introduction

Structure of metallic and also majority of ceramic alloys is one of the factors, which significantly influence their physical and mechanical properties. Formation of structure is strongly affected by production technology, casting and solidification of these alloys. Solidification is a critical factor in the materials industry, e.g. (Chvorinov, 1954). Solute segregation either on the macro- or micro-scale is sometimes the cause of unacceptable products due to poor mechanical properties of the resulting non-equilibrium phases. In the areas of more important solute segregation there occurs weakening of bonds between atoms and mechanical properties of material degrade. Heterogeneity of distribution of components is a function of solubility in solid and liquid phases. During solidification a solute can concentrate in inter-dendritic areas above the value of its maximum solubility in solid phase. Solute diffusion in solid phase is a limiting factor for this process, since diffusion coefficient in solid phase is lower by three up to five orders than in the melt (Smrha, 1983). When analysing solidification of these alloys so far no unified theoretical model was created, which would describe this complex heterogeneous process as a whole. During the last fifty years many approaches with more or less limiting assumptions were developed. Solidification models and simulations have been carried out for both macroscopic and microscopic scales. The most elaborate numerical models can predict micro-segregation with comparatively high precision. The main limiting factor of all existing mathematical micro-segregation models consists in lack of available thermodynamic and kinetic data, especially for systems of higher orders. There is also little experimental data to check the models (Kraft & Chang, 1997).

Many authors deal with issues related to modelling of a non-equilibrium crystallisation of alloys. However, majority of the presented works concentrates mainly on investigation of modelling of micro-segregation of binary alloys, or on segregation of elements for special cases of crystallisation – directional solidification, zonal melting, one-dimensional thermal field, etc. Moreover these models work with highly limiting assumption concerning phase diagrams (constant distribution coefficients) and development of dendritic morphology

(mostly one-dimensional models of dendrites); e.g. overview works (Boettingen, 2000; Rappaz, 1989; Stefanescu, 1995). Comprehensive studies of solidification for higher order real alloys are rarer. Nevertheless, there is a strong industrial need to investigate and simulate more complex alloys because nearly all current commercial alloys have many components often exceeding ten elements. Moreover, computer simulation have shown that even minute amounts of alloying elements can significantly influence microstructure and micro-segregation and cannot be neglected (Kraft & Chang, 1997). Dendritic crystallisation is general form of crystallisation of salts, metals and alloys. At crystallisation of salts from solutions a dendritic growth of crystals occurs at high crystallisation rate, which requires high degree of over-saturation. Findings acquired at investigation of crystallisation of salts were confirmed at investigation of crystallisation of metals. If negative temperature gradient is present in the melt before the solidification front, this leads to a disintegration of the crystallisation front and to formation of dendritic crystallisation (Davies, 1973). High crystallisation rate is characteristic feature of dendritic crystallisation. Solutes have principal influence on the crystallisation character, as they are the cause of melt supercooling before the crystallisation front and formation of the negative temperature gradient. This kind of supercooling is called constitutional supercooling. For example a layer of supercooled melt is formed in a steel ingot in the immediate vicinity of the interface melt-solid, in principle at the very beginning of crystallisation as a result of segregation of solutes, which causes decrease in solidification temperature of this enriched steel. Increased concentration of solutes creates soon a broad zone of constitutionally supercooled steel, in which the crystallisation rate is high. During subsequent solidification, when the crystallisation rate is low, the value of temperature gradient is also low, which means that conditions for dendritic crystallisation are fulfilled again (Šmrha, 1983). More detailed information on dendritic crystallisation - see classical works (Chalmers, 1940), (Flemings, 1973), (Kurz &Fisher, 1986). According Chvorinov (1954), Smrha (1983) and others metallic alloys and also majority of ceramic alloys in technical application are always characterised by their dendritic crystallisation. It is therefore of utmost importance that their final desirable dendritic structure has appropriate properties that can be used in technical practice. These properties depend of the kind of practical use and they comprise flexibility, elasticity, tensile strength, hardness, but also for example toughness. In the case of ceramic materials the properties of importance are brittleness, fragility and very often also refractoriness or resistance to wear. This chapter presents numerical models of crystallisation of steel, ductile cast iron and ceramics EUCOR aimed at optimisation of their production and properties after casting.

#### 2. Numerical models of the temperature field and heterogeneity

Crystallization and dendritic segregation of constitutive elements and admixtures in solidifying (crystallising) and cooling gravitationally cast casting or continuously cast blank (shortly concast blank) is directly dependent on character of formation of its temperature field. Especially rate and duration of the running crystallisation at any place of the blank, so called local solidification time, is important. Solidification and cooling-down of a gravitationally cast casting as well as the simultaneous heating of a metal or non-metal mould is a rather complex problem of transient heat and mass transfer. This process in a system casting- mould-ambient can be described by the Fourier's equation (1) of 3D transient conduction of heat.

$$\frac{\partial T}{\partial \tau} = \frac{\lambda}{\rho c} \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + \frac{Q_{\text{SOURCE}}}{\rho c}$$
(1)

In equation (1) are T temperature [K],  $\tau$  time [s],  $\lambda$  heat conductivity [W.m<sup>-1</sup>.K<sup>-1</sup>],  $\rho$  density [kg.m<sup>-3</sup>], c specific heat capacity [J.kg<sup>-1</sup>.K<sup>-1</sup>], Q<sub>SOURCE</sub> latent heat of the phase or structural change [W.m<sup>-3</sup>], x,y,z axes in given directions [m].

Implementation of continuously casting (shortly concasting), which considerably increased rate of melt cooling between temperatures of liquidus and solidus brought about time necessary for crystallic structure homogenisation. 3D transient temperature field of the of the system of concast blank-mould or concast blank-ambient is described by Fourier-Kirchoff's equation (2).

$$\frac{\partial T}{\partial \tau} = \frac{\lambda}{\rho c} \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + \left( w_x \frac{\partial T}{\partial x} + w_y \frac{\partial T}{\partial y} + w_z \frac{\partial T}{\partial z} \right) + \frac{Q_{\text{SOURCE}}}{\rho c}$$
(2)

In equation (2)  $w_x$ ,  $w_y$ ,  $w_z$  are velocity in given directions [m.s<sup>-1</sup>]

These equations are solvable only by means of modern numerical methods. Therefore original models of the transient temperature field (models **A**) of both systems of gravitational casting or continuous casting were developed. Both models are based on the 1<sup>st</sup> and 2<sup>nd</sup> Fourier's laws on transient heat conduction, and the 1<sup>st</sup> and 2<sup>nd</sup> law of thermodynamics. They are based on the numerical method of finite differences with explicit formula for the unknown temperature of the mesh node in the next time step, which is a function of temperatures of the same node and six adjacent nodes in Cartesian coordinate system in the previous time step. Models take into account non-linearity of the task, it means dependence of thermo-physical properties of all materials of the systems on temperature and dependence of heat transfer coefficients on temperature of all external surfaces. Models are equipped with and interactive graphical environment for automatic generation of a mesh, and for evaluation of results, it means by so called pre-processing and post-processing.

