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# A MATHEMATICAL MODEL OF SEGREGATION DURING COOLING OF THE MELT OF IRON WITH PHOSPHORUS

***A.D. Drozin***, *drozinad@susu.ru,*
***E.Yu. Kurkina***, *kurkinaei@susu.ru*
*South Ural State University, Chelyabinsk, Russian Federation*

The purpose of this work is to study in detail the process of phosphorus segregation during steel solidification. A mathematical model considering a spherical melt cell with the nucleus of a solid phase in the center has been created. It has assumed that the thermal processes in this system are in accordance with the law of thermal conductivity and the mass transfer of phosphorus in the liquid and solid phases obeys the law of diffusion. In addition, it has assumed that a local equilibrium is maintained at the interface between these phases and the parameters of this equilibrium can be determined from the equilibrium phase diagram Fe–P. It has been assumed that the outer boundary of the system is cooled according to a mode that is set arbitrarily. Based on the obtained equations, a computer program has been created, that allows obtaining the temperature and the phosphorus content at any point at any time. The calculations have shown that the temperature alignment in of the system is almost instantaneous, and the concentration of phosphorus in the liquid phase has aligned quickly. However, the phosphorus concentration in the solid phase aligns much slower due to the small phosphorus diffusion coefficient in the solid phase. The principal factors determining the segregation of phosphorus are the initial concentration and the melt cooling mode. The results will help to calculate the cooling mode of the melt to produce a metal with the desired properties.

*Keywords: mathematical model, physical metallurgy, phase diagram, segregation, local equilibrium.*

## Introduction

The segregation of steel impurities during its solidification largely determines its quality [1–10]. A promising method of its research is mathematical modeling [11–13].

We have developed a mathematical model based on the following basic principles. A two-component melt is investigated. The whole melt has been divided into cells with the size equal to the average size of the mature grains observed in the crystallized metal. A nucleus of the solid phase grows in each cell. It was assumed that the solid phase nucleus and the outer boundary of the melt are spherical. The temperature of the outer surface of the melt cell decreases according a mode that is set arbitrarily.

Naturally, there is no equilibrium in the melt or in the solid phase during real cooling. However, we assumed that a local equilibrium is maintained at the interface between these phases and the parameters of this equilibrium can be determined from the equilibrium phase diagram.

Due to the small size of the system under consideration, convective flows can be ignored, so it has assumed that thermal processes are in accordance with the laws of thermal conductivity and the mass transfer of phosphorus in the liquid and solid phases obeys the laws of diffusion.

The mathematical model is based on the equations of thermal conductivity and diffusion in the solid and liquid phases and the equations of the equilibrium concentrations of phosphorus in the solid and liquid phases near the surface of the solid particle.

## 1. The mathematical model of the system

In accordance with general theory of the growth of chemical reactions products particles, described in [13], the equations of thermal conductivity and diffusion of phosphorus are as follows.

1. The equations for the solid phase $(S)$ consist of the heat conduction equation

$$\frac{\partial T}{\partial t}=\frac{1}{\rho^S c_P^S}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\lambda^S\frac{\partial T}{\partial r}\right)$$

and the phosphorus diffusion equation

$$\frac{\partial c^S}{\partial t}=\frac{D^S}{\rho^S}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\rho^S\frac{\partial c^S}{\partial r}\right).$$

Here $r$ is the distance from the current point to the center of the solid particle (the center of the whole system), $t$ is time, $c\left(\tilde{n}=\tilde{n}(t,r)\right)$ is the mass fraction of phosphorus, $\rho$ is density, $\lambda$ is thermal conductivity coefficient, $c_P$ is specific heat capacity, and $D$ is diffusion coefficient of phosphorus. The superscript $S$ indicates the solid phase.

