

Solidifying ceramics EUCOR and its tendency to the cracks and fractures

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ABSTRACT. *Corundum-baddeleyit material (CBM) – EUCOR – is a ceramic material, which is a heat- and wear-resistant even at extreme temperatures. A numerical model of the solidification and cooling of this material – which was cast into a non-metal form – had been applied. The model is capable of determining the total solidification time of the casting and also the place of the casting which solidifies last. Furthermore, it is possible to calculate the temperature gradient in any point and time. The local solidification time is one of the input parameters for the cooperating model of chemical heterogeneity which is applied next. This second model and its application provide detailed quantitative information on the material structure and make it possible to analyse the solidification process which entails statistical processing of the results of the measurements of the chemical heterogeneity of EUCOR and performs the correlation of individual components during solidification. The crystallisation process seems to be very complicated, where the macro- and microscopic segregations differ significantly. The verification of both numerical models was conducted on a real 350 x 200 x 400 mm cast block. If the heterogeneity of EUCOR does not exceed the pre-defined limits, its tendency to crack is considerably reduced.*

INTRODUCTION

Material EUCOR belongs to the not too well known system of the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-ZrO}_2$ oxide ceramics. Throughout the world, it is produced only in several plants – in the Czech Republic under the name of EUCOR [1]. The melting of this material is done in electric-arc furnaces lined with material of the same chemical composition. The information relating to the properties of EUCOR is covered in [1 to 6]. The basic approximate chemical composition of CBM (in weight %) is 13-17% SiO_2 , 49-52% Al_2O_3 , 30-33% ZrO_2 , 0.1% TiO_2 , 0.2 CaO, 0.2% FeO and (1.0-2.0%) alkaline oxides. Mineralogical, i.e. the phase composition of this ceramic material is given in weight % as: 48-50% corundum, 30-32% baddeleyite (ZrO_2 – monocline system) and 18-20% glass phase [1]. From the foundry property viewpoint, EUCOR has certain characteristics that are similar to the behaviour of cast metal materials, especially steel

for castings. For example, the cooling of EUCOR blocks was monitored and measured with the aim of determining the solidification constant K [$\text{cm}\cdot\text{min}^{-1/2}$] according to Chvorinov (see [2]). During the calculation of this constant according to Chvorinov, the release of heat was considered only in the direction perpendicular to the wall of the casting, together with the corresponding calculated modulus of cast blocks $M = 10$ cm. This corresponded according to the basic relationship $M = K\sqrt{t}$, where t is the solidification time in minutes, the solidification constant:

$K = 0.669$ [$\text{cm}\cdot\text{min}^{-1/2}$] for a casting in a mixture of sand and water-glass without metal chills, and

$K = 0.890$ [$\text{cm}\cdot\text{min}^{-1/2}$] for a casting in a mixture of sand and water-glass with approximately 50% of metal chills.

EUCOR castings must also be risered – to a certain extent in a similar way as casting steel for castings. In order to ensure their correct functioning, it is necessary to perforate the crust several times during solidification, for the surface layer of the melt solidifies quickly and prevents the further flow of the melt from the riser to the actual casting. Regarding the high volume contraction during solidification (6.5%), it is necessary to select a riser where the ratio of casting-to-riser is 7:3, and count with 70% utilization of melt even when the level (of the riser) is insulated with *Sibral* and its multiple perforation. With risers that are prone to cracking, it is necessary, within the temperature range from 970°C to 560°C , to ensure cooling at a rate of less than $50^\circ\text{C}/\text{hour}$ [4]. This question and also other problems can be solved by means of numerical three-dimensional (3D) model of temperature field and model of chemical heterogeneity.

NUMERICAL MODEL OF THREE-DIMENSIONAL TEMPERATURE FIELD

A three-dimensional (3D) model of transient heat transfer, considering the system made up of the casting, mould and ambience had been used for the research. The solidification and cooling of a classically cast casting, together with the simultaneous heating and successive cooling of the mould can be described by the well-known Fourier equation. The application of this model to the massive casting from EUCOR material was described in report [2] in detail.

A real $350 \times 200 \times 400$ mm EUCOR block had been used for the numerical calculation and the experiment. Temperature measurement (using thermocouples) and its successive confrontation with the calculation proved that it is possible to apply the numerical model on basic calculations of solidification and cooling of EUCOR. It is also possible to determine the temperature gradients, the rate of solidification and the local solidification times θ (i.e. the time for which the given point of the casting finds itself between the liquidus and solidus temperatures). The local solidification time θ significantly affects – according to the analogy from steels – the forming of the pouring structure of the given material. Since the research [2] also covered measurement of chemical heterogeneity of the oxides of EUCOR, the previous conclusion was used to develop the numerical model of chemical heterogeneity.