Another model, which has also been already mastered is model of chemical heterogeneity of chemical elements (model **B**), enables description and measurement of dendritic segregation of constitutive elements and admixtures in crystallising and cooling blank (casting or concasting). This model is based on the 1<sup>st</sup> and 2<sup>nd</sup> Fick's laws of diffusion and it comprises implicitly also the law of conservation of mass. The solution itself is based on the Nernst distribution law, which quantifies at crystallisation distribution of chemical elements between liquid and solid phases of currently crystallising material in the so called mushy zone (i.e. in the zone lying between the temperature of liquidus and solidus). Majority of parameters necessary for application of the models **A** is known, but parameters necessary for use of the model **B** had to be determined by measurements on the work itself, i.e. on suitably chosen samples from continuously crystallised blanks.

Measurement was realised in the following manner: at selected segments of the cast blank concentration of main constitutive, additive and admixture elements was determined from the samples taken in regular steps. In dependence on chemical heterogeneity and structure of a blank the segments with length of 500 to 1000  $\mu$ m were selected, and total number of

steps, in which concentration of elements was measured, was set to 101. Measurement of concentration of elements was performed by methods of quantitative energy dispersive analysis (EDA) and wave dispersive analysis (WDA) of X-ray spectral microanalysis, for which special software and special measurement device was developed for use in combination with the analytical complex JEOL JXA 8600/KEVEX.

After completion of measurement the sample surface was etched in order to make visible the original contamination of surface by electron beam, and the measured traces were photographically documented, including the mean distance of dendrites axes within the measured segment. It was verified that the basic set of measured concentration data of elements (8 to 11 elements) makes it possible to obtain a semi-quantitative to quantitative information on chemical heterogeneity of the blank, and that it is possible to apply at the same time for evaluation of distribution of elements in the blank structure the methods of mathematical- statistical analysis. It is possible to determine the distribution curve of the element concentration in the measured segment of the analysed blank and their effective distribution coefficient between the solid and liquid phase during crystallisation. In this way the crucial verified data necessary for creation of the conjugated model (AB) of crystallising, solidifying and cooling down blank were obtained. It was verified that re-distribution of constitutive, additive elements and admixtures can be described by effective distribution coefficient, which had been derived for parabolic growth by Brody and Flemings (Brody&Flemings, 1966). At the moment of completed crystallisation, at surpassing of an isosolidic curve in the blank, it is possible to express the ratio of concentration of dendritically segregating element  $C_S$  to the mean concentration of the same element at the given point of the blank  $C_0$  by the relation

$$C_{\rm S}/C_0 = k_{\rm ef} [1 - (1 - 2\alpha k_{\rm ef})g_{\rm S}]^{(k_{\rm ef} - 1)/(1 - 2\alpha)}$$
(3)

where  $k_{ef}$  is effective distribution coefficient,  $g_S$  is mass share of the solidified phase, and  $\alpha$  is dimensionless Fourier's number of the 2<sup>nd</sup> kind for mass transfer. This number is given by the relation

$$\alpha = D_S \theta_{\rm IS} / L^2 \tag{4}$$

in which  $D_s$  is diffusion coefficient of the segregating element in solid phase,  $\theta_{ls}$  is local time of crystallisation (i.e. time of persistence of the assumed dendrite between the temperature of liquidus and solidus) and L is mean half distance of dendritic axes (namely of axes of secondary dendrites). In the next step it is necessary to express the ratio of concentrations  $C_s/C_0$  express as a function of concrete heterogeneity index  $I_H$  and of statistical distribution of the measured element, expressed by distributive curve of crystallization segregation. In this manner the following equation is available for each measured element:

$$C_{\rm S}/C_0 = I_{\rm H} \tag{5}$$

which expresses by concrete numbers the parameters, defined by the equation (3). By solving equations (3, 4) it is then possible to determine for each analysed element (i.e. for its measured index of dendritic heterogenity, effective distribution coefficient and distribution curve of dendritic segregation, i.e. for the established statistic character of distribution of the analysed element in structure of the blank) certain values of dimensionless criterion  $\alpha$ . Afterwards on the basis of semi-empiric relations and rates of movement of the crystallisation front, calculated from the thermal field model in confrontation with the

results of experimental metallographic analysis, the mean value of distances between branches of secondary dendrites *L* was determined for 9 samples of the blank. The values  $\theta_{ls}$  and *L* for the criterion  $\alpha$ , are calculated from the model for each sample, which were determined for individual measured elements in each sample of the blank. It is possible to make from the equation (4) an estimate of the diffusion coefficient of each analysed element in individual samples of the blank. At the moment, when temperature of any point of the mesh drops below the liquidus temperature, it is valid that the share of the forming solid phase  $g_s$  grows till its limit value  $g_s = 1$  (i.e. in solid phase). In this case segregation of the investigated element achieves in the residual inter-dendritic melt its maximum.

The combination of mentioned models and methodology of chemical heterogeneity investigation are presented on following technical applications.

#### 3. Gravitational casting

#### 3.1 Solidification of massive casting of ductile cast iron

The quality of a massive casting of cast iron with spheroidal graphite is determined by all the parameters and factors that affect the metallographic process and also others. This means the factors from sorting, melting in, modification and inoculation, casting, solidification and cooling inside the mould and heat treatment. The centre of focus were not only the purely practical questions relating to metallurgy and foundry technology, but mainly the verification of the possibility of applying two original models – the 3D model of transient solidification and the cooling of a massive cast-iron casting and the model of chemical and structural heterogeneity.

#### 3.1.1 Calculation and meassurement of the temperature field

The application of the 3D numerical model on a transient temperature field requires systematic experimentation, including the relevant measurement of the operational parameters directly in the foundry. A real 500×1000×500 mm ductile cast-iron block had been used for the numerical calculation and the experiment. They were cast into sand moulds with various arrangements of steel chills of cylindrical shape. The dimensions of the selectid casting, the mould, the chills and their arrangements are illustrated in Figure 1. The



Fig. 1. The forming of casting no. 1 with chills on one side

courses of the temperatures on casting No.1 were measured for 19 hours 11 min after pouring. The iso-zones, calculated in castings No.1 and in the chills in the total solidification time after casting, are illustrated in Figure 2 (Dobrovska et al., 2010).



Fig. 2. The calculated iso-zones in casting No. 1 (5 hours)

## 3.1.2 The relation between the model of the temperature field and the model of structural and chemical heterogeneity

The 3D numerical model of the temperature field of a system comprising the casting-moldambient is based on the numerical finite-element method. The software ANSYS had been chosen for this computation because it enables the application of the most convenient method of numerical simulation of the release of latent heats of phase and structural changes using the thermodynamic enthalpy function. The software also considers the nonlinearity of the task, i.e. the dependence of the thermophysical properties (of all materials entering the system) on the temperature, and the dependence of the heat-transfer coefficients (on all boundaries of the system) on the temperature of the surface-of the casting and mold. The original numerical model had been developed and used for estimation of structural and chemical heterogeneity. Initial and boundary conditions had been defined by means of theory of similarity. The verifying numerical calculation of the local solidification times  $\theta$  – conducted according to the 3D model proved that, along the height, width and length of these massive castings, there are various points with differences in the solidification times of up to two orders. The aim was to verify the extent to which the revealed differences in the local solidification times affect the following parameters (Stransky et al., 2010):

- a. The average size of the spheroidal graphite particles;
- b. The average density of the spheroidal graphite particles;
- c. The average dimensions of the graphite cells, and
- d. The chemical heterogeneity of the elements in the cross-sections of individual graphite cells.