2. The equations for the liquid phase $(L)$ consist of the heat conduction equation

$$\frac{\partial T}{\partial t}=\frac{1}{\rho^L c_P^L}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\lambda^L\frac{\partial T}{\partial r}\right)+$$
$$+\frac{\rho_{\mathcal{F}}^L-\rho_{\mathcal{F}}^S}{\rho^L}\frac{R^2}{r^2}\frac{dR}{dt}\frac{\partial T}{\partial r}$$

and the phosphorus diffusion equation

$$\frac{\partial c^L}{\partial t}=D^L\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c^L}{\partial r}\right)+$$
$$+\frac{\rho_{\mathcal{F}}^L-\rho_{\mathcal{F}}^S}{\rho^L}\frac{R^2}{r^2}\frac{dR}{dt}\frac{\partial c^L}{\partial r}.$$

Members $\frac{\rho_{\mathcal{F}}^L-\rho_{\mathcal{F}}^S}{\rho^L}\frac{R^2}{r^2}\frac{dR}{dt}\frac{\partial T}{\partial r}$, $\frac{\rho_{\mathcal{F}}^L-\rho_{\mathcal{F}}^S}{\rho^L}\frac{R^2}{r^2}\frac{dR}{dt}\frac{\partial c^L}{\partial r}$ appear because a growing particle of the solid phase “pushes” the liquid phase around itself, causing its mechanical movement. In these expressions, the superscript $L$ indicates the liquid phase, the subscript $\mathcal{F}$ indicates the value refers to the interphase boundary.

3. The basic equations of the interface boundary consist of the heat transfer equation

$$\lambda_{\mathcal{F}}^S\frac{\partial}{\partial r}T\left[t,R(t)-0\right]-\lambda_{\mathcal{F}}^L\frac{\partial}{\partial r}T\left[t,R(t)+0\right]+$$
$$+\left(I_{\text{Fe}}\Delta H_{\text{Fe}}+I_{\text{P}}\Delta H_{\text{P}}\right)=0,$$

the equations of mass transfer of the phosphorus between the phases

$$\rho_{\mathcal{F}}^S D^S\frac{\partial}{\partial r}c_{\mathcal{F}}^S\left[t,R(t)-0\right]+$$
$$+c_{\mathcal{F}}^S\left(t,R(t)\right)\left(I_{\text{Fe}}+I_{\text{P}}\right)-I_{\text{P}}=0,$$
$$\rho_{\mathcal{F}}^L D^L\frac{\partial}{\partial r}c_{\mathcal{F}}^L\left[t,R(t)+0\right]+$$
$$+c_{\mathcal{F}}^L\left(t,R(t)\right)\left(I_{\text{Fe}}+I_{\text{P}}\right)-I_{\text{P}}=0,$$

and the equation of the solid phase particles growth

$$\frac{dR}{dt}=\frac{1}{\rho_{\mathcal{F}}^S}\left(I_{\text{Fe}}+I_{\text{P}}\right).$$

Here, $\Delta H_{\text{Fe}}$, $\Delta H_{\text{P}}$ are the specific enthalpies of the transition of iron and phosphorus from solid to liquid, $I_{\text{Fe}}$, $I_{\text{P}}$ are the mass transfer rates of Fe and P from the liquid phase to the solid phase per unit surface area.

## 2. Solution method

The boundary between the phases $L$ and $S$ moves. We used difference scheme with front rectification for solving multifront problems of the Stefan type [14] in which the boundary is not moving. After that a finite difference method [15] has been applied and then an algorithm for solving the resulting difference problem has been developed.

A computer program for calculating the temperature and the phosphorus content at any point of the solid particle and the melt at any time and drawing the corresponding graphs was developed.

## 3. The source data for the calculation

A fragment of the Fe–P phase diagram has been used (Fig. 1).

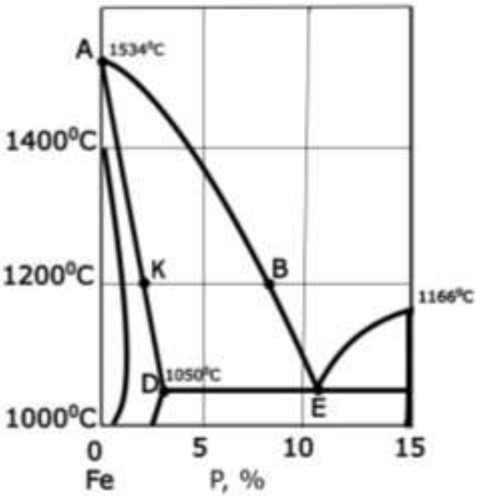

**Fig. 1. A fragment of the Fe–P phase diagram**

The coordinates of points $A, B, E, K, D$ were determined and the line $AD$ was approximated by a linear dependence, and the line $ABE$ by quadratic dependence:

$$c^S=-6.198347\cdot10^{-5}T+0.09508264463,$$
$$c^L=-6.30282\cdot10^{-5}T^2+$$
$$+14.7369036\cdot10^{-2}T-77.7488824.$$

The following physical characteristics of the system components were used [16–19] (Table 1).

