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THERMODYNAMIC INVESTIGATION OF BRIQUETTE OBTAINED FROM WASTE FAYALITE WITH CALCIUM CARBIDE

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ABSTRACT

The iron content in fayalite, wasted from the copper production, is high and can be used as a raw material in the ferrous extractive metallurgy. This material has a fine dispersal structure, and it is necessary to be agglomerated for next refining processes. An experimental investigation for briquetting was carried out. X-Ray analysis of the initial sample showed fayalite and magnetite as main phases.

Thermodynamics of the reduction of the fayalite using calcium carbide as a reductor was studied. Calcium carbide was used also as a regulator of the basicity of the charge. The experiments were carried out at ratios for fayalite - calcium carbide 1:1 and 1:10, relative to the stoichiometrically calculated quantity of calcium carbide, in the temperature range from 773 K to 1173 K.

The oxygen potential, respectively Gibbs energy, has been calculated using EMF method with galvanic cell with solid electrolyte $ZrO_2(Y_2O_3)$ and reference electrode Ni/NiO. Equations for DGT = f (T) for different temperature ranges were derived from the data experimentally obtained.

The obtained briquettes were heat treated at temperatures 1125 K and 1423 K. The toughness, physical and mineral structure of the heated briquettes, were investigated. It was established that the melting temperature of the investigated mixtures decreased by increasing the amount of calcium carbide.

Keywords: thermodynamics, briquettes, Gibbs energy, EMF method.

INTRODUCTION

Annually considerable quantity of wasted fayalite is generated from copper production. The main phase is fayalite $2FeO.SiO_2$, whose content in the dry mass reaches 85 mass % [1, 2]. The fayalite from copper slag flotation is located on significant areas and their landfilling is a reason for secondary environmental pollution [3, 4]. This waste could be used as a raw material in the manufacture of iron or steel. The iron content is high, but this material is a fine powder with a predominant content (about 95 %) of fraction below 100 μm [5]. The fine particles in the charge cause difficulty of circulation of gases in the furnace, normal running of the processes and consequently reduces the productivity of the furnace [6 - 8]. It is necessary the fine dispersal charge materials to be sintered before their remelting and refining.

The mechanism of the slag fayalite waste reduction was described in the literature. The monosilicate slag reduces relatively difficult. The results show that fayalite can not be reduced with carbon monoxide at high temperatures. A more effective reduction is the direct reduction [9 - 11].

Calcium carbide is used as a reducing agent to regulate basicity and help in the desulfurization processes. There are data for injection of calcium carbide in the molten slag. [12]. Calcium carbide is used as a reducing agent in the electric furnace smelting [13, 14]. In the same time, the exothermic effect of the reaction (1) can be used:

$$CaC_2 + 3(FeO.SiO_2) = CaO.(SiO_2)_3 + 3Fe + 2CO + Q \quad (1)$$

The experimental and thermodynamic studies

Table 1. Chemical composition of the initial wasted fayalite, %.

Fe	Si	Mn	K	Na	Al	Ca	Mg	Ti	Mo	Zn	Pb	Cu
47,96	12,71	0,05	0,91	0,67	1,99	1,66	0,72	0,27	0,11	1,36	0,49	0,47

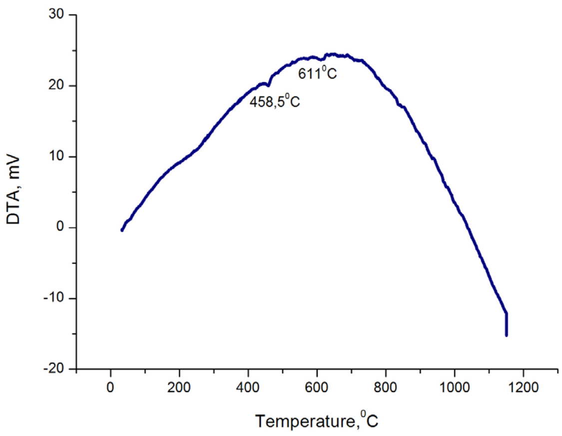

Fig. 1. Temperature dependence of DTA at ratio 1:1.

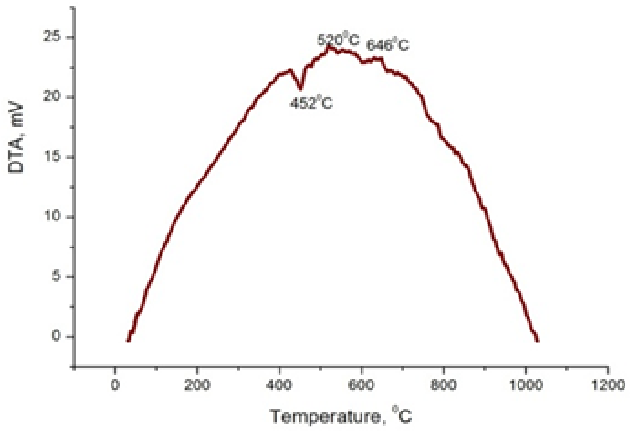

Fig. 2. Temperature dependence of DTA at ratio 1:10.

of MgO reduction with calcium carbide [15, 16] and chromium containing slag [17] have been investigated.

