

DOI: 10.24425/122430

B. MACHULEC<sup>\*#</sup>, W. BIALIK<sup>\*\*</sup>, S. GIL<sup>\*\*</sup>

## APPLICATION OF THE MINING INDUSTRY WASTES AS RAW MATERIAL FOR MELTING OF THE COMPLEX FESIAL FERROALLOYS

An economical alternative for the steel industry which uses a separate ferrosilicon and aluminum for the deoxidization of steel is a complex deoxidizer in the form of FeSiAl alloys. The effectiveness of complex deoxidizers is higher and they have a positive effect on quality improvement and also for mechanical properties of the finished steel. It is associated with a smaller number of non-metallic inclusions and a more favorable its distribution in the structure of steel. Noteworthy are the waste from the mining industry simultaneously contains SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> oxides with a few of dopants in the form of CaO, MgO, FeO, TiO<sub>2</sub> oxides. These wastes are present in large quantities and can be a cheap raw material for obtaining complex FeSiAl ferroalloys by an electrothermal method. "Poor" hard coal grades which so far did not apply as a reducing agent in the ferroalloy industry because of the high ash content can also be a raw material for the electrothermal FeSiAl process. The electrothermal FeSiAl melting process is similar to the ferrosilicon process in the submerged arc furnace. For this reason, a model based on Gibbs' free enthalpy minimization algorithm was used to analyze the simultaneous reduction of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> oxides, which was originally elaborated for the ferrosilicon smelting process. This is a system of two closed reactors: the upper one with the lower temperature and the lower one with the higher temperature. Between the reaction system and the environment, and between the reactors inside the system, there is a cyclical mass transfer in moments when the state of equilibrium is reached in the reactors. Based on the model, the basic parameters of the electrothermal reduction process of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> oxides were determined and a comparative analysis was made towards the ferrosilicon process.

*Keywords:* FeSiAl, FeSi75, model, submerged arc furnace, Gibbs energy minimization method

### 1. Introduction

The FeSiAl alloys could be melted by the carbothermal process of simultaneous reduction SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> oxides in the submerged arc furnace [1,2]. In nature, there are large quantities of minerals that could be the good raw materials for the production of FeSiAl alloys due to a simultaneous content of silica and aluminum oxides with a few impurities such as iron, calcium, magnesium and titanium oxides. Large resources of cheap raw materials for the FeSiAl production is a selected waste from hard coal mines (Table 1). Also, the "poor" hard coals, which so far have not found any application in the ferroalloys industry due to their high ash content (Table 2) are also worth mentioning. The FeSiAl process in the submerged arc furnace is very similar to the carbo-thermic reduction of silica in the ferrosilicon process. With regard to the unique properties of complex FeSiAl deoxidizers in comparison to traditional de-oxidizers [3,4], and to the economic considerations at the Re Alloys LLC ferroalloys has been started a pilot installation for the FeSiAl melting in the 2017 year. The basic element of the installation is the submerged arc furnace with two transformers of 7.75 MVA. It is the six-electrode furnace

with the rectangular furnace body. Two three-phase transformers independently supply 3 electrodes with a diameter of  $d = 0.9$  m, arranged linearly in two rows separated by a partition through the middle of the bath. The basic raw material for FeSiAl production is a selected waste from hard coal mines and also "poor" hard coal with high ash content. It was assumed that FeSiAl alloy will be a substitute for FeSi65 and FeSi75 ferrosilicon produced in a furnace with six electrodes previously in which 10% Si will be replaced by 10% Al, These alloys are analogous to FS55A10 and FS65A10 alloys produced in Kazakhstan [1].