The diffusion coefficients of P in the liquid and solid phases were taken equal to $1\cdot10^{-9}\ \text{m}^2\text{s}^{-1}$ and $1\cdot10^{-13}\text{m}^2\text{s}^{-1}$ respectively.

Here are the calculation results for a melt with a mass fraction of phosphorus equaled

**Table 1**

**Data for the calculation**

| Parameter | Fe | P |
|---|---|---|
| Specific heat of melting (kJ·kg$^{-1}$) | 270 | 917 |
| Specific heat capacity, sol. (J·kg$^{-1}$·K$^{-1}$) | 770 | 685 |
| Specific heat capacity liq. (J·kg$^{-1}$·K$^{-1}$) | 673 | 436 |
| Density, sol. (kg·m$^{-3}$) | 7700 | 2200 |
| Density, liq (kg·m$^{-3}$) | 7000 | 900 |
| Thermal conductivity, sol. (W·m$^{-1}$·K$^{-1}$) | 37 | 0.24 |
| Thermal conductivity,liq. (W·m$^{-1}$·K$^{-1}$)) | 34 | 0.16 |

$c_0 = 0{,}05\%$. The liquidus and solidus temperatures of such a system equal, respectively, $T_L$ = 1532.2010 °C and $T_S$ = 1525.6260 °C.

Based on the approximate volume of the melt per grain, the radius of the whole system was assumed equal to $R_{sur} = 10\ \mu\text{m}$, and the initial size of the solid particle was assumed equal to $R_0 = 10\ \text{nm}$. It was assumed that at the initial moment the whole system was at the same temperature $T_0 = T_L$, the composition of the liquid and solid phases was the same everywhere and equal to $c_0$. The cooling rate of the outer surface of the system is assumed linear and such that solidification occurs in 10 minutes.

## 4. The calculation results

Calculations have shown that the temperature alignment in both the liquid and solid phases is almost instantaneous.

Fig. 2 shows that in less than 0.03 seconds, the solid phase particle grows to two-thirds of its maximum possible size (10 microns) and then grows relatively slowly.

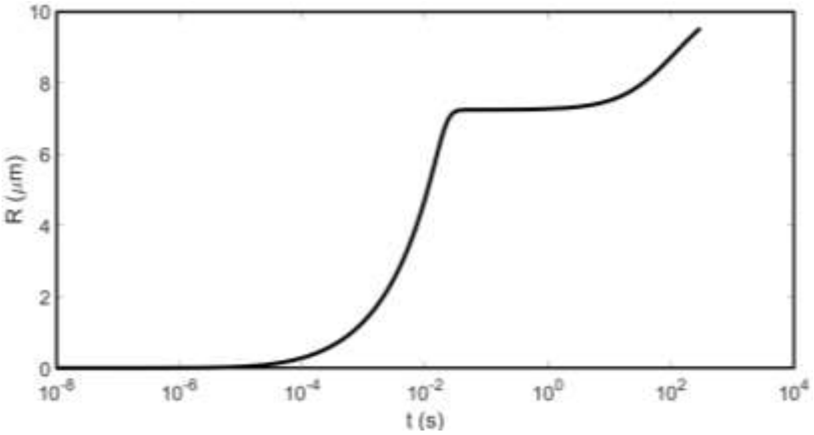

Fig. 2. Growth of the solid phase particle

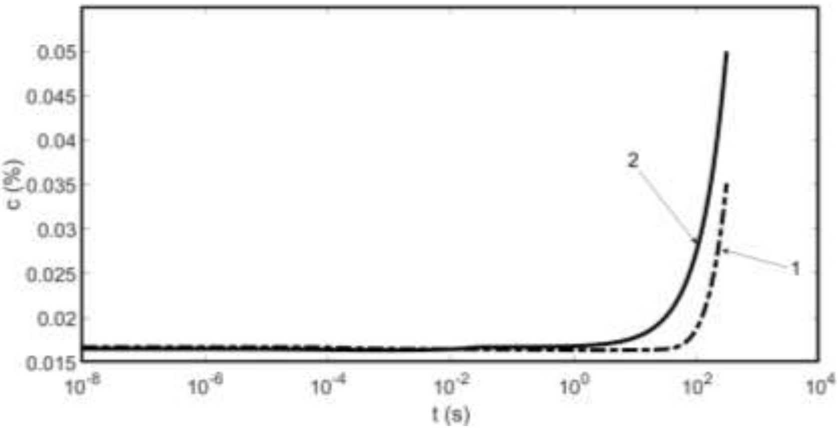

Fig. 3. The changes in the phosphorus concentration in the solid phase over time:
1 – in the center, 2 – on the surface