The aim of this paper is to investigate the possibility to briquette mixtures of wasted fayalite with calcium carbide and a thermodynamic investigation of the reduction process in the produced briquettes.

EXPERIMENTAL

The chemical composition of the wasted fayalite, defined by weight and ICP-OES analysis, is shown in Table 1. The phase composition is determined by scanning electron microscope JEOL JSM 35 CF with X-ray microanalyser TRACOR NORTHERN TN-2000. The main phases are $FeSiO_4$- 65,93 mass % and Fe_3O_4 - 16,33 mass %.

Two mixtures with wasted fayalite and calcium carbide in ratios 1:1 (Mixture 1) and 1:10 (Mixture 2) were prepared.

The thermodynamics of mixtures was studied by EMF method using galvanic cells with a solid electrolyte ZrO_2 (Y_2O_3) and reference electrodes Ni/NiO.

The following galvanic cells were used in this work:

$$\underset{}{\mathrm{Pt}} \,|\, \underset{P'_{O_2}}{\text{studied sample}} \,||\, \mathrm{ZrO_2(CaO)} \,||\, \underset{P''_{O_2}}{\mathrm{Ni,NiO}} \,|\, \mathrm{Pt}$$

The mixtures were investigated also by DTA method (apparatus STA PT1600) within the temperature range 293 K - 1473 K.

RESULTS AND DISCUSSION

In the initial wasted material, iron is bound as magnetite and fayalite. Theoretically, the reduction process with calcium carbide can be carried out by the reaction (2):

$$7Fe_3O_4 + 2\,CaC_2 + Fe_2SiO_4 = \\ = 23\,FeO + Ca_2SiO_4 + 2CO + 2CO_2 \qquad (2)$$

The data for the thermodynamic characteristics: specific heat capacity C_p, enthalpy H^o_{298}, and entropy S^o_{298} were used for the calculation of reaction (2) [18]. An equation for ΔG of the reaction (2) was deduced.

$$\Delta G = 231584\text{-}2299.\ T,\ J/mol \quad R^2 = 0.9993 \qquad (3)$$

On the base of stoichiometric calculations for reaction 2, two ratios (1:1 and 1:10) between fayalite and calcium carbide were prepared.