### 2. Model of the FeSiAl melting process

It has been assumed that the electro-thermal melting process of the FeSi65Al10 and FeSi55Al10 alloys in the submerged arc furnace is close to the ferrosilicon FeSi75 and FeSi65 melting in which part of the silica in charge is replaced by sillimanite (Al<sub>2</sub>O<sub>3</sub>\*SiO<sub>2</sub>) so that in the final alloy about 10% of Si will be replaced with Al. Therefore, in the model, the total content of Si + Al in the FeSiAl alloys should be 75% and 65%

\* SILESIAAN UNIVERSITY OF TECHNOLOGY, DEP. OF ENGINEERING PRODUCTION, 8 STR KRASIŃSKIEGO, 40-019 KATOWICE, POLAND

\*\* SILESIAAN UNIVERSITY OF TECHNOLOGY, INSTITUTE OF METALS TECHNOLOGY, 8 STR KRASIŃSKIEGO, 40-019 KATOWICE, POLAND

# Corresponding author: boleslaw.machulec@polsl.pl

TABLE 1

Chemical composition of waste rocks from different coal mines in Poland

Mine	Component, wt. %				Ash chemical composition, wt. %					
	$A^r$	$V^r$	$W^r$	$C_{fix}$	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
Bogdanka	84,62	11,95	0,79	2,64	57,11	23,51	12,46	1,14	1,45	0,14
Bolesław Śmiały	85,4	9,37	0,81	4,42	60,44	25,74	5,15	1,07	1,93	0,08
Pniówek	84,92	9,67	1,12	4,29	53,64	27,56	6,29	1,08	0,35	0,36
Staszic	87,99	9,17	0,61	2,23	64,22	22,25	5,01	1,04	0,31	0,06

TABLE 2

Chemical composition of hard coal grades with high ash content which so far have not found any use in the ferroalloys industry as reducing agents

Mine	Component, wt. %				Ash chemical composition, wt. %					
	$A^r$	$V^r$	$W^r$	$C_{fix}$	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
Marcel	21,5	24	8,5	46	52,67	25,28	5,65	1,03	3,67	0,27
Piast-Ziemowit	22,50	39,75	6,50	31,25	49,03	24,48	9,66	1,04	4,20	0,13
Powstanców Śląskich	21	30,5	3,8	44,7	38,1	21,43	5,24	1,59	5,36	0,08

respectively, similar to Si content in ferrosilicon. To simulate a continuous process of simultaneous reduction SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> oxides in submerged arc furnace the model was used that had been firstly developed for the ferrosilicon melting process. It is a system of two closed isothermal reactors: an upper one with a lower temperature  $T_1$ , and a lower one with a higher temperature  $T_2$ . Between the reactors and the environment, as well as between the reactors inside the system, a periodical exchange of mass occurs at the time when the equilibrium state is reached in the reactors. In each cycle, a reaction mixture with the molar composition corresponding approximately to the batch mixture of raw materials for the process is fed into the upper reactor [5]. At the same time, the condensed products of chemical reactions move from the top to the bottom, and the gas phase components move in the opposite direction. The gas flow problems in a lump deposit are presented in the publication [6,7]. Simulation of the continuous process is implemented recursively. In Cycle 1, a portion of the reaction mixture is fed into the upper reactor where the reactions take place until the equilibrium state at the temperature  $T_1$  is reached. Then, the gas-phase products leave the Reactor 1 and after cooling to the temperature  $T_w = 850^\circ\text{C}$ , they do not participate in the further process. Simultaneously, the products of condensed phases of the Reactor 1 flow down and are introduced into the Reactor 2 where they react with each other until the equilibrium at the temperature  $T_2$  is reached. Then, the condensed phase products leave the Reactor 2 and, after cooling to the temperature  $T_1$ , they form metallic and slag phases and do not participate in the further process. The gaseous products with the equilibrium composition leave the Reactor 2 and, after cooling to temperature  $T_1$ , they are introduced back into the Reactor 1 where they react to reach the equilibrium state again at temperature  $T_1$  in the next cycle. Cycle 2 and each next cycle of the reaction system starts with an introduction of a new portion of the reactants to the Reactor 1. They react together with the gaseous products of the previous cycle until the equilibrium is reached