The relationships – among the given four parameters and the corresponding local solidification times – were determined in the series of samples that had been selected from defined positions of the massive casting. The bottom part of its sand mould was lined with (a total number of) 15 cylindrical chills of a diameter of 150 mm and a height of 200 mm. The upper part of the mould was not lined with any chills. The average chemical composition of the cast-iron before casting is given in Table 1.

Element	С	Mn	Si	Р	S	Ti	Al	Cr	Ni	Mg
wt.%	3.75	0.12	2.15	0.039	0.004	0.01	0.013	0.07	0.03	0.045

Table 1. Chemical composition of ductile cast-iron (casting No. 1)

A 500×500×40 mm plate had been mechanically cut out of the middle of the length by two parallel transversal cuts. Then, further samples were taken from exactly defined points and tested in terms of their structural parameters and chemical heterogeneity. Samples in the form of testing test-samples for ductility testing, with threaded ends, were taken from the bottom part of the casting (A), from the middle part (C) and from the upper part (G). The 15 mm in diameter and 12 mm high cylindrical samples served the actual measurements in order to determine the structural parameters and chemical heterogeneity. In the points of the defined positions of the samples prepared in this way, the quantitative metallographic analysis was used to establish the structural parameters of cast-iron, the in-line point analysis to establish the chemical composition of selected elements and numerical calculation using the 3D model to establish the local solidification time. Quantitative analyses of the basic micro-structural parameters in the samples have been the subject of a special study. On each sample a total number of 49 views were evaluated. On the basis of average values of these results the structural parameters of graphite, i.e. the radius of the spheroids of graphite –  $R_g$ , the distances between the edges of graphite particles –  $L_g$  and the radius of the graphite cells –  $R_c$  have been determined for each sample. The concentration of selected elements in each of the samples was measured on the line of  $L_g$  between the edges of two particles of spheroidal graphite. The actual measurements of concentrations of ten elements - Mg, Al, Si, P, S, Ti, Cr, Mn, Fe, Ni - was carried out. On each of the samples, the concentrations of all ten elements had been measured in three intervals with each individual step being 3  $\mu$ m. Before the actual measurement, the regions were selected on an unetched part of the surface and marked with a micro-hardness tester. After the micro-analysis, the samples were etched with nitric acid in alcohol in order to make the contamination of the ground surface visible using an electron beam. Then, using a Neophot light microscope, the interval within which the concentrations were measured was documented. The method of selection of the measurement points is illustrated in Figures 3a,b.



Fig. 3. An example of the chemical micro-heterogeneity measurement of ductile cast-iron a)  $L_g = 165 \ \mu\text{m}$ , b)  $L_g = 167 \ \mu\text{m}$  ( in Fig.  $L_g \equiv z$ )

The results of the measurements of the chemical heterogeneity were evaluated statistically. The element heterogeneity index  $I_{H(i)}$  is defined by the quotient of standard deviation of element concentration  $\sigma_{c(i)}$  and average element concentration  $C_i^{av}$  in the analysed area, i.e.  $I_{H(i)} = \sigma_{c(i)}/C_i^{av}$ . The element segregation index  $I_{S(i)}$  is defined by the quotient of element maximum concentration  $C_i^{max}$  and average element concentration  $C_i^{av}$  in the analysed area, i.e.  $I_{S(i)} = C_i^{max}/C_i^{av}$ . The local solidification times of the selected samples of known coordinates within the massive experimental casting were calculated by the 3D model. The calculation of the temperature of the liquidus and solidus for a melt with a composition according to the data in Table 1 was performed using special software with the values: 1130 °C and 1110 °C (the liquidus and solidus temperature). If the local solidification time is known, then it is also possible to determine the average rate of cooling w of the mushy zone as a quotient of the results that in the vertical direction y from the bottom of the massive casting (sample A: y = 50 mm) to the top (gradually samples C: y = 210 mm and G: y = 450 mm) the characteristic and significant relations are as follows:

- a. The average size of the spheroids of graphite  $R_g$ , the average size of the cells of graphite  $R_c$  and also the average distance between the individual particles of the graphite  $L_g$  are all increasing. This relation was confirmed by the quantitative metallographic analysis.
- b. The chemical heterogeneity within the individual graphite cells is also changing. The increase in the chemical heterogeneity is reflected most significantly in the increase in the indexes of segregation  $I_S$  for titanium which are increasing in the direction from the bottom of the massive casting to the top in the following order:  $I_{S(Ti)} = 5.79$ -to-9.39-to-11.62
- c. The local solidification time increases very significantly from the bottom of the casting to the top from 48 s more than 50× (near the centre of the casting) and 95× (at the top of the massive casting).

The relationships between the structural characteristics of graphite in the casting and the local solidification time were expressed quantitatively using a semi-logarithmic dependence:

$$R_{\sigma} = 19.08 + 2.274 \ln \theta$$
,  $R_{c} = 61.33 + 5.567 \ln \theta$ ,  $L_{\sigma} = 84.50 + 6.586 \ln \theta$  [µm,s] (6, 7, 8)

As far as chemical heterogenity of the measured elements is concerned, the analogous relation was established only for the dependence of the segregation index of titanium on the local solidification time, which has a steadily increasing course from the bottom of the casting all the way up to the top. The relevant relation was expressed in the form of a logarithmic equation

$$\ln I_{\rm S}^{\rm Ti} = 1.201 + 0.1410 \ln \theta_{\rm 1s}, \quad [s] \tag{9}$$

The local solidification time  $\theta$  naturally affects the mechanical properties of cast-iron however with regard to the dimensions of the test pieces; it is not possible to assign the entire body a single local solidification time. To assess relationship among structural parameters, chemical microheterogenity and mechanical properties of analysed cast-iron casting, the selected mechanical properties have been measured. The samples for testing of the tensile strength were taken from the test-sample of the experimental casting in such a way that one had been taken from under the metallographic sample and the second was taken from above. The testing indicates that the local solidification time  $\theta$  has significant influence on the ductility  $A_5$ . The relationship between the ductility and the local solidification time (equation 10) indicates that the reduction in the ductility of cast-iron in the state immediately after pouring is – in the first approximation – directly proportional to the square of the local solidification time.

$$A_5 = 23.399 - 8.1703\theta^2 \quad [\%, hr] \tag{10}$$

It can be seen from previous experimentation and the evaluations of the results that – in the general case of the solidification of ductile cast-iron – there could be a dependence of the size of the spheroids of graphite, the size of the graphite cells and therefore even the distance among the graphite particles on the local solidification time. The described connection with the 3D model of a transient temperature field, which makes it possible to determine the local solidification time, seems to be the means via which it is possible to estimate the differences in structural characteristics of graphite in cast-iron and also the effect of the local solidification time on ductility in the poured casting. The main economic goal observed is the saving of liquid material, moulding and insulation materials, the saving of energy and the already mentioned optimization of pouring and the properties of the cast product.

