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BACK-DIFFUSION IN CRYSTAL GROWTH. EUTECTICS

DYFUZJA WSTECZNA WE WZROŚCIE KRYSZTAŁU. EUTEKTYKI

Solute segregation/redistribution model for some eutectic alloys is presented. The differential equation for the solute micro-segregation during solidification accompanied by the back-diffusion is formulated. The solution to this equation results in the definitions of: solidification path, solid/liquid (s/l) interface path and redistribution path. An equation for the estimation of the amount of equilibrium and non-equilibrium precipitates is also delivered. It is proved that the current model is universal one. Thus, the model reduces perfectly, mathematically to both description of diffusion-less solidification and model of equilibrium solidification.

Keywords: micro-segregation; redistribution; precipitates

Przedstawiono model segregacji/redystrybucji składnika dla stopów eutektycznych. Sformułowano równanie różniczkowe dla mikrosegregacji składnika podczas krystalizacji, której towarzyszy dyfuzja wsteczna. Rozwiązanie tego równania pozwoliło na zdefiniowanie ścieżek: krystalizacji, frontów krystalizacji i redystrybucji. Sformułowano równanie dla oceny ilości wydzieleń równowagowych i nierównowagowych. Pokazano, że model jest uniwersalny. Dlatego, redukuje się perfekcyjnie, matematycznie do opisu krystalizacji bez dyfuzji a także do modelu krystalizacji równowagowej.

Notation

D_s – coefficient of diffusion into the solid, [m^2/s]
i_D – amount of the non-equilibrium precipitate, [dimensionless]
i_E – amount of the equilibrium precipitate, [dimensionless]
i_K – total amount of precipitates, [dimensionless]
k – equilibrium partition ratio, [mole fr./mole fr.]
L_0 – amount of the liquid at the beginning of solidification; $L_0 = 1$, [dimensionless]
N^B – current solute redistribution in the solid, [mole fr.]
N^L – current solute concentration in the liquid, [mole fr.]
N^S – current solute concentration at the s/l interface, [mole fr.]
N_0 – nominal solute concentration of a studied alloy, [mole fr.]
$\bar{N}_s$ – average solute concentration within the solid, [mole fr.]
R – half the space of the crystal, [m]
t^f – local solidification time, [s]
t^d – homogenization time for the diffusion length, [s]
T – temperature, [K]
x – current amount of a growing crystal; $x \in [0,1]$, [dimensionless]
x_K – finale amount of the crystal, [dimensionless]
X^0 – amount of a growing crystal at a given solidification stage, [dimensionless]
α – back-diffusion parameter (*Fourier* Number); $\alpha \in [0,1]$, [dimensionless]
β^{ex} – coefficient of the extent of redistribution, [dimensionless]
β^{in} – coefficient of the intensity of redistribution, [dimensionless]

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Introduction

Most castings show some evidences of a fine-scale solute redistribution. This compositional inhomogeneity can be revealed as a solute concentration gradient on a micro-scale, and additionally, it can result in the formation of a second phase.

One of the most important challenges encountered in the alloy's solidification is the ability to predict the effects of processing parameters on nature and extent of both micro-segregation and solute redistribution. This kind of approach is highly desirable in view of recent development in the thermodynamic modelling and phase diagrams estimation. The description of the solute redistribution should involve the application of some parameters of the full physical meaning. Moreover, the model is to be an universal approach applicable in the case of plate-like morphology formation (1D), oriented structure solidification (2D), and equiaxed grains growth (3D).

1. Micro-segregation without back-diffusion

The origin of micro-segregation comes from the partitioning of the solute between solid and liquid during a crystal growth. The solute segregation as a result of the non-equilibrium solidification was the subject of the Scheil, [1] and Krupkowski, [2], treatments. Scheil, [1], was able to deliver the equation which can be used to predict micro-segregation in the case of non-equilibrium crystal growth while applying the simplest equilibrium partition ratio, Eq. (1). The back-diffusion does not operate in this approach, therefore, $\alpha = 0$, Eq. (1).