at the temperature  $T_1$ . In the subsequent cycles, the process is the same as in Cycle 2. In a real process, temperature  $T_w$  corresponds to the temperature of gases that are by-products of the reduction process, measured immediately after leaving the furnace charge surface. It can be assumed in the model that Reactor 1 corresponds to the charge zone of submerged arc furnace where heat is released as a result of resistive heating and Reactor 2 corresponds to the zones of the furnace where heat is produced by the electric arc. For a fixed composition of the initial reaction mixture and for set conditions of temperature and pressure ( $T_1, T_2, P = 1$  bar), the equilibrium composition of the Reactors 1, and 2 was determined by a non-stoichiometric algorithm of the Gibbs Free Energy Minimization using the HSC 7.1 thermochemical software. It allows for the use a thermochemical database and solution of the Gibbs Minimization problems directly in the Excel spreadsheet [8]. The non-stoichiometric algorithm of the Gibbs Free Energy Minimization arrives at solving the non-linear optimization problem with limitations resulting from the mass balances of individual elements [9]:

$$\left. \begin{array}{l} \min_n \frac{G(T_i, P, \mathbf{n}_i)}{RT_i} \\ \mathbf{A} \cdot \mathbf{n}_i = \mathbf{B} \\ \mathbf{n} \geq \mathbf{0} \end{array} \right\} \quad (1)$$

where:

$G(T_i, P, \mathbf{n}_i)$  – Gibbs free enthalpy function for the reactor  $i$ ,  $i = 1, 2$  MJ/kmol,

$$\mathbf{n}_i = (\mathbf{n}_i^1, \mathbf{n}_i^2, \dots, \mathbf{n}_i^f)^T, \quad \mathbf{n}_i^r = (\mathbf{n}_{1,i}^r, \mathbf{n}_{2,i}^r, \dots, \mathbf{n}_{k^r,i}^r)^T,$$

$\mathbf{n}_i^r$  – vectors which elements are numbers of kmol of the various phase  $r$  components,  $r = 1, 2, \dots, f$ ,

$\mathbf{A}$  – atomic matrix with dimensions  $N \times n$ , which elements are number of particular atoms in phase components (Table 3),

TABLE 3

The components of specific phases of the Fe-Si-Al,-O-C system  
 ( $N = 5, f = 5, n = 84, k^1 = 28, k^2 = 25, k^3 = 1, k^4 = 1, k^5 = 13$ )

§ PHASE 1:	C5(g)	C6(g)	C7(g)	C8(g)	C60(g)	C70(g)	CO(g)	CO2(g)
	C2O(g)	C3O2(g)	Fe(g)	Fe2(g)	Fe(CO)5(g)	FeO(g)	FeO2(g)	O(g)
	O2(g)	O3(g)	Si(g)	Si2(g)	Si3(g)	Si4(g)	SiC(g)	SiC2(g)
	Si2C(g)	SiO(g)	SiO2(g)	Si2O2(g)				
§ PHASE 2:	Al4CO4	AlO	Al2O3	Al2O3*SiO2	Al2O3*2SiO	*3Al2O3*2Si	Al2SiO5(A)	FeAl2O4
	Fe2Al4Si5O	Fe3Al2Si3O	FeCO3	Fe(CO)5	Fe2(CO)9	Fe3(CO)12	Fe0.945O	Fe0.947O
	FeO	FeO1.056	Fe2O3	Fe3O4	FeO*SiO2	*2FeO*SiO2	FeSiO3	Fe2SiO4(B)
	SiO2							
§ PHASE 3:	C							
§ PHASE 4:	SiC							
§ PHASE 5:	Al4C3	Al4SiC4	Fe2C	Fe3C	Al	Fe	FeSi	FeSi2
	Fe3Si	Fe5Si3	Si	FeSi2.33	FeSi2.43			

$n = k^1 + k^2 + \dots + k^f$ , number of components in the reaction system,

$\mathbf{B}$  – vector  $N \times 1$ ,  $\mathbf{B} = (e_1, e_2, \dots, e_N)^T$ ,

$e_i$  – mass of the element type  $i$  in the system, kmol,  
 $i = 1, 2, \dots, N$ ,

$f$  – number of phases in the system,

$N$  – the number of elements in the system,

$R$  – gas constant, kJ/(kmol · K).