MODEL OF CHEMICAL HETEROGENEITY

The concentration distribution of individual oxides, making up the composition of the ceramic material EUCOR, was determined using an original method developed by the authors and applied in the process of measuring the macro- and micro-heterogeneity of elements within ferrous alloys [3]. This method was initially modified with respect to the differences during solidification of the ceramic material compared to ferrous alloys.

It had been presumed that within EUCOR the elements are together with oxygen already distributed according to the stoichiometric ratio (i.e. chemical equation), which characterises the resulting composition of the oxides of individual elements after solidification.

The preconditions for the application of the model of chemical heterogeneity on EUCOR material are:

If the analytically expressed distribution of micro-heterogeneity of the oxides of the ceramic material are available, if their effective distribution coefficient is known and 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 is applied for the description of the segregation of oxides of the solidifying ceramic material [3] and if an analogy with metal alloys is assumed, then it is possible to express a relationship between the heterogeneity index I_{het} of the relevant oxide, its effective distribution coefficient k_{ef} and the dimensionless parameter α using the equation

$$\ln(2\alpha k_{ef}) / (1 - 2\alpha k_{ef}) = \{ \ln(1 + nI_{het}^{(m)} / k_{ef}) \} / (k_{ef} - 1), \quad (1)$$

whose right side $\{ \ln(1 + nI_{het}^{(m)} / k_{ef}) \} / (k_{ef} - 1)$, based on the measurement of micro-heterogeneity, is already known and through whose solution it is possible to determine the parameter α , which is also on the right hand side of the equation in $2\alpha k_{ef} = X$. The quantity n has a statistical nature and expresses what percentage of the measured values can be found within the interval $\bar{x}_s \pm ns_x$ (where \bar{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 α is known for each oxide, then there exists a key to the clarification of the relationship between the local solidification time θ of EUCOR, to the diffusion coefficient D of the relevant oxide within the solidifying phase and to the structure parameter L , which characterises the distances between individual dendrites (in steels) or cells (in ceramics). The equation of the dimensionless parameter α is

$$\alpha = D\theta/L^2. \quad (2)$$

As a structure parameter of EUCOR material it is possible to take the dimension of structure cell.

APPLICATION OF THE MODEL OF CHEMICAL HETEROGENEITY

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). The primary results from the measurements of chemical heterogeneity of the oxides of EUCOR are contained in the works [4,5].

Both the measured and computed parameters of chemical micro-heterogeneity and the computed parameters of the local solidification time θ (according to the temperature-field model) were calculated. The local solidification time of sample B is $\theta_B = 112.18 \text{ s}$ and of sample C is $\theta_C = 283.30 \text{ s}$. The computed values of parameter α and the local solidification time θ 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:

$$\alpha/\theta = D/L^2 \text{ [1/s]} \quad (3)$$

The calculated values of relation (3) for oxides of samples B and C are arranged in the following table together with parameters α :

Table 1. Calculated value of relation Eq. 3 and of parametr α

Oxide	Na ₂ O	Al ₂ O ₃	SiO ₂	ZrO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	HfO ₂
B: α	0.0732	0.0674	0.0741	0.00035	0.0721	0.0750	0.0759	0.0732	0.0165
$\alpha/\theta_B \cdot 10^4$	6.53	6.01	6.61	0.0312	6.43	6.69	6.77	6.53	1.47
C: α	0.0691	0.0662	0.0663	0.00008	0.0665	0.0703	0.0757	0.0711	0.00017
$\alpha/\theta_C \cdot 10^4$	2.44	2.34	2.34	0.0028	2.35	2.48	2.67	2.51	0.0060

It comes as a surprise that the values of the parameter $\alpha/\theta = D/L^2$ of the oxides of elements Na, Al, Si, K, Ca, Ti and Fe differ 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 have the highest melting temperature. From the melt, both oxides segregate first, already in the solid state. Further redistribution of the oxides of both elements runs on the interface of the remaining melt and the successive segregation of other oxides only to a very limited extent. It is therefore possible to count with the fact that the real diffusion coefficients of zirconium and hafnium in the successively forming crystallites are very small (i.e. D_{Zr}

→ 0 a $D_{Hf} \rightarrow 0$). On the other hand, the very close values of the parameters $\alpha/\theta = D/L^2$ of the remaining seven analysed oxides:

$$D/L_B^2 = (6.51 \pm 0.25) \cdot 10^{-4} \quad \text{and} \quad D/L_C^2 = (2.45 \pm 0.12) \cdot 10^{-4} \quad [1/s]. \quad (4)$$