$$k = N^S(x;0)\,/\,N^L(x;0) \tag{1}$$

The major assumptions made in this derivation are: no diffusion into the solid, $\alpha = 0$, complete mixing in the liquid and local equilibrium at the solid/liquid (s/l) interface. Some consequences for the behavior of solid result from these assumptions. A heterogeneous nucleus can be introduced in the liquid just before the beginning of solidification, [3]. In some situations the nucleus can present the nominal solute concentration, [4,5]. The crystal seed is consequently surrounded with the solid sub-layers which appear in sequence due to the temperature drop. The solute concentration in the first sub-layer is equal to the product of the partition ratio and nominal concentration of a given alloy, $N^S(0,0) = kN_0$. Every subsequent sub-layer conserves the solute concentration which corresponds with appropriate temperature at which it came into existence. Finally, the ***solidification path*** is described as follows:

$$N^L(x;0) = N_0\,(1-x)^{k-1} \tag{2}$$

Eq. (2) has been obtained due to the solution of an adequate differential equation to which an initial condition was applied: $N^L(0;0) = N_0$. Consequentially, the ***s/l interface path*** is given as: $N^S(x;0) = kN^L(x;0) = kN_0\,(1-x)^{k-1}$. The ***redistribution path*** $N^B(x;0)$ means the same as the ***s/l interface path***, $N^B(x;0) \equiv N^S(x;0)$, since, $\alpha = 0$, [6]. The mass balance is satisfied in this description, [7,8].

2. Micro-segregation with complete back-diffusion

The mass balance applied to the description of the so-called equilibrium crystal growth (Lever Rule) can be referred to the current universal model for micro-segregation/ redistribution. In the case of the equilibrium solidification, the solute concentration in the liquid is defined as follows:

$$N^L(x;1) = N_0\,(1+kx-x)^{-1} \quad x \in [0,1] \tag{3a}$$

$$N^L(0;1) = N_0; \quad N^L(1;1) = N_0\,/\,k \tag{3b}$$

The ***solidification path***, Eq. (3), is written for the so-called complete diffusion into the solid, $\alpha = 1$. The ***s/l interface path*** is given: $N^S(x;1) = kN^L(x;1) = kN_0\,(1+kx-x)^{-1}$ whereas the ***redistribution path*** is written: $N^B(x;X^0;1) = N^S(X^0;1)$; $N^B(1;1;1) = N_0$.

3. Micro-segregation with finite back-diffusion

The theory for the equiaxed crystal growth presented by Eq. (2) has been subsequently developed by Brody & Flemings, [9] for directional solidification. The definition for the α – back diffusion parameter has been introduced, [9]:

$$\alpha = D_S\,t^f R^{-2} \tag{4}$$

The Brody & Flemings theory, [9], presents some simplifications and assumptions which are not acceptable. First of all, the α – back diffusion parameter tends to infinity, [9]. Then the solute redistribution is identical to the micro-segregation which appears at the s/l interface and consequentially the mass balance is not conserved in such a system described by the mentioned approach, [9]. Thus, the theory, [9] was subjected to many modifications and generalizations, [10-21]. Nevertheless, the mass balance violation was not removed from the model, [9], and back-diffusion parameter tends to infinity. In the consequence, the mentioned models [9-21], are mathematically reducible to the non-equilibrium solidification, Eq. (2), but not reducible to the Lever Rule, Eq. (3). The current model improves the imperfections involved by the mentioned models, [9-21]. Thus, the following equation is formulated:

$$d\left(x\bar{N}_S\left(x;\alpha\right)\right) = N^S\left(x;\alpha\right)dx + \frac{D_S}{R\,v_p}\,x\,\frac{dN^S\left(x;\alpha\right)}{dx}\,dx \tag{5}$$

The l.h.s. of Eq. (5) presents the amount of solute, which entered inside the crystal due to back-diffusion, when the newly growing dx – layer appeared; the first term of the r.h.s. of Eq. (5) presents the amount of solute, which is actually within this layer, (s/l interface); the second term of the r.h.s. of Eq. (5) presents the amount of solute which passed across the s/l interface and entered inside the crystal. Eq. (5) has been written, however, with some simplifications analogous to those, known in the Brody & Flemings theory, [9]. It causes mass balance in the solid-liquid system to not be yet satisfied. Eq. (5) determines increase of solute, which is passing from the liquid to the solid, only while considering the increment, dx.