First, a model was developed for the Fe-Si-O-C-Al system [6]. However, in addition to SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> oxides, the chemical composition of mining waste includes minerals containing small amounts of oxides: CaO, MgO, TiO<sub>2</sub>. Therefore, in this publication, the model has been extended to the Fe-Si-O-C-Al-Ca-Mg-Ti system. Based on the HSC 7.1 database, it was determined that there may be  $n = 150$  components in this system and  $f = 5$  phases. The phase selection method is shown in Table 3, but due to a large number of components, it is limited to the Fe-Si-O-C-Al system only.

This approach does not specify the chemical reactions or stoichiometric equations. For each cycle, the equilibrium composition of the reaction system as well as the mass, and energy balances can be determined [10]. Based on the energy balance, the components  $Q_R, Q_{Arc}$  of the heat balance that characterize the distribution of heat in the reaction zones located around the electrodes of the submerged arc furnace were determined [6]. The component  $Q_R$  corresponds to the charge zones where heat is released as a result of resistive heating and the  $Q_{Arc}$  corresponds to gas chambers localized around the electrode tips where heat is released by radiation of arc. The distribution of heat in the process can be characterized by percentages  $Q_1, Q_2$  related to  $Q_R$  and  $Q_{Arc}$  as follows:

$$Q_1 = 100 \cdot \frac{Q_w}{Q}, \quad Q_2 = 100 \cdot \frac{Q_{Arc}}{Q}, \quad \% \quad (2)$$

where:

$h$  – factor related to the thermal efficiency of the furnace,  
 $\eta \approx 0.88$ ,

$Q$  – total energy demand in the process, MJ.

Fig. 1 presents a comparison of calculation results for models simulating FeSi75 and FeSi65Al10 melting processes. The ferrosilicon smelting process is well known and the calculations results for the FeSi75 model are in good agreement with industrial data. This applies not only to the Si yield and energy consumption index but also to the trace elements in the chemical composition (Al, Ca, Mg, Ti, C). It can, therefore, be assumed that the obtained results of calculations with the help of the model can provide some explanations which will be useful in the production of FeSiAl alloys under industrial conditions. The calculations show that the FeSiAl electrothermal melting process is more energy-consuming and requires much higher temperatures of reaction zones compared to the ferrosilicon process. This also shows that in industrial practice, the melting processes of FeSiAl alloys will be more difficult compared to the ferrosilicon process. It results not only from higher temperatures but also from the proportion of energy demand in the upper and lower zones of the furnace. Obtaining the suitable proportions in the energy distribution as a result of resistive heating and as a result of the arc radiation in the submerged arc furnace causes great difficulties and is one of the most common reasons for the disturbances in the ferrosilicon smelting process. In the melting of the FeSi65Al10 process, obtaining the correct heat distribution in the furnace working space will be even more difficult. This requires a deeper placement of the electrodes tips and the operation of the furnace with the higher current load of the electrodes compared to the ferrosilicon process.

Below on Figs. 2-4 the most interesting dependencies regarding the FeSi65Al10 process obtained using the model has been presented. This applies to the influence of the coal reducer contribution in the reaction mixture and the temperature conditions of the reaction zones on the FeSiAl melting process.