Fig. 3 shows that for a given such a small coefficient of phosphorus diffusion in the solid phase, the composition of the solid phase does not have time to equalized even in 5 minutes. The concentration of phosphorus in the center and on the surface of the particle by the end of the three hundred seconds differs by 0.15 %. But, as Fig. 4 shows, the concentration of phosphorus in the liquid phase at the surface of the solid particle and at the outer surface of the system begin to coincide after 0.038 s.

Fig. 5 shows the redistribution dynamics of the phosphorus mass contained in the initial melt between the liquid and the solid phases

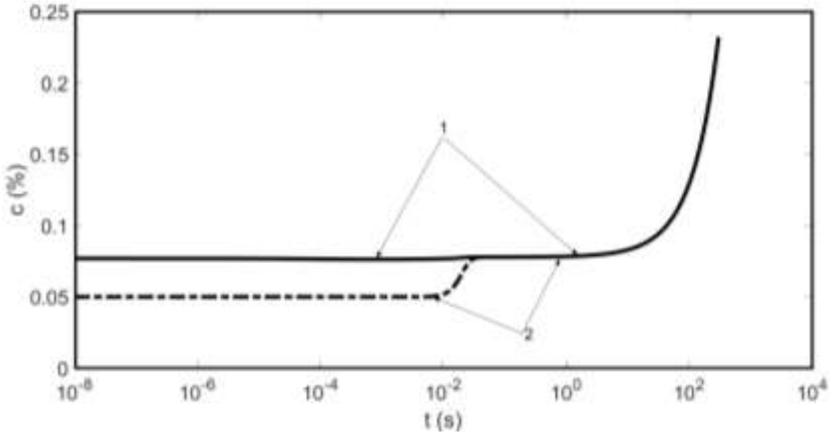

**Fig. 4. Changes in the concentration of phosphorus in the liquid phase over time: 1 – on the border with the solid phase, 2 – on the outer border**

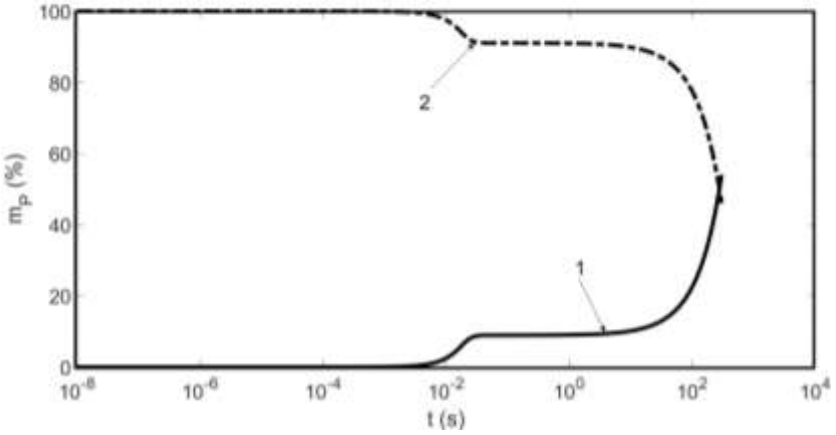

**Fig. 5. Change of the relative mass of phosphorus (relative to the total mass of phosphorus in the system under consideration) over time: 1 – in the solid phase, 2 – in the liquid phase**