#### 3.2 Casting of corundo-baddeleyit ceramic material

The corundo-baddeleyit material (CBM) belongs to the not too well known system of the Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-ZrO<sub>2</sub> oxide ceramics. Throughout the world, it is produced only in several plants, in the Czech Republic under the name of EUCOR. This production process entails solely the utilisation of waste material from relined furnaces from glass-manufacturing plants. EUCOR is heat resistant, wear resistant even at extreme temperatures and it is also resistant to corrosion. It was shown that from the foundry property viewpoint, EUCOR has certain characteristics that are similar to the behavior of cast metal materials, especially steel for castings (Chvorinov, 1954; Smrha, 1983 and others).

#### 3.2.1 Measurements and computation results (the original riser)

The assignment focussed on the investigation of the transient 3D temperature field of a system comprising a casting-and-riser, the mold and ambient, using a numerical model (Heger et al., 2002; Kavicka et. al., 2010). The dimensions of the casting — the so-called "stone" — were 400 x 350 x 200 mm (Figure 4). The results attained from the numerical analysis of the temperature field of a solidifying casting and the heating of the mold represent only one quadrant of the system in question. Figure 5 shows the 3D temperature field of the casting with the original riser and the mold at two times after pouring. The riser-mold interface is an interesting place for monitoring. Once this point solidifies, the riser can no longer affect the process inside the casting. The initial temperature of the mold was 20°C. The pouring temperature of the melt was 1800°C. That was approximately 300°C higher, when compared with, for example, the steel pouring temperature. The temperature of the liquidus was 1775°C and the solidus 1765°C. The temperature field was symmetrical along the axes, i.e. it was sufficient for the investigation of the temperature field of a single quadrant only.



Fig. 5. a) The 3D teperature field of one quadrant of the casting wirh riser- mold, b) The 2D temperature field on the riser mold and riser casting interferace

#### 3.2.2 The model of the chemical heterogeneity and its application

The concentration distribution of individual oxides, making up the composition of the ceramic material EUCOR, was determined using an original method (Dobrovska, et al., 2009) and applied in the process of measuring the macro- and micro-heterogeneity of elements within ferrous alloys. This method was initially modified with respect to the differences occurring during solidification of the ceramic material, when compared to ferrous alloys. It was presumed that within EUCOR, the elements had been already distributed, together with oxygen, at the stoichiometric ratio (i.e. the chemical equation), which characterized the resulting composition of the oxides of individual elements after

solidification. The preconditions for the application of the model of chemical heterogeneity on the EUCOR material are as follows:

If the analytically expressed distribution of micro-heterogeneity of the oxides of the ceramic material is available, if their effective distribution coefficient is known, and if it is assumed that it is possible to describe the solidification of the ceramic material via analogical models as with the solidification of metal alloys, then it is possible to conduct the experiment on the mutual combination of the calculation of the temperature field of a solidifying ceramic casting with the model describing the chemical heterogeneity of the oxides.

If the Brody-Flemings Model (Brody & Flemings, 1966) is applied for the description of the segregation of oxides of the solidifying ceramic material and if an analogy with metal alloys is assumed, then it is possible to express the relationship between the heterogeneity index  $I_H$  of the relevant oxide, its effective distribution coefficient  $k_{ef}$  and the dimensionless parameter *a* using the equation

$$[\ln(2\alpha k_{\rm ef})]/(1 - 2\alpha k_{\rm ef}) = \{\ln[(1 + nI_{\rm H}^{(m)})/k_{\rm ef}]\}/(k_{\rm ef} - 1)$$
(11)

the right-hand side of which  $\{ln[(1+nI_H^{(m)})/k_{ef}]\}/(k_{ef} - 1)$ , based on the measurement of microheterogeneity, is already known and through whose solution it is possible to determine the parameter *a*, which is also on the right-hand side of the equation in  $2ak_{ef} = X$ . The quantity *n* has a statistical nature and expresses what percentage of the measured values could be found within the interval  $x_s \pm ns_x$  (where  $x_s$  is the arithmetic mean and  $s_x$  is the standard deviation of the set of values of the measured quantity). If n = 2, then 95% of all measured values can be found within this interval. If the dimensionless parameter *a* is known for each oxide, then a key to the clarification of the relationship exists between the local EUCOR solidification time  $\theta$ , the diffusion coefficient *D* of the relevant oxide within the solidifying phase and the structure parameter *L*, which characterizes the distances between individual dendrites in metalic and ceremic alloys (Figure 6). The equation of the dimensionless parameter *a* is

$$\alpha = D\theta/L^2$$
 [-], [m<sup>2</sup>s<sup>-1</sup>, s, m] (12)

It is possible to take the dimension of a structure cell as the structure parameter for the EUCOR material. The verification of the possibility of combining both methods was conducted on samples taken from the EUCOR blocks – from the edge (sample B) – and from the centre underneath the riser (sample C). Both the measured and the computed parameters of chemical micro-heterogeneity and the computed parameters of the local solidification time  $\theta$  (according to the temperature-field model) were calculated. The local solidification time of the sample B was  $\theta_B$  = 112.18 s and of the sample C was  $\theta_C$  = 283.30 s. The computed values of parameter *a* and the local solidification time  $\theta$  determine, via their ratio, the quotient of the diffusion coefficient *D* and the square of the structure parameter *L*, which means that the following relation applies:

$$\alpha/\theta = D/L^2 \quad [s^{-1}] \tag{13}$$

The calculated values of relation (13) for oxides of the samples B and C are arranged in Table 2 together with the parameters *a* 

Oxide	Sample B: <b>a</b>	$\alpha/ heta_{ m B}\cdot 10^4[1/s]$	Sample C: <b>a</b>	$a/\theta_{\rm C} \cdot 10^4  [1/s]$
Na <sub>2</sub> O	0.0732	6.53	0.0691	2.44
$Al_2O_3$	0.0674	6.01	0.0662	2.34
SiO <sub>2</sub>	0.0741	6.61	0.0663	2.34
ZrO <sub>2</sub>	0.00035	0.0312	0.00008	0.0028
K <sub>2</sub> O	0.0721	6.43	0.0665	2.35
CaO	0.075	6.69	0.0703	2.48
TiO <sub>2</sub>	0.0759	6.77	0.0757	2.67
Fe <sub>2</sub> O <sub>3</sub>	0.0732	6.53	0.0711	2.51
HfO <sub>2</sub>	0.0165	1.47	0.00017	0.006

Table 2. Calculated values of the equation (13)

It comes as a surprise that the values of the parameter  $a/\theta = D/L^2$  of the oxides of elements Na, Al, Si, K, Ca, Ti, and Fe differed by as much as an order from the value of the same parameter of the oxide of zirconium and hafnium. This could be explained by the fact that zirconium contains hafnium as an additive and, therefore, they segregate together and the forming oxides of zirconium and hafnium show the highest melting temperatures. From the melt, both oxides segregated first, already in their solid states. Further redistribution of the oxides of both elements ran on the interface of the remaining melt and the successive segregation of other oxides only to a very limited extent. It was therefore possible to count on the fact that the real diffusion coefficients of zirconium and hafnium in the successively forming crystallites were very small (i.e.  $D_{Zr} \rightarrow 0$  and  $D_{Hf} \rightarrow 0$ ). On the other hand, the very close values of the parameters  $a/\theta = D/L^2$  of the remaining seven analyzed oxides:

$$D/L_{B^2} = (6.51 \pm 0.25).10^{-4} \text{ and } D/L_{C^2} = (2.45 \pm 0.12).10^{-4} \text{ [s-1]} (14,15)$$

indicated that the redistribution of these oxides between the melt and the solid state ran in a way, similar to that within metal alloys, namely steels.