Taking into account that average thickening rate, v_p, perpendicular to the direction of crystal growth, is $v_p = R/t^f$, the definition of the α – back-diffusion parameter, Eq. (4), can be separated from Eq. (5) because $D_S/(Rv_p) = D_S t^f/R^2 = \alpha$. Hence, Eq. (5) can be rewritten as follows: $d(x\overline{N}_S(x;\alpha)) = N^S(x;\alpha)\,dx + \alpha x dN^S(x;\alpha)$. The assumed conservation of solute within the solid-liquid system is expressed in function of an average solute content within the solid: $d((1-x)N^L(x;\alpha)) + d(x\overline{N}_S(x;\alpha)) = 0$. Finally, the studied formula becomes:

$$\begin{aligned}\left[N^L(x;\alpha) - N^S(x;\alpha)\right]dx = (1-x)\,dN^L(x;\alpha) + \\ + \alpha\,x\,dN^S(x;\alpha)\end{aligned} \tag{6}$$

Eq. (6) should be rewritten adequately to the current description which takes into account both the back-diffusion phenomenon and applicability of Eq. (1).

$$\begin{aligned}(1-k)N^L(x;\alpha)\,dx = (1-x)\,dN^L(x;\alpha) + \\ + \alpha\,k\,x\,dN^L(x;\alpha)\end{aligned} \tag{7}$$

It can be easily deduced from Eq. (7), that the definition of the back-diffusion parameter satisfies the following limitation: $0 \le \alpha \le 1$, [22,23].

The solution to Eq. (7) is obtained while applying the condition: $N^L(0;\alpha) = N_0$.

$$N^L(x;\alpha) = N_0\left(1+\alpha kx - x\right)^{\frac{k-1}{1-\alpha k}}; \quad x \in \left[0, x_K\right] \tag{8}$$

Contrary to the analogous equations delivered in approaches [9-21], Eq. (8) is reducible to the Lever Rule, Eq. (3) while applying $\alpha = 1$ and Eq. (8) reduces to Eq. (2), with $\alpha = 0$, as expected.

The s/l interface path results from Eq. (8): $N^S(x;\alpha) = k\,N_0\left(1+\alpha kx - x\right)^{\frac{k-1}{1-\alpha k}}$. However, the redistribution path is to be formulated by a new relationship, [8,24]:

$$\begin{aligned}N^B\left(x; X^0, \alpha\right) = \left[k + \beta^{ex}\left(x; X^0\right)\beta^{in}\left(X^0, \alpha\right)\right]N^L(x;\alpha), \\ x \in [0, X^0], \quad X^0 \in [0, x_K]\end{aligned} \tag{9}$$

$$\beta^{ex}\left(x; X^0\right) = k(1-k)\left(X^0 - x\right)/\left(1 + k\,X^0 - X^0\right) \tag{9a}$$

which yields from the condition: $N^S(x;1) + \beta^{ex}(x;X^0)\beta^{in}(X^0;1)\,N^L(x;1) = N^S(X^0;1)$

$$\begin{aligned}&\beta^{in}\left(X^0, \alpha\right) = \frac{A\,B}{C\left[D + E\,F\right]} \\ &A = \alpha\left(1 + k - 2\alpha k\right)\left(1 + k\,X^0 - X^0\right) \\ &B = \left[\left(1 + k\,X^0 - X^0\right)\left(1 + \alpha\,k\,X^0 - X^0\right)^{\frac{k-1}{1-\alpha k}} - 1\right] \\ &C = (1-k) \\ &D = k\,X^0(1-\alpha) \\ &E = \left(1 + \alpha\,k\,X^0 - X^0\right)\end{aligned} \tag{9b}$$

$$F = \left(\left(1 + \alpha\,k\,X^0 - X^0\right)^{\frac{k-\alpha k}{1-\alpha k}} - 1\right)$$

which yields from the mass balance: $\int\limits_0^{X^0} N^B\left(x; X^0, \alpha\right)dx + \left(1 - X^0\right)N^L\left(X^0; \alpha\right) = 1\,N_0$

The equilibrium solidification ($N_K(\alpha, N_0) = N^L(1,\alpha) = N_0/k$)) results in:

$$(\alpha k)^{(k-1)/(1-\alpha k)} = 1/k \tag{10}$$

Eq. (10) yields $\alpha = 1$, as expected. Exceptionally, $N_K(\alpha, N_0) = N^L(1, \alpha_E) = N_E$. In this case, $x_K = 1$ and no precipitates are observed. It gives: $(\alpha_E k)^{(k-1)/(1-\alpha_E k)} = N_E/N_0$. It can be shown that: $\alpha_E(N_0) = 1$ when $N_0 = k\,N_E$. Generally, $\alpha_E(N_0) \le 1$ when $x_K \le 1$ with $0 < N_0 \le N_E$. However, $\alpha_E(N_0) = 1$ when $N^L(1;1) \ge N_E$.