DTA analysis

Thermogravimetric analysis was carried out and the

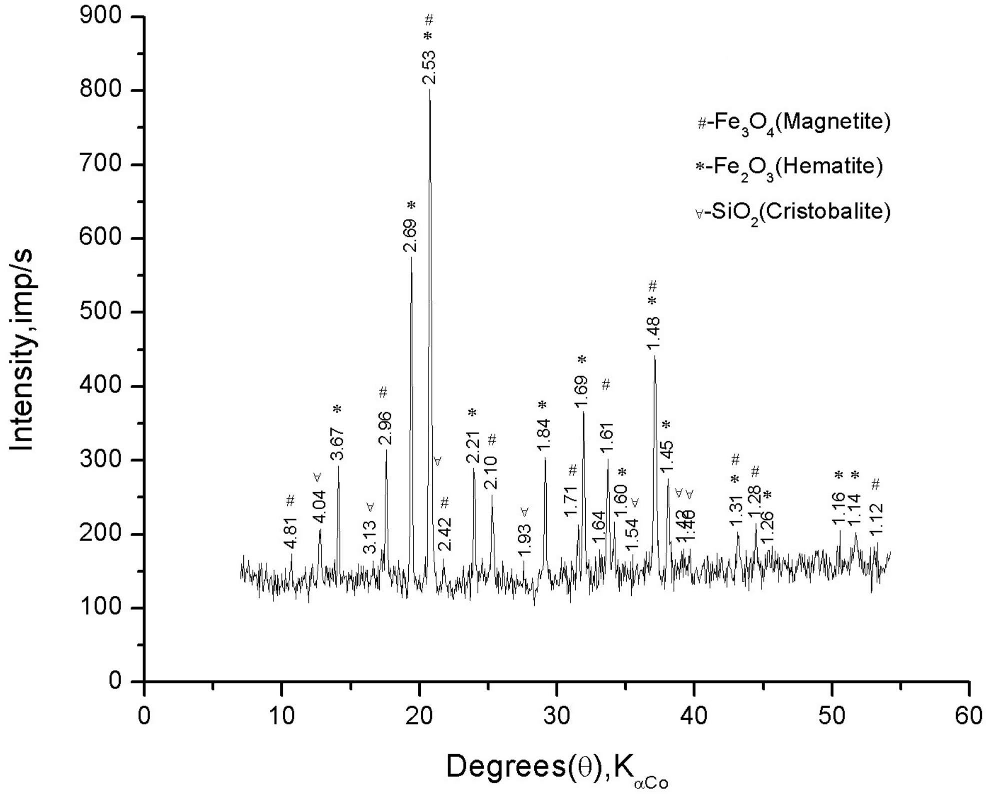

Fig. 3. X-Ray analysis of the product of heat-treated sample - fayalite /calcium carbide 1:1 ratio.

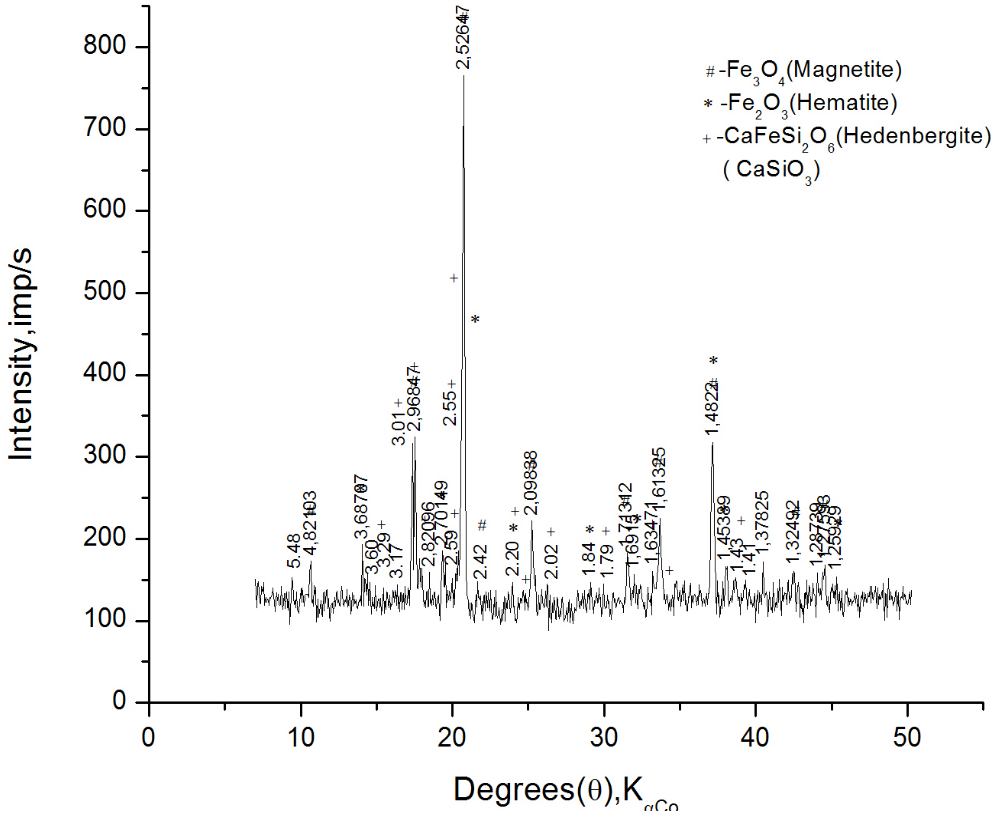

Fig. 4. X-Ray analysis of the product of heat-treated sample - fayalite /calcium carbide 1:10 ratio.

results are presented in Figs. 1 and 2. DTA transformations of both mixtures are similar. Two endothermic peaks with weak intensity - at T ~ 731 K and at T ~ 884 K in the case of ratio 1:1 were observed. The first peak is due to the reaction $Fe_2O_3 \leftrightarrow Fe_3O_4$, whereas the second one is due to the fayalite dissociation. This is confirmed by X-Ray analysis presented in Fig. 3. The main phases after heat treatment in mixture 1 are magnetite - Fe_3O_4, hematite Fe_2O_3, and cristobalite SiO_2.

For mixture 2, where the amount of CaC_2 is higher, the endothermic peaks are with stronger intensity at T ~ 725 K and T ~ 823 K. An exothermal effect at T ~ 911 K which corresponds to the formation of calcium silicate reaction chain was noticed in mixture 2 as opposed of mixture 1. This was confirmed by an X-Ray analysis shown in Fig. 4.