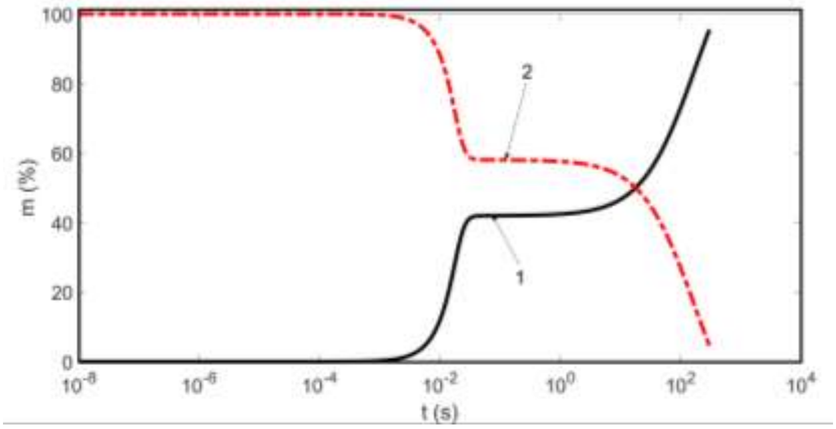

**Fig. 6. Change in relative mass (relative to the total mass of the system) over time: 1 – solid phase, 2 – liquid phase**

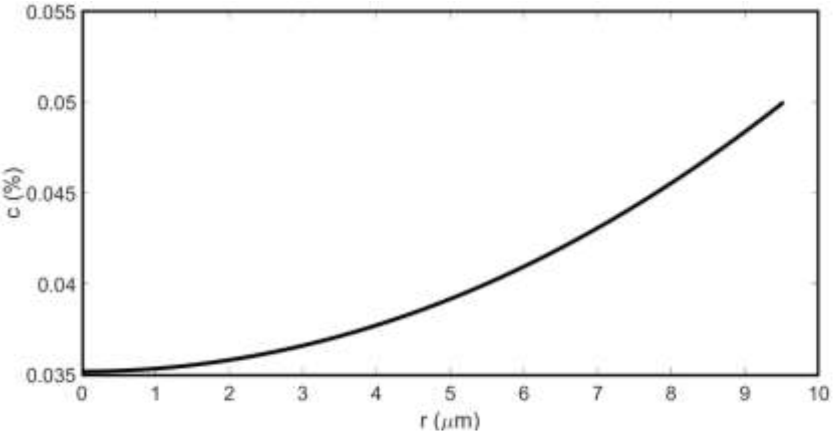

**Fig. 7. Distribution of the phosphorus concentration in the solid phase after 300 s**

over time.

Fig. 6 shows the solidification dynamics of the melt.

Fig. 7 shows the unevenness of phosphorus distribution in solid phase particles after 300 s. The composition of the liquid phase is leveled after 0.038 s.

## Conclusions

Calculations have shown that the temperature alignment is almost instantaneous, and the liquid phase composition alignment is also quite fast. Alignment of the solid phase composition with a small diffusion coefficient is not achieved in real time.

Calculations also showed that the initial concentration of phosphorus and the nature of changes in external temperature play a principal role in the inhomogeneity of the crystallized metal. A computer program that implements the proposed mathematical model allows selecting cooling modes for obtaining solid phase with the specified properties.

## References

1. Kushner V.S., Vereshchaka A.S., Skhirtlazdze A.G., Negrov D.A., Burgonova O.Yu. *Materialovedenie* [Materials technology]. Omsk, OGTU, 2008. 232 p.

2. Roshchin V.E., Roshchin A.V. *Elektrometallurgiya i metallurgiya stali* [Electrometallurgy and metallurgy of steel]. Chelyabinsk, SUSU, 2013. 571 p.

3. Zhukova S.Yu. [Distribution of chemical elements in dendrites and inter-dendritic areas of cast metal]. *Metallurg* [Metallurgist], 2009, no. 1, pp. 46–49. (in Russ.)

4. Rabinovich S.V., Chermenskij V.I., Ogorodnikova O.M., Harchuk M.D. [Mathematical modeling of nickel dendritic liquation in casting invar and superinvar alloys]. *Litejnoe proizvodstvo* [Foundry], 2002, no. 6, pp. 9–12. (in Russ.)

5. Martyushev N.V. [Effect of crystallization conditions on the structure and properties of lead-containing bronzes]. *Metallurgiya mashinostroeniya* [Metallurgy of mechanical engineering], 2010, no. 4, pp. 32–36. (in Russ.)

6. Kondratyuk S.E., Stoyanova E.N., Plyahtur A.A., Parhomchuk Zg.V. [Structure and segregation of steel P6M5L depending on the crystallization conditions]. *Metallurgiya mashinostroeniya* [Metallurgy of mechanical engineering], 2014, no. 1, pp. 23–25. (in Russ.)