4. Effect of the back-diffusion upon precipitates appearance

Micro-segregation is usually accompanied by precipitates. However, a/ there are not precipitates when: $\alpha > \alpha_E(N_0)$; b/ there are equilibrium precipitates, i_E, only, when $\alpha = \alpha_E(N_0)$, for $kN_E < N_0 \le N_E$; c/ there are non-equilibrium precipitates, i_D, only, when $\alpha < \alpha_E(N_0)$, for $0 < N_0 \le kN_E$; d/ there are non-equilibrium, i_D, and equilibrium precipitates, i_E, when $\alpha < \alpha_E(N_0)$, for $kN_E \le N_0 \le N_E$.

In the case of solidification of the alloys from the eutectic phase diagrams, the solute concentrations in the last portion of the liquid before an appearance of precipitates are given:

$$N_K(\alpha, N_0) = N_E, \qquad 0 \le \alpha \le \alpha_E(N_0) \tag{11}$$

$$N_K(\alpha, N_0) = N^L(1;\alpha), \qquad \alpha_E(N_0) < \alpha \le 1 \tag{12}$$

Final amount of the crystal can also be calculated:

$$\begin{aligned}x_K(\alpha, N_0) = \left(1/(1-\alpha k)\right)\left[1 - \left(N_E/N_0\right)^{\frac{1-\alpha k}{k-1}}\right], \\ 0 \le \alpha \le \alpha_E(N_0)\end{aligned} \tag{13a}$$

$$x_K(\alpha, N_0) = 1, \qquad \alpha_E(N_0) < \alpha \le 1 \tag{13b}$$

The total amount of precipitates, i_K, is given as:

$$i_K(\alpha, N_0) = 1 - x_K(\alpha, N_0) \tag{14}$$

whereas, $i_E(N_0) = i_K(1, N_0)$, and $i_D(\alpha, N_0) = i_K(\alpha, N_0) - i_E(N_0)$; $i_E(N_E) = 1$; $i_E(kN_E) = 0$.

5. Concluding remarks

The current model for solute segregation/redistribution is coherent with the fundamental models for: a/ non-equilibrium solidification, [1,2], b/ equilibrium solidification (Lever Rule). First of all, however, the physical limitation for the α – back-diffusion parameter (Diffusional *Fourier* Number) is to be determined. Thus, the definition of the time required for homogenization, $t^d = R^2/D_S$, is to be introduced into Eq. (4). Then, the mentioned definition becomes: $\alpha = t^f/t^d$. The equilibrium solidification takes part when, $t^f = t^d$, and full homogeneity of a given crystal is obtained with, $\alpha = 1$. On the other hand, $\alpha = 0$, when no diffusion into the solid is assumed.

Thus, when: a/ $\alpha = 0$, then Eq. (7) reduces to the differential equation for micro-segregation formulated by Scheil, [1] and Krupkowski, [2], b/ $\alpha = 1$, then Eq. (7) results in the description of the equilibrium solidification. Consequentially, for, $\alpha = 0$, Eq. (8) reduces to Eq. (2), and to Eq. (3) for, $\alpha = 1$. Additionally, the ***redistribution path***, Eq. (9) reduces to the ***s/l interface path***, $N^B(x;X^0,0) \Rightarrow N^S(x;0)$, when, $\alpha = 0$, and to $N_0 = \text{const}$, when, $\alpha = 1$.

The current model can be used for the estimation of the diffusion coefficient due to the solute redistribution measurement and a fitting of the measurement points by Eq. (9). It requires to select a proper value of the α – *Fourier* Number, and results in estimation of the D_S – parameter, [25].

The proposed description of the solute redistribution can also be applied to the assignment of the solidification path for ternary alloys, [26].

The current model is universal approach of solidification and is able to describe the rapid solidification experiments, [27], when, $k \Rightarrow 1$, according to the Aziz's concept, [28]. In this case, Eq. (8) changes its form into: $N^L(x;\alpha) = N_0$ (***solidification path***). Consequentially, the ***s/l interface path*** is: $N^S(x;\alpha) = kN^L(x;\alpha) = kN_0 = N_0$, when, $k = 1$. It means that *liquidus* line is juxtaposed by *solidus* line, for, $k = 1$. Finally, the ***redistribution path*** is defined as: $N^B(x;X^0,\alpha) \equiv N^S(x;\alpha) = N_0$. Therefore, the back-diffusion phenomenon is not forced to occur in this experiment or in an adequate technology.