It would be possible to count – in the first approximation – the diffusion coefficients of the oxides in the slag having the temperatures of 1765°C (solidus) and 1775°C (liquidus), the average value of  $D = (2.07\pm0.11) \times 10^{-6} \text{ cm}^2/\text{s}$  (the data referred to the diffusion of aluminum in the slag of a composition of 39% CaO-20% Al<sub>2</sub>O<sub>3</sub>-41% SiO<sub>2</sub>). For these cases, and using Equation (13), it was possible to get the magnitude of the structure parameters that governed the chemical heterogeneity of the values:

$$L_{\rm B} = \sqrt{\left[\left(2.07 \, {\rm x} \, 10^{-6}\right) / \left(6.51 \, {\rm x} \, 10^{-4}\right)\right]} = 0.05639$$

$$L_{\rm C} = \sqrt{\left[\left(2.07 \, {\rm x} \, 10^{-6}\right) / \left(2.45 \, {\rm x} \, 10^{-4}\right)\right]} = 0.09192$$
[cm] (16,17)

It corresponded to 564 µm in the sample B (which was taken from the edge of the casting block) and 919 µm in the sample C (which was taken from underneath the riser of the same casting block). The comparison of the micro-structures of the analyses samples B and C (Figures 6a,b) has clearly shown that the sample B micro-structure ( $L_B$ ) was significantly finer than the micro-structure of the sample C ( $L_C$ ), which semi-quantitatively corresponded to the qualified estimate of the structure parameters L, conducted on the basis of calculations using the data obtained from both models.



Fig. 6. a)The structure of the sample B ( $L_b$  = 564 µm), b) The structure of the ample C ( $L_c$  = 919 µm)

#### 4. Continuously casting

#### 4.1 Chemical microheterogeneity of continuously cast steel slab

Structure of metallic alloys is one of the factors, which significantly influence their physical and mechanical properties. Formation of structure is strongly affected by production technology, casting and solidification of these alloys. Solidification is a critical factor in the materials industry (Kavicka et al., 2007). Solute segregation either on the macro- or microscale is sometimes the cause of unacceptable products due to poor mechanical properties of the resulting non-equilibrium phases. In the areas of more important solute segregation there occurs weakening of bonds between atoms and mechanical properties of material degrade. Heterogeneity of distribution of components is a function of solubility in solid and liquid phases. During solidification a solute can concentrate in inter-dendritic areas above the value of its maximum solubility in solid phase. Solute diffusion in solid phase is a limiting factor for this process, since diffusion coefficient in solid phase is lower by three up to five orders than in the melt. When analysing solidification of steel so far no unified theoretical model was created, which would describe this complex heterogeneous process as a whole. During the last fifty years many approaches with more or less limiting assumptions were developed. Solidification models and simulations have been carried out for both macroscopic and microscopic scales. The most elaborate numerical models can predict micro-segregation with comparatively high precision. The main limiting factor of all existing mathematical micro-segregation models consists in lack of available thermodynamic and kinetic data, especially for systems of higher orders. There is also little experimental data to check the models. Many authors deal with issues related to modelling of a non-equilibrium crystallisation of alloys. However, majority of the presented works concentrates mainly on investigation of modelling of micro-segregation of binary alloys, or on segregation of elements for special cases of crystallisation - directional solidification, zonal melting, onedimensional thermal field, etc. Moreover these models work with highly limiting assumption concerning phase diagrams (constant distribution coefficients) and development of dendritic morphology (mostly one-dimensional models of dendrites. Comprehensive studies of solidification for higher order real alloys are rarer. Nevertheless, there is a strong industrial need to investigate and simulate more complex alloys because

nearly all current commercial alloys have many components often exceeding ten elements. Moreover, computer simulation have shown that even minute amounts of alloying elements can significantly influence microstructure and micro-segregation and cannot be neglected.

#### 4.1.1 Methodology of chemical heterogeneity investigation

Original approach to determination of chemical heterogeneity in structure of polycomponent system is based on experimental measurements made on samples taken from characteristic places of the casting, which were specified in advance. Next procedure is based on statistical processing of concentration data sets and application of the original mathematical model for determination of distribution curves of dendritic segregation of elements, characterising the most probable distribution of concentration of element in the frame of dendrite (Dobrovska et al., 2009), and the original mathematical model for determination of effective distribution coefficients of these elements in the analysed alloy.

## 4.1.2 Application of methodology of chemical heterogeneity investigation – investigation into chemical micro-heterogeneity of CC steel slab

A continuously cast steel slab (CC steel slab, Figure 7) with dimensions 1530x250 mm was chosen for presentation of results, with the following chemical composition in (wt. %): 0.14C; 0.75Mn; 0.23Si; 0.016P; 0.010S; 0.10Cr; 0.050Cu; 0.033Al<sub>total</sub>.

After solidification and cooling of the cast slab a transversal band was cut out, which was then axially divided into halves. Nine samples were taken from one half for determination of chemical heterogeneity according to the diagram in Figure 8. The samples had a form of a cube with an edge of approx. 20 mm, with recorded orientation of its original position in the CC slab. Figure 9 shows an example of microstructure of the analysed slab. On each sample a concentration of seven elements (*aluminium, silicon, phosphor, sulphur, titanium, chromium and manganese*) were measured along the line segment long 1000 µm. The distance between the measured points was 10 µm.



Fig. 7. The steel slab caster



Fig. 8. Scheme of sampling from a slab and marking of samples



Fig. 9. Example of structure of the sample 21 with a microscopic trace of 1000 μm long

Analytical complex unit JEOL JXA 8600/KEVEX Delta V Sesame was used for determination of concentration distribution of elements, and concentration was determined by method of energy dispersive X-ray spectral micro-analysis. As an example, Figures 10 a,b present *the basic concentration spectrum* of Mn, Si, P and S.