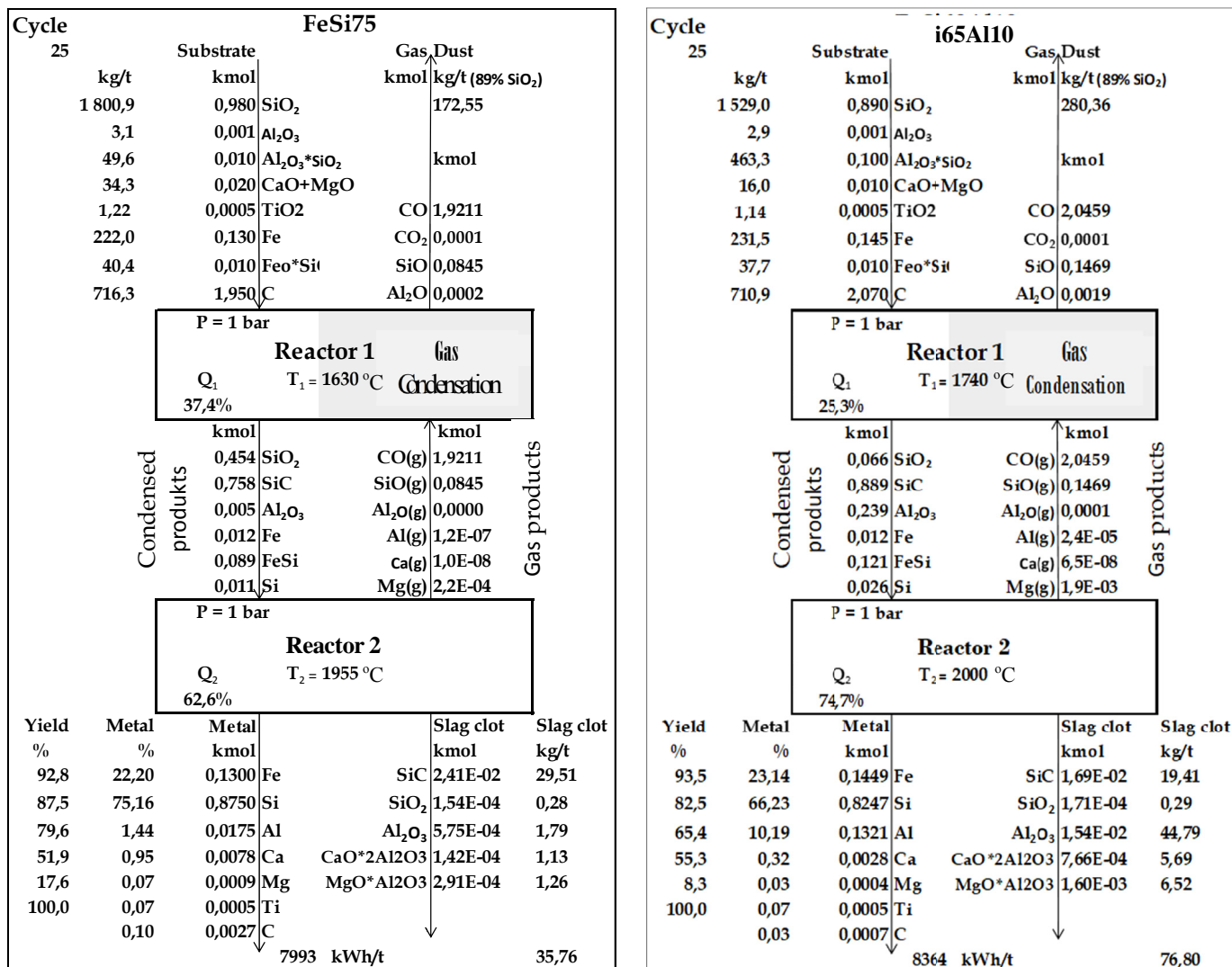


Fig. 1. Comparison of the results of calculations for the ferrosilicon FeSi75 and ferrosilicon-aluminum FeSi65A110 process models. The main components of the Fe-Si-O-C-Al-Ca-Mg-Ti system and efficiency of the recurrent process for experimentally determined parameters:  $T_1, T_2$  and composition of the reaction mixture after 25 cycles