The solute redistribution is the only parameter measurable by the EDS technique. The practical definition, applicable for the measurement of the solute redistribution is: $N^B(x_j;x_{0j},\alpha) = N^B\left[(\bar{\lambda}_j/L)^w;\ (\bar{L}_{oj}/\bar{L})^w,\alpha\right]$. All these parameters have already been well characterized, [24]. It should, however, be emphasized that the w – parameter depends on the geometry of solidification. Thus, $w = 1$, when the plate-like morphology is formed (1D solidification); $w = 2$, when the columnar grains appear during oriented crystal growth (2D solidification), and $w = 3$, when the equiaxed grains are exclusive form of an alloy (3D solidification), Fig. 1.

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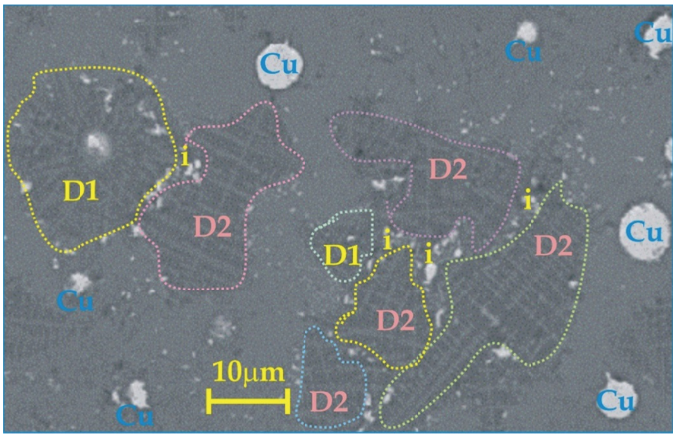

Fig. 1. 3D solidification of some (Fe)-equiaxed grains which appear within the slag used in the KGHM – plant conditions; a/the **D1** – (Fe)-equiaxed crystals growing due to the heterogeneous nucleation on the (Cu)-particle, b/ the **D2** – (Fe)-equiaxed crystals growing due to the homogeneous nucleation (according to the mechanism described in [4], [5]); c/ the **i** – precipitates resulting from the **D1** and **D2** crystal growth; d/ the **Cu** – particles after coagulation due to the special treatment of the slag by the complex reactant (it is generally described in [29,30]).

REFERENCES

[1] E. Scheil, Über die Eutektische Kristallization. Zeitschrift für Metallkunde **34**, 70-76 (1942).

[2] A. Krupkowski, General Solution of the Equation Characterizing the Crystallization Process in Binary Alloys of Dendritic Type, Bulletin of the Polish Academy of Sciences, Technical Sciences **13**, 61-66 (1965).

[3] W. Krajewski, A.L. Greer, T.E. Quested, W. Wołczyński, Identification of the Substrate of Heterogeneous Nucleation in Zn-Al Alloy Inoculated with Zn-Ti Based Master Alloy, Chapter 16 in: Solidification and Crystallization, p. 137-147, ed. Wiley-VCH, Weinheim, Germany, 2004, eds. D.M. Herlach.

[4] T. Lipiński, Modification of Al-Si Alloys with the Use of a Homogenous Modifiers. Archives of Metallurgy and Materials **53**, 193-197 (2008).

[5] T. Lipiński, P. Szabracki, Modification of the Hypo-eutectic Al-Si Alloys with an Exothermic Modifier. Archives of Metallurgy and Materials, **58**, 453-458 (2013).

[6] H. Nguyen-Thi, B. Drevet, W. Wołczyński, Influence of Microgravity on the Back-diffusion Phenomenon in the Al-3.5Li Alloy Solidified Directionally, Archives of Metallurgy and Materials **44**, 365-371 (1999).

[7] J. Kloch, B. Billia, T. Okane, T. Umeda, W. Wołczyński, Experimental Verification of the Solute Redistribution in Cellular/Dendritic Solidification of the Al-3.5Li and Fe-4.34Ni Alloys, Materials Science Forum **329/330**, 31-36 (2000).

[8] W. Wołczyński, J. Kloch, Mass Conservation for Micro-segregation and Solute Redistribution in Cellular/Dendritic Solidification with Back-Diffusion, Materials Science Forum **329/330**, 345-351 (2000).

[9] H.D. Brody, M.C. Flemings, Solute Redistribution in Dendritic Solidification, Transactions of the Metallurgical Society of AIME, **236**, 615-624 (1966).