Fig. 10. Sample 21. Basic concentration spectrum a) of Mn and Si, b) of S and P

Chemical micro-heterogeneity, i.e. segregation of individual elements at distances, order of which is comparable to dendrite arms spacing, can be quantitatively evaluated from the

basic statistical parameters of the measured concentrations of elements in individual samples. These parameters comprise:  $C_x$  average concentration of element (arithmetic average) in the selected section,  $s_x$  standard deviation of the measured concentration of element,  $C_{min}$  minimum concentration of element and  $C_{max}$  maximum concentration of element measured always on the selected section of the sample. It is possible to calculate from these data moreover *indexes of dendritic heterogeneity*  $I_H$  of elements in the measured section of individual samples as ratio of standard deviation  $s_x$  and average concentration  $C_x$  of the element. Then the element distribution profiles can be plotted according to the Gungor's method (Gungor, 1989) from the concentration data sets measured by the method ED along the line segment 1000 µm long. Data plotted as the measured weight percent composition versus number of data (Figures 10 a,b) were put in an ascending or descending order and x-axis was converted to the fraction solid ( $f_{S \sim g_S}$  in Equation 3) by dividing each measured data number by total measured data number. The element composition versus fraction solid, i.e. element distribution profile (distribution curve of dendritic segregation) was then plotted; Figures 11 a,b represent such dependences for manganese, silicon, phosphor and sulphur. The slope of such curve (ascending or descending) depended on the fact, whether the element in question enriched the dendrite core or the inter-dendritic area in the course of solidification.

From these statistical data it is also possible to determine with use of original mathematical model for each analysed element from the given set of samples the values of *effective distribution coefficients*  $k_{ef}$ . The procedure of the effective distribution coefficient calculation will be outlined here as follows:

The sequence of such arranged concentrations (Figures 11 a,b) was seen as a distribution of concentrations of the measured element in the direction from the axis ( $f_S = 0$ ) to the boundary ( $f_S = 1$ ) of one average dendrite.



Fig. 11. Experimentally determined distribution curve of dendritic segregation (sample 21) a) for Mn and Si ,b) for P and S

The effective distribution coefficient  $k_{ef}$  was in this case defined by the relation

$$k_{ef}(f_{s}) = C_{s}(f_{s}) / C_{L}(f_{s})$$
(18)

where  $C_S$  is the solute concentration in the solidus and  $C_L$  is its concentration in liquidus and argument ( $f_S$ ) expressed the dependence of both concentrations on the fraction solid. A perfect mixing of an element in the interdendritic melt was then assumed (this assumption.

It was therefore possible to substitute the equation (18) by the formula

$$k_{ef}(i) = C_i / C_R(i)$$
 (19)

where  $C_i$  is the concentration in *i*-th point of the sequence (i.e. in the *i*-th point of the curve in Figures 11 a, b) and  $C_R(i)$  is the average concentration of the element in the residual part of the curve (i.e. for  $f_S \in \langle i, 1 \rangle$ ), expressed by the relation:

$$C_{R}(i) = \left[1 / (n - i + 1)\right] \sum_{j=1}^{n} C_{j}$$
(20)

where *n* was the number of the measured points. In this way it was possible to determine the values of effective distribution coefficients for all  $i \in \langle 1, n \rangle$ , i.e. for the entire curve characterising the segregation during solidification. The effective distribution coefficients of all the analysed elements were calculated by this original method. The average values of determined effective distribution coefficients are listed in Table 3. No segregation occurs when  $k_{\text{ef}} = 1$ ; the higher is the deviation from the number 1, the higher is the segregation ability.

The effective distribution coefficients calculated in this way inherently include in themselves both the effect of segregation in the course of alloy solidification and the effect of homogenisation, occurring during the solidification as well as during the cooling of alloy.

Sample				Eleı	nent			
		Al	Si	Р	S	Ti	Cr	Mn
11	$I_H$	1.24	0.28	1.22	1.45	0.30	0.22	0.14
11	<i>k</i> <sub>ef</sub>	0.32	0.78	0.33	0.26	0.76	0.83	0.88
12	$I_H$	1.54	0.30	1.12	1.74	0.29	0.27	0.15
12	<i>k</i> <sub>ef</sub>	0.24	0.77	0.36	0.20	0.78	0.79	0.88
12	$I_H$	1.44	0.30	1.25	1.48	0.30	0.29	0.15
15	<i>k</i> <sub>ef</sub>	0.27	0.78	0.32	0.26	0.77	0.78	0.88
21	$I_H$	1.33	0.29	1.58	1.49	0.31	0.24	0.13
21	k <sub>ef</sub>	0.29	0.78	0.24	0.25	0.76	0.81	0.89
22	$I_H$	1.14	0.28	1.31	1.41	0.30	0.26	0.14
22	<i>k</i> <sub>ef</sub>	0.35	0.78	0.30	0.27	0.77	0.80	0.88
22	$I_H$	1.56	0.29	1.34	1.86	0.26	0.28	0.13
23	<i>k</i> <sub>ef</sub>	0.24	0.78	0.29	0.18	0.80	0.78	0.89
21	$I_H$	1.11	0.28	1.22	2.34	0.31	0.23	0.16
51	<i>k</i> <sub>ef</sub>	0.37	0.78	0.33	0.18	0.76	0.82	0.87
27	$I_H$	1.44	0.27	1.16	1.49	0.34	0.25	0.14
52	<i>k</i> <sub>ef</sub>	0.27	0.79	0.34	0.25	0.74	0.80	0.88
22	$I_H$	1.32	0.29	1.24	1.64	0.35	0.26	0.13
55	<i>k</i> <sub>ef</sub>	0.30	0.78	0.32	0.22	0.74	0.80	0.89

Average values of measured and calculated quantities in the set of samples are in Table 4.

Table 3. The average values of the heterogeneity index  $I_H$  and the effective distribution coefficient  $k_{ef}$  of elements in the individual samples

	$C_X$	$I_H$	$k_{ef}$	k <sup>(ref)</sup>
	±	±	±	according to
	$S_X$	$s_I$	Sk	Dobrovska et al., 2009
Δ1	0.0136	1.352	0.294	0.12 0.02
AI	0.0029	0.162	0.046	0.12 -0.92
C:	0.1910	0.285	0.781	0.66 0.01
51	0.0068	0.011	0.005	0.00 -0.91
D	0.0141	1.270	0.314	0.06 0.50
ľ	0.0023	0.133	0.035	0.08 -0.30
c	0.0136	1.657	0.232	0.02, 0.10
5	0.0030	0.297	0.035	0.02 -0.10
т:	0.0951	0.306	0.765	0.05 0.60
11	0.0032	0.027	0.019	0.05 -0.80
Cr	0.1758	0.255	0.799	0.20 0.07
	0.0076	0.023	0.017	0.30 -0.97
Ma	0.8232	0.143	0.873	0.72 0.00
Ivin	0.0169	0.009	0.033	0.72 -0.90

Table 4. Average values of the measured and calculated quantities in the set of all samples

Data represented in Table 3 and Table 4 make it possible to evaluate dendritic heterogeneity (micro-heterogeneity) of elements, as well as their effective distribution coefficients in individual samples, and also in the frame of the whole analysed half of the slab cross-section. It is obvious from these tables that dendritic heterogeneity of accompanying elements and impurities is comparatively high. This is demonstrated by the index of dendritic heterogeneity  $I_H$ . It follows from Table 3, that distinct differences exist between micro-heterogeneity of individual elements. Figures 12 a, b show distribution of indexes of micro-heterogeneity of sulphur (the most segregating element) and manganese (the least segregating element) on slab cross-section.