7. Koltygin A.V., Belov V.D., Bazhenov V.E. [Peculiarities of crystallization of magnesium alloy ML10 on the segregation of zirconium during the melting process]. *Metally* [Metals], 2013, no. 1, pp. 78–83. (in Russ.)

8. Avdonin N.A. *Matematicheskoe opisanie processov kristallizacii* [Mathematical description of crystallization processes]. Riga, Zinatne, 1980. 180 p.

9. Ljubov B.Ja. *Teoriya kristallizatsii v bol’shikh ob”yemakh* [Theory of crystallization in large volumes]. Moscow, Nauka, 1975. 256 p.

10. Skripov V.P., KoverdaV.P. *Spontannaya kristallizatsiya pereokhlazhdennykh zhidkostey* [Spontaneous crystallization of supercooled liquids]. Moscow, Nauka, 1984. 232 p.

11. Galenko P.K., Jou D. Rapid solidification as non-ergodic phenomenon. *Physics Reports*, 2019, 818, pp. 1–70.

12. Alexandrov D.V., Ivanov A.O. Dynamic stability analysis of the solidification of binary melts in the presence of a mushy region: changeover of instability. *J. Crystal Growth*, 2000, 210, pp. 797–810.

13. Drozin A.D. *Rost mikrochastic produktov himicheskih reakcij v zhidkom rastvore: monografija* [The growth of the microparticle products of chemical reactions in a liquid solution: a monograph]. Cheljabinsk, SUSU, 2007. 56 p.

14. Budak B.M., Gol'dman N.L., Uspenskij A.V. [Difference scheme with front rectification for solving multifront problems of the Stefan type]. *Reports of the USSR Academy of Sciences*, 1966, vol. 167, no. 4, pp. 735–738. (in Russ.)

15. Samarskij A.A. *Teorija raznostnyh shem* [Theory of difference schemes]. Moscow, Nauka, 1977. 656 p.

16. Lyakishev N.P. *Diagrammy sostoyaniya dvojnyh metallicheskih sistem* [Phase diagrams of double metal systems]. Moscow, Mashinostroenie, 1996. 996 p.

17. Zaharov A.M. *Diagrammy sostojanija dvojnyh i trojnyh sistem* [State diagrams of double and triple systems]. Moscow, Metallurgija, 1990. 250 p.

18. Grigor'eva I.S., Mejlihova E.Z. *Fizicheskie velichiny. Spravochnik* [Physical magnitudes. Guide]. Moscow, Jenergoatomizdat, 1991. 1250 p.

19. Rabinovich V.A., Havin Z.Ja. *Kratkij himicheskij spravochnik* [Brief chemical reference]. Leningrad, Himija, 1978. 392 p.

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# МАТЕМАТИЧЕСКАЯ МОДЕЛЬ ЛИКВАЦИИ ПРИ ОХЛАЖДЕНИИ РАСПЛАВА ЖЕЛЕЗА С ФОСФОРОМ

***А.Д. Дрозин, Е.Ю. Куркина***
*Южно-Уральский государственный университет, г. Челябинск, Россия*

Целью данной работы явилось детальное изучение процесса ликвации фосфора при затвердевании стали. Создана математическая модель, рассматривающая сферическую ячейку расплава с ядром твердой фазы в центре. Приняли, что тепловые процессы в системе протекают в соответствии с законом теплопроводности, а массоперенос фосфора в жидкой и твердой фазах подчиняется закону диффузии. Кроме того, приняли, что на границе раздела этих фаз поддерживается локальное равновесие, и параметры этого равновесия могут быть определены из равновесной диаграммы состояния. Внешняя граница расплава охлаждается по произвольному режиму. На основе полученных уравнений была создана компьютерная программа, позволяющая определять содержание фосфора в любой точке расплава в любой момент времени. Расчеты показали, что выравнивание температуры в системе происходит практически мгновенно, а концентрация фосфора в жидкой фазе быстро выравнивается. Однако концентрация фосфора в твердой фазе выравнивается гораздо медленнее из-за малого коэффициента диффузии фосфора в твердой фазе. Основными факторами, определяющими сегрегацию фосфора, являются начальная концентрация и режим охлаждения расплава. Полученные результаты помогут подбирать режим охлаждения расплава для получения металла с заданными свойствами.