[10] M. Solari, H. Biloni, Micro-segregation in Cellular and Cellular--Dendritic Growth, Journal of Crystal Growth **49**, 451-457 (1980).

[11] T. Clyne, W. Kurz, Solute Redistribution during Solidification with Rapid Solid State Diffusion, Metallurgical Transactions **12A**, 965-971 (1981).

[12] A. Roosz, Z. Gacsi, G. Fuchs, Solute Redistribution during Solidification and Homogeneisation of Binary Solid Solution, Acta Metallurgica **32**, 1745-1754 (1984).

[13] D.H. Kirkwood, Micro-segregation, Materials Science and Engineering **65**, 101-109 (1984).

[14] I. Ohnaka, Mathematical Analysis of the Solute Redistribution during Solidification with Diffusion in the Solid Phase, Transactions of the ISIJ **26**, 1045-1051 (1986).

[15] S. Kobayashi, A Mathematical Model for Solute Redistribution during Dendritic Solidification, Transactions of the ISIJ **28**, 535-542 (1988).

[16] S. Kobayashi, Mathematical Analysis of Solute Redistribution during Solidification Based on a Columnar Dendrite Model, Transactions of the ISIJ **28**, 728-735 (1988).

[17] S. Kobayashi, Solute Redistribution during Solidification with Diffusion in the Solid Phase, Journal of Crystal Growth, **88**, 87-96 (1988).

[18] S.W. Chen, Y.A. Chang, Micro-segregation in Solidification for Ternary Alloys, Metallurgical Transactions, **23A**, 1038-1043 (1992).

[19] L. Nastac, D.M. Stefanescu, An Analytical Model for Solute Redistribution during Solidification of Planar, Columnar, or Equiaxed Morphology, Metallurgical Transactions **24A**, 2107-2118 (1993).

[20] N.F. Dean, A. Mortensen, M.C. Flemings, Micro-segregation in Cellular Solidification, Metallurgical Transactions **25A**, 2295-2301 (1994).

[21] T. Himemiya, T. Umeda, Solute Redistribution Model of Dendritic Solidification Considering Diffusion in both the Liquid and Solid Phases. ISIJ International **38**, 730-738 (1998).

[22] W. Wołczyński, J. Kloch, R. Ebner, W. Krajewski, The Use of Equilibrium Phase Diagram for the Calculation of Non-Equilibrium Precipitates in Dendritic Solidification. Validation, Calphad **25**, 391-400 (2002).

[23] W. Wołczyński, W. Krajewski, R. Ebner, J. Kloch, The Use of Equilibrium Phase Diagram for the Calculation of Non-Equilibrium Precipitates in Dendritic Solidification. Theory, Calphad **25**, 401-408 (2002).

[24] W. Wołczyński, Back-Diffusion Phenomenon during the Crystal Growth by the Bridgman Method, Chapter 2. in the book: Modelling of Transport Phenomena in Crystal Growth, p. 19-59, WIT Press, Southampton (UK) – Boston (USA), 2000, eds. J.Szmyd & K.Suzuki.

[25] W. Wołczyński, W. Gąsior, Z. Moser, Interpretation and Meaning of the Diffusion Coefficient in Solid Al-3.5Li Alloy by Measurement of the Li-Solute Redistribution, Archives of Metallurgy and Materials **47**, 231-238 (2002).

[26] T. Himemiya, W. Wołczyński, Prediction of Solidification Path and Solute Redistribution of an Iron-Based Multi-Component Alloy Considering Solute Diffusion in the Solid, Materials Transactions of the Japan Institute of Metals **43**, 2890-2896 (2002).

[27] C. Senderowski, Z. Bojar, W. Wołczyński, A. Pawłowski, Microstructure Characterization of D-Gun Sprayed Fe-Al Intermetallic Coatings, Intermetallics **18**, 1405-1409 (2010).

[28] M.J. Aziz, Model for Solute Redistribution during Rapid Solidification, Journal of Applied Physics **53**, 1158-1168 (1982).

[29] A. W. Bydałek, S. Biernat, A. Bydałek, P. Schlafka, The Innovative Analysis of the Refinement Ability Extractive Slag, International Journal of Engineering and Innovative Technology **4**, 186-197 (2014).

[30] A.W. Bydałek, A. Bydałek, W. Wołczyński, S. Biernat, The Concept of Slag Decopperisation in the Flash Furnace Process by Use of Complex Reagents, Archives of Metallurgy and Materials **60**, 319-322 (2015).

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