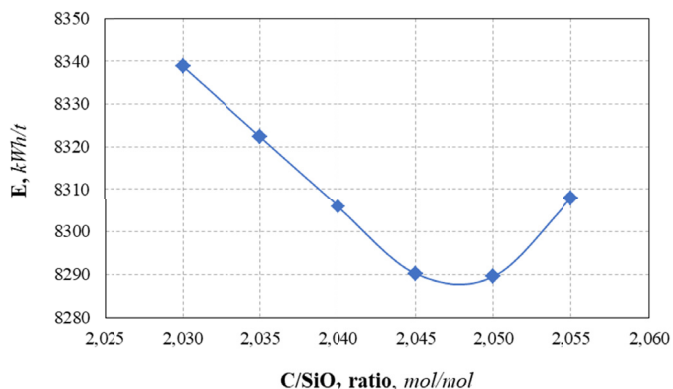


Fig. 2. The impact of reducer participation in the reaction mixture on the energy consumption index E in the smelting process FeSi65A110 for specified temperature conditions of the process:  $T_1 = 1640^\circ\text{C}$ ,  $T_2 = 2000^\circ\text{C}$

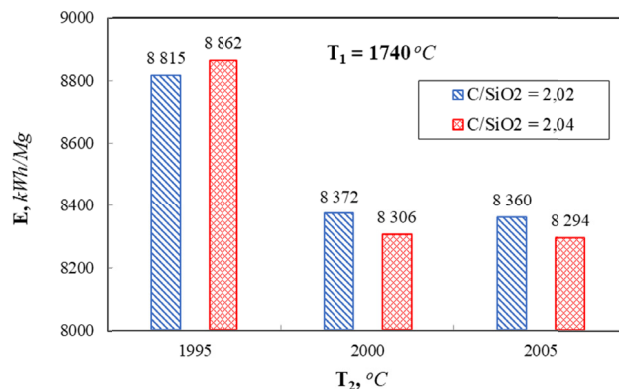


Fig. 3. Influence of the temperature  $T_2$  and the contribution of the reducer in the reaction mixture to the energy consumption index E in the melting process FeSi65A110 (other parameters as in Fig. 1)

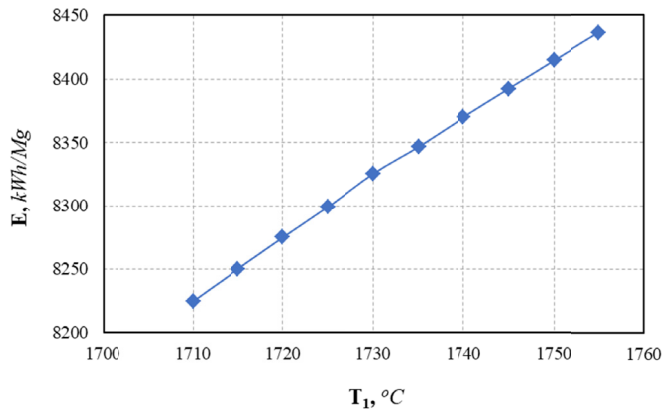


Fig. 4. Influence of temperature  $T_1$  on energy consumption indicator in the FeSi65Al10 melting process, for set temperature  $T_2 = 2000^\circ\text{C}$  (other parameters as in Fig. 1)

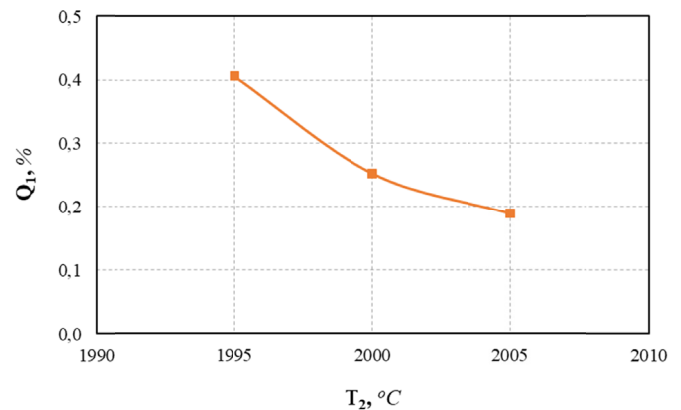


Fig. 5. The influence of temperature  $T_2$  on the distribution of energy in the reaction system at a constant temperature  $T_1 = 1740^\circ\text{C}$  (other parameters as in Fig. 1)

### 3. Summary

The calculations show that the FeSiAl electrothermal melting process is more energy-consuming and requires much higher temperatures of reaction zones compared to the ferrosilicon process.