Fig. 12. a) Differences in sulphur micro-heterogeneity in samples taken from one-half of slab cross-section. b) Differences in manganese micro-heterogeneity in samples taken from one-half of slab cross-section.

Average value of this coefficient for all the analysed elements and the whole set of nine samples is given in Table 4. It follows from this table that dendritic heterogeneity of slab decreases in this order of elements: sulphur, aluminium, phosphor, titanium, silicon, chromium and manganese, which has the lowest index of heterogeneity. Dendritic heterogeneity of the analysed elements is expressed also by the values of their effective distribution coefficients, arranged for individual samples in Table 3 and for the set of samples in Table 4.

It is obvious from the tables that pair values of the index of dendritic heterogeneity and effective distribution coefficient for the same element do mutually correspond. The higher the value of the heterogeneity index, the lower the value of effective distribution coefficient and vice versa. The lowest value of the effective distribution coefficient is found in sulphur and the highest value is found in manganese. It follows from the Table 4, that effective distribution coefficient increases in this order of elements: sulphur, aluminium, phosphor, titanium, silicon, chromium and manganese. All the analysed elements segregate during solidification into an inter-dendritic melt, and their distribution coefficient is smaller than one. For comparison, the Table 4 contains also the values of distribution coefficients found in literature. It is obvious that our values of effective distribution coefficients, calculated according to the original model, are in good agreement with the data from literature, only with the exception of sulphur (and titanium). The reason for this difference is probably the means of calculation of the effective distribution coefficient – the value of this parameter is calculated from concentration data set measured on solidified and cooled casting. Consequently, the effective distribution coefficients calculated in this way inherently include in themselves both the effect of segregation in the course of alloy solidification and the effect of homogenisation, occurring during the solidification as well as during the cooling of alloy.

#### 4.2 Effect of elelectromagnetic stirring on the dendritic structure of steel billets

Currently, casters use rotating stators of electromagnetic melt-stirring systems. These stators create a rotating magnetic induction field with an induction of **B**, which induces eddycurrent **J** in a direction perpendicular to **B**, whose velocity is **v**. Induction **B** and current **J** create an electromagnetic force, which works on every unit of volume of steel and brings about a stirring motion in the melt. The vector product ( $\mathbf{v} \times \mathbf{B}$ ) demonstrates a connection between the electromagnetic field and the flow of the melt. The speeds of the liquid steel caused by the elelectromagnetic stirring is somewhere from 0.1-to-1.0 m/s. The stirring parameters are within a broad range of values, depending on the construction and technological application of the stirrer. The power output is mostly between 100 and 800 kW, the electric current between 300 and 1000 A, the voltage up to 400 V and with billet casting the frequency from 5 to 50 Hz.

The elelectromagnetic stirring applied on the steel caster is basically a magneto-hydraulic process together with crystallisation processes and solidification of billet steel. The complexity of the entire process is enhanced further by the fact that the temperatures are higher than the casting temperatures of concast steel. The temperature of the billet gradually decreases as it passes through the caster down to a temperature lying far below

the solidus temperature. From the viewpoint of physics and chemistry, the course of the process is co-determined by a number of relevant material, physical and thermokinetic characteristics of the concast steel and also electrical and magnetic quantities. There is also a wide range of construction and function parameters pertaining to the caster and elelectromagnetic stirring as well as parameters relating to their mutual arrangement and synchronisation. Numerous works from recent years relate that exact mathematical modelling of elelectromagnetic stirring on a caster is still unsolvable (Stransky et al., 2009).

The basic elelectromagnetic stirring experiment was conducted on a continuously steel billet caster where two individual mixers were working (Figure 13). The first stirrer, entitled MEMS (Mould Electromagnetic Stirring), is mounted directly on the mould and the second stirrer, entitled SEMS (Strand Electromagnetic Stirring), is mounted at the beginning of the flow directly after the first cooling zones but in the secondary-cooling zone. Here the outer structure of the billet is already created by a compact layer of crystallites, however, in the centre of the billet there is still a significant amount of melt that is mixed by the SEMS.



Fig. 13. The steel billet caster of 150x150 mm. The positions of the MEMS and SEMS stirrers

#### 4.2.1 The temperature field of a billet

The temperature field of the billet of 150x150 mm computed via original numerical model (Stransky et al., 2009,2011) is in Figures 14-15.



Fig. 14. The temperature history of marked points of the cross-section of the steel billet 150x150 mm



Fig. 15. Computed iso-solidus and iso-liquidus curves in the axial longitudinal section

#### 4.2.2 The experiment

The first stirrer (MEMS) stirs the melt still in the mould while the billet is undergoing crystallization and solidification. The second stirrer (SEMS) works at a time when the melt is already enclosed by a shell of crystallites around the perimeter of the billet and inside the billet there is less melt than above in the active zone of the first stirrer. When both stirrers were switched off, the crystallisation and solidification continued in the normal way, i.e. the solidifying melt did not undergo a forced rotational movement. Samples were taken throughout the course of the experiment – from parts of the billet cast using the MEMS and SEMS and without and also using either one. The samples were taken in the form of cross-sections (i.e. perpendicular to the billet axis). The samples were fine-ground and etched with the aim of making visible the dendritic structure which is characteristic for individual variants of the solidification of the billet. The verification of the influence of MEMS and SEMS on the macrostructure of the billet was carried out on two melts of almost the same chemical composition (Table 5).

Melt	С	Mn	Si	Р	S	Cu	Cr	Ni	Al	Ti
А	0.14	0.31	0.22	0.014	0.009	0.03	0.05	0.02	0.02	0.002
В	0.13	0.32	0.22	0.018	0.012	0.09	0.06	0.04	0.02	0.002

Table 5. Chemical composition of experimental melts [wt.%]

The timing of the concasting process of the billets – without the involvement of the stirrers and with the working of the elelectromagnetic stirring of individual variants of stirrers (MEMS and SEMS) – is given in Table 6. The speed of the concasting (i.e. the movement, the proceeding of the billet through the mould) of the billet was maintained constant during the experimentation at a value of 2.7 m/min. Table 6 shows that as many as nine concasting variants were verified. The lengths of individual experimental billets – from which samples had been taken – were always a multiple of the metallurgical length. The average superheating of the steel above the liquidus was  $32.8 \pm 3.1$  °C in melt A and  $28.0 \pm 4.6$  °C in melt B, which lies within the standard deviation of the temperature measurements.