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

According to [6], it would be possible to count – in the first approximation – with the diffusion coefficients of the oxides in the slag at temperatures of 1765 °C (solidus) and 1775 °C (liquidus) with an average value of $(2.07 \pm 0.11) \times 10^{-6} \text{ cm}^2/\text{s}$ (the data refers to the diffusion of aluminium in the slag with a composition of 39% CaO-20% Al₂O₃-41% SiO₂). For these cases, and using Eq. (3), it is possible to get the magnitude of the structure parameters that govern the chemical heterogeneity of the values:

$$\begin{aligned} L_B &= \sqrt{(2.07 \times 10^{-6}) / (6.51 \times 10^{-4})} = 0.05639 \text{ cm and} \\ L_C &= \sqrt{(2.07 \times 10^{-6}) / (2.45 \times 10^{-4})} = 0.09192 \text{ cm,} \end{aligned} \quad (5)$$

which corresponds to 564 μm in sample B (which was taken from edge of casting block) and 919 μm in sample C (which was taken from underneath the riser of the same casting block).

From the comparison of the micro-structures of the analyses samples B and C (Fig. 1 and 2 are taken from [6]), it is obvious that the micro-structure of sample B (L_B) is significantly finer than the micro-structure of sample C (L_C), which semi-quantitatively corresponds to the qualified estimate of the structure parameters L , conducted on the basis of calculations from the data obtained from both models.

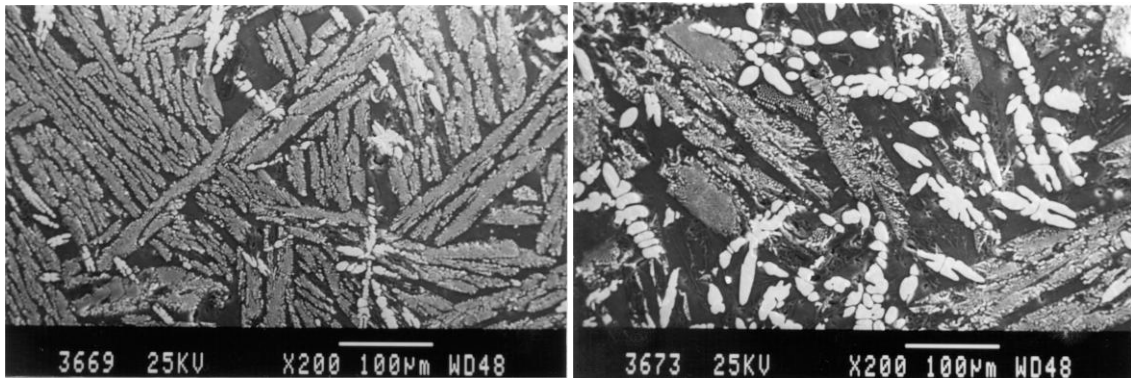


Figure 1. Sample B – $L_B = 563.9 \mu\text{m}$ Figure 2. Sample C – $L_C = 919.2 \mu\text{m}$

CONSEQUENCES OF CHEMICAL HETEROGENEITY MODEL

The structure of sample B on the Fig. 1 characterizes more cooling velocity of EUCOR material from solidus temperature as the structure C on the Fig. 2. From these two

figures it is possible to see that the higher diameter of the structure parameter L corresponds with the lower cooling velocity of the same material. The booth structure parameters L_B, L_C was calculated using the combination of two models (numerical model of temperature field and model of chemical heterogeneity). Numerical model of temperature field of the casting block solidification gives the information about the local solidification time in the anyone point of casting, it means also in anyone critical point of casting which has tendency to the cracking, or to the fracture. The model of chemical heterogeneity creates a possibility to estimate the structures parameters in this critical point of castings.

After fracture mechanics it is possible in the first approximation to write equation

$$K_{IC} \geq \sigma_B \sqrt{\pi L_B} = \sigma_C \sqrt{\pi L_C}, \quad (6)$$

where K_{IC} is fracture toughness [MPa.m^{1/2}], σ_B, σ_C are the strain on the tips of structure defects [MPa] and L_B, L_C are the diameters the structure parameters (cells) in the samples B and C [m]. On their grains is a high probability of the creating of the primary technological defects in castings (micro-shrinkage porosity, micro-shrinkage cavity, and so on). From the Eq. 6 follows that

$$\left(\frac{\sigma_B}{\sigma_C} \right)^2 = \frac{L_C}{L_B} = \frac{919.2}{563.9} = 1.63. \quad (7)$$

It means, that the relation between the structure parameters L_C and L_B makes (gives) the relation between of quarter of σ_B and σ_C strain on the tips of potential structure defects of the samples B and C. At the same fracture toughness can be the strain on the sample B 1.27 time higher as the strain on the sample C.

CONCLUSIONS

This paper discusses the numerical model of the transient temperature field and the numerical model of chemical heterogeneity, their application and combination.

The combining of both models makes it possible to estimate the structure parameter, which expresses the size of the crystallites of the resultant material structure.

The combining of both models creates a tool to the estimating of the tendency to the cracks and fractures in a critical point of casting from EUCOR material.

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