This also shows that in industrial practice, the FeSi65Al10 technological processes will be more difficult compared to ferrosilicon process. It results not only from higher temperatures but also from the proportion of energy demand in the upper and lower zones of the furnace.

Obtaining the suitable proportions in the energy distribution as a result of resistive heating and as a result of the arc radiation in the upper and lower zones of the furnace causes great difficulties and is one of the most common reasons for the disturbances in the technological process of smelting of FeSi.

In the melting process of the FeSi65Al10 alloy, obtaining the correct heat distribution in the furnace working space will be even more difficult.

This requires a deeper placement of the electrodes tips and the operation of the furnace at a higher current load of the electrodes compared to the ferrosilicon FeSi75 process.

### Acknowledgements

This paper was created with the financial support of Polish Ministry for Science and Higher Education under internal grant BK-221/RM0/2018 for Faculty of Materials Engineering and Metallurgy, Silesian University of Technology, Poland.

### REFERENCES

- [1] V.S. Shkolnik, A.A. Zharmenov, M.Zh. Tolymbekov, S.O. Baisanov, S.O. Chekimbaev, Prospects of production complex aluminum silicon Alloy, Infacon XIII, The Thirteenth International Ferroalloys Congress. Efficient technologies in ferroalloy industry, Almaty, Kazakhstan, 311-315 (2013).
- [2] M. Gasik, [red.], Handbook of Ferroalloys Theory and Technology. Waltham: Elsevier Ltd. (Butterworth-Heinemann), (2013).
- [3] A.A. Загородный, А.В. Кольба, О.В. Сыкчин, А.И. Соколов, Ферросиликоалюминий – один из резервов для уменьшения экономических потерь в металлургической промышленности, Индустрия. – 2011. – №3. – С.29-30. 8. О.
- [4] A.V. Kol'ba, C.V. Tret'ykov, A.A. Zagorodniy, II Ferrosilicoaluminiiy – vygodniy ferrosplavl' Stal'. 2008. N118. S. 71.
- [5] B. Machulec, W. Bialik, Effects of raw material contaminants on the ferrosilicon melting process in the submerged arc furnace. 21<sup>st</sup> Conference on Technologies and Properties of Modern Utility Materials (TPMUM) Location: Silesian Univ. Technol. Fac. Mat. Engn. Katowice, POLAND Date: May 17, 2013. Technologies and Properties of Modern Utility Materials XXI. Book Series: Solid State Phenomena **212**, 183-186 (2014).
- [6] S. Gil, J. Góral, J. Ochman, M. Saternus, W. Bialik, An experimental study on the air delivery and gas removal method in a model of furnace for ferroalloy production, Metalurgija **53** (4), 447-450 (2014).
- [7] B. Panic, Influence of the bed type on the flow resistance change during the two-phase (gas+ powder) flow through the descending packed bed., Archives of Metallurgy and Materials **59** (2), 795-800 (2014).
- [8] A. Roine, HSC Chemistry 7.0 Users Guide, Outotec Information Center (2009).
- [9] C.W. Bale, A.P. Pelton, W.T. Thomson, Facility of the Analysis of Chemical Thermodynamics. FACT-Win-User Manual, Ecole Polytechnique de Montreal, Quebec (1999).
- [10] H. Buchowski, W. Ufnalski, Roztwory Wykłady z chemii fizycznej, Wydawnictwo Naukowo-Techniczne, Warszawa (1995).