*Ключевые слова: математическая модель, металловедение, диаграмма состояния, ликвация, локальное равновесие.*

### *Литература*

*1. Материаловедение / В.С. Кушнер, А.С. Верещака, А.Г. Схиртладзе и др.; под ред. В.С. Кушнера. – Омск: Изд-во ОмГТУ, 2008. – 232 с.*

*2. Рощин, В.Е. Электрометаллургия и металлургия стали / В.Е. Рощин, А.В. Рощин. – 4-е изд., перераб. и доп. – Челябинск: ЮУрГУ, 2013. – 571 с.*

*3. Жукова, С.Ю. Распределение химических элементов в дендритах и междендритных участках литого металла / С.Ю. Жукова // Металлург. – 2009. – № 1. – С. 46–49.*

*4. Математическое моделирование дендритной ликвации никеля в литейных инварных и суперинварных сплавах / С.В. Рабинович, В.И. Черменский, О.М. Огородникова, М.Д. Харчук // Литейное производство. – 2002. – № 6. – С. 9–12.*

*5. Мартюшев, Н.В. Влияние условий кристаллизации на структуру и свойства бронз, содержащих свинец / Н.В. Мартюшев // Металлургия машиностроения. – 2010. – № 4. – С. 32–36.*

*6. Структура и ликвация стали Р6М5Л в зависимости от условий кристаллизации / С.Е. Кондратюк, Е.Н. Стоянова, А.А. Пляхтур, Ж.В. Пархомчук // Металлургия машиностроения. – 2014. –№ 1. – С. 23–25.*

*7. Колтыгин, А.В., Влияние особенностей кристаллизации магниевого сплава мл10 на ликвацию циркония в процессе плавки / А.В. Колтыгин, В.Д. Белов, В.Е. Баженов // Металлы. – 2013. – № 1. – С. 78–83.*

*8. Авдонин, Н.А. Математическое описание процессов кристаллизации / Н.А. Авдонин. – Рига: Зинатне, 1980. – 180 с.*

*9. Любов, Б.Я. Теория кристаллизации в больших объемах / Б.Я. Любов. – М.: Наука, 1975. – 256 с.*

*10. Скрипов, В.П. Спонтанная кристаллизация переохлажденных жидкостей / В.П. Скрипов, В.П. Коверда. – М.: Наука, 1984. – 232 с.*

*11. Galenko, P.K. Rapid solidification as non-ergodic phenomenon / P.K. Galenko, D. Jou // Physics Reports. – 2019. – Vol. 818. – P. 1–70.*

*12. Alexandrov, D.V. Dynamic stability analysis of the solidification of binary melts in the presence of a mushy region: changeover of instability / D.V. Alexandrov, A.O. Ivanov// Journal of Crystal Growth. – 2000. – Vol. 210, no. 4. – P. 797–810.*

*13. Дрозин, А.Д. Рост микрочастиц продуктов химических реакций в жидком растворе: моногр. / А.Д. Дрозин // Челябинск: Изд-во ЮУрГУ, 2007. – 56 с.*

*14. Будак, Б.М. Разностная схема с выпрямлением фронтов для решения многофронтовых задач типа Стефана / Б.М. Будак, Н.Л. Гольдман, А.Б. Успенский // Докл. АН СССР. –1966. – Т. 167, № 4. – С. 735–738.*

*15. Самарский, А.А. Теория разностных схем / А.А. Самарский. – М.: Наука, 1977. – 656 с.*

*16. Диаграммы состояния двойных металлических систем: справ. / под. ред. Н.П. Лякишева. – М.: Машиностроение, 1996. – Т. 1. – 992 с.*

*17. Захаров, А.М. Диаграммы состояния двойных и тройных систем / А.М. Захаров. – М.: Металлургия, 1990. – 250 с.*

*18. Физические величины: справ. / под ред. И.С. Григорьева, Е.З. Мейлихова. – М: Энергоатомиздат, 1991. – 1250 с.*

*19. Рабинович, В.А. Краткий химический справочник / В.А. Рабинович, З.Я. Хавин. – Л: Химия, 1978. – 392 с.*

**Дрозин Александр Дмитриевич**, д-р техн. наук, профессор, директор Центра элитного образования, Южно-Уральский государственный университет, г. Челябинск; drozinad@susu.ru.

**Куркина Елена Юрьевна**, заместитель директора Центра элитного образования, Южно-Уральский государственный университет, г. Челябинск; kurkinaei@susu.ru.

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