Melt	Concasting	Superheating of	MEMS	SEMS	Fig.
	mode –	steel above	stirring	stirring	_
	sampling	liquidus [°C]	[Amperes]	[Amperes]	
А	1A	37	210	0	
	2A	31	0	0	Fig. 16a
	3A	33	0	29	
	4A	30	210	57	Fig. 16b
В	1B	35	210	0	
	2B	30	0	0	
	3B	27	0	57	
	4B	24	210	57	
	5B	24	210	29	

Table 6. The billet concasting modes and sampling

Note: Detailed records of the experimental verification of the effects of MEMS and SEMS during concasting on the relevant device pertain to Table 6. The data are appended with a time history of the MEMS and SEMS connection and with information relating to the lengths of individual billets and the points from which the actual samples had been taken (i.e. the cross-sections from which the dendritic structures had been created). Evaluation of all nine variants of concasting (Table 6) indicates that the arrangement of dendrites in the cross-section follow the same tendency in the first phase of crystallization. The structure is created by columnar crystals – dendrites – perpendicular to the walls of the billet (Figure 16a).

In the billets that were not stirred the dendrites gradually touch one another on the diagonals of the cross-section. Here their growth either ceases, or the dendrites bend in the directions of the diagonals and their growth continues all the way to the centre of the billet. The columnar dendrites that grow from the middle part of the surface maintain their basic orientation – perpendicular to the surface – almost all the way to the centre of the billet. In the central part of the cross-section there is an obvious hollow on all nine macroscopic images. This is most probably a shrinkage.



Fig. 16. a) Dendrite growth in the concasting structure without elelectromagnetic stirring – mode 2A, b) The growth of dendrites in the billet structure using the MEMS and SEMS – mode 4A (Table 6)

The above-described mechanism of dendrite growth during concasting without stirring is frequently the object of interest (Figure 16a). Inside the billets, when using the MEMS stirrer (or both MEMS and SEMS), the kinetics of solidification and dendrite growth is initially the same as without stirring. This also creates columnar dendrites which touch along the diagonals, however, soon their growth ceases still near the surface. Dendrites, which are called equiaxed dendrites continue to grow – their orientation is more random and only partly directed towards the centre of the billet (Figure 16b). It appears that this dendrite growth mechanism manifests itself the most when both stirrers are working simultaneously (Table 6: 4A, 4B and 5B). If MEMS and SEMS are working simultaneously, the stirring effect significantly destroys the formation of columnar crystals. If only MEMS is working and SEMS is switched off (1A and 1B), then the descruction of columnar crystals is less evident. The working mode of SEMS alone (modes 3A and 3B) cannot be clearly differentiated from the changes in the dendritic structure in relation to the structure formed without stirring (2A and 2B).

Figure 16b (the macro-ground dendritic structure) shows the depth of the columnar band of dendrites in the direction away from the surface of the billet (Figure 16b – see arrows) and its value, which (with the simultaneous stirring of MEMS and SEMS) is 23.4±1.8 mm. The same qualified guess was made for ordinary billet casting (i.e. without stirring). Here, the depth of the dendrites can be guessed almost all the way to the central shrinkage at 70 mm (Figure 16a – see arrows). It is known that additives and impurities during solidification are often concentrated in points of contact of the growing dendrites, where the maximum of segregated additives and impurities and the greatest probability of technological defects occurs. In the given case, this undesirable effect can be expected along the diagonals which have a length of up to 100-to-103 mm towards the central shrinkage. This point of contact of the dendrites during the simultaneous working of SEMS and MEMS is only 29.8±1.9 mm,

i.e. 3.4× less. The central area of the billet containing a hollow as a result of a shrinkage is then filled with dendrites growing into a vacuum (i.e. underpressure) (Figure 17).



Fig. 17. Dendrites in the centre of the billet

Under the assumption that the maximum of defects (i.e. vacancies, impurities, additives and micro-shrinkages) are formed along the diagonals it is possible to expect that in the areas of the corners – specifically on the edges – the nucleation of cracks will be higher than on the walls of the billet. If the first approximation of the fracture toughness of the relevant billet made from low-carbon steel is  $K_{IC} \sim 75.0$  MPa.m<sup>1/2</sup>, then in the ordinary concasting process it can be assumed that the length of the contact of columnar dendrites along the diagonal will be approximately  $\Delta l_{normal} \approx 101.5$  mm (Figure 16a). On the other hand, if both electromagnetic stirrers (MEMS and SEMS) are engaged simultaneously, the contact length of the columnar dendrites along the diagonal decreases to  $\Delta l_{el.magnl} \approx 29.8$  mm (Figure 16b). Along these lengths (i.e. the areas) it could be expected that during concasting the concentration of the primary defects will increase.

A comparison of limit stresses and strains in the area of the edges of the billets during concasting without elelectromagnetic stirring and if both MEMS and SEMS stirrers are engaged indicates that the billets (otherwise cast under the same conditions) cast without stirring are almost twice as susceptible to cracking along the edges as billets cast using both stirrers. A similar assumption can be made even in the case of assessing the effect of columnar dendrites in the central part of the surface of the billet where, without stirring, their length grows from the surface of the wall all the way to the central shrinkage (Figure 16a), while with the stirrers the dendrites are significantly shorter. The boundaries of the dendrites are however much less damaged by technological defects (vacancies, etc.) than the areas of their touching – of the peaks along the diagonals. Long-term statistical monitoring of the quality of 150×150 mm billets and the chemical composition has proven that the application of elelectromagnetic stirring has significantly reduced the occurrence of defects (in this case cracks).

#### 5. Conclusion

Progressive creation of numeric model of unsteady thermal field A connected with the model of chemical heterogeneity B, leads to a completely novel conjugated numeric model,

which necessarily requires respecting reality of poly-component crystallising metallic system, formed usually by eight to eleven constitutive elements. Constitutive elements forming conjugated model have during crystallisation completely different physical-chemical properties in dependence of temperature. Their redistribution in the volume of crystallising tangible macroscopic system is governed by the 2<sup>nd</sup> Fick's law. Mutual functional connection of both models A and B into one mutually cooperating conjugated model AB represents a completely new step resting on real crystallising poly-component system. This connection of two models AB necessarily requires large amount of consistent concentration data of constitutive elements forming real crystallising tangible macroscopic poly-component system. These data concern alloying elements (e.g. Ni, Cr), basic tramp elements (Mn, Si, Ti, V, Mo), data on admixture elements and impurities (S, P), as well as data on de-oxidising elements (AI, Ca, etc.).

The most complicated conjugated model will be the model for continuous casting. The authors have prepared for its creation 50,000 experimentally verified and mutually consistent data on elements. These data, make it possible to express concentrations *C*, effective distribution coefficient of elements between melt and crystallising solid phase  $k_{ef}$ , diffusion coefficients  $D_s$  in the melt of all segregating elements of dendritically crystallising system in the sense of the equation (3), express also the degree of heterogeneity and shares of solidified phase  $g_s$ . It contains also the equation (4), which is dimensionless Fourier's number  $\alpha$  of the second kind for mass transfer, which contains implicitly, apart from the diffusion coefficient also share of local solidification time and squares of half distance of dendritic axes  $\theta_{ls}/L^2$ . Equation (5) postulates by share of concentrations at the interface of the melt and solid phase (dendrite) the degree of heterogeneity – these mutually consistent and already verified data on elements form the basic starting point for progressive functional creation of the above mentioned conjugated model AB.

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