This pattern shows that the higher amount of CaC_2 is a result due to the formation of hedenbergit $CaFeSi_2O_6$ or calcium silicate $CaSiO_3$. It is seen also that the lines of hematite are weaker than those for ratio 1:1.

EMF method results

On the basis of the experimentally measured values by the EMF method in non- isothermal heating of the studied samples, the Gibbs energy for mixtures 1 and 2 were calculated.

The apparent partial pressure of the oxygen (generated by the mixtures) could be determined by the equation (4)

$$E = \frac{R.T}{n.F}\left(\lg P''_{O_2} - \lg P'_{O_2}\right) \qquad (4)$$

where E - measured EMF, [V]; R - gas constant, 8,314 [deg $K^{-1}mol^{-1}$]; n - number of the electrons taking part in the reaction; F - Faraday constant, $9{,}6489.10^4$ [$C.mol^{-1}$]; ln P'_{O_2} - oxygen pressure of reference electrode; ln P''_{O_2} - oxygen pressure of the system under investigation.

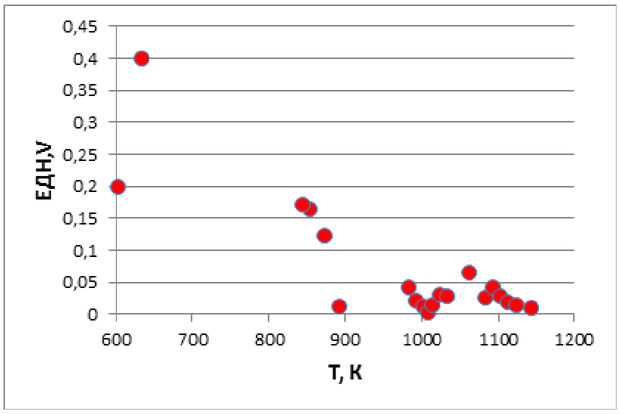

Fig. 5. EMF values obtained vs temperature in 1:1 ratio.

Using the Ni/NiO reference electrode, the partial pressure of the oxygen in the mixtures was

$$\lg P'_{O_2} = -\frac{E.20193}{T} - \frac{12225}{T} + 4.44 \qquad (5)$$

Experimental data for the temperature dependence of EMF at ratios 1:1 and 1:10 are shown in Figs. 5, 6.

The Gibbs energy results for mixture 1 and mixture 2 are presented in Figs. 7 and 8. The equations of the relationship ΔG = f (T) for both mixtures were derived. Processes in mixture 2 (1:10) were described by two equations for Gibbs energy. The first equation is valid for the temperature range 773 - 993 K. It is related to the reversible reaction $Fe_2O_3 \leftrightarrow Fe_3O_4$. Delta G data, received for the reversible reaction by S.I. Filippov [19] are similar to those obtained from the experimental data of the deduced equation (6) in this work. The second equation

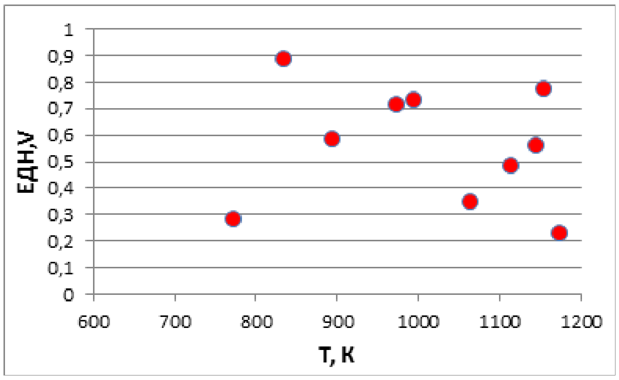

Fig. 6. EMF values obtained vs temperature in 1:10 ratio.

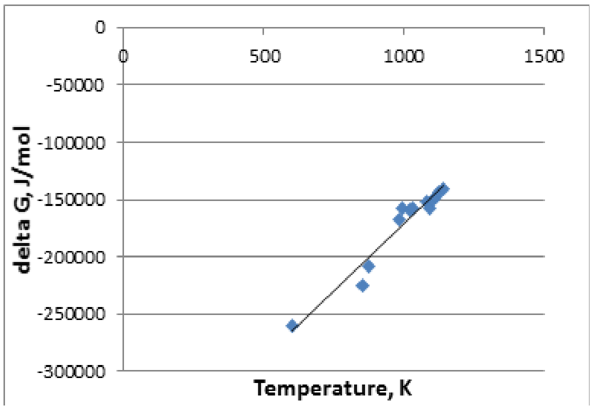

Fig. 7. Gibbs energy as a function of temperature, for fayalite/CaC_2 in 1:1 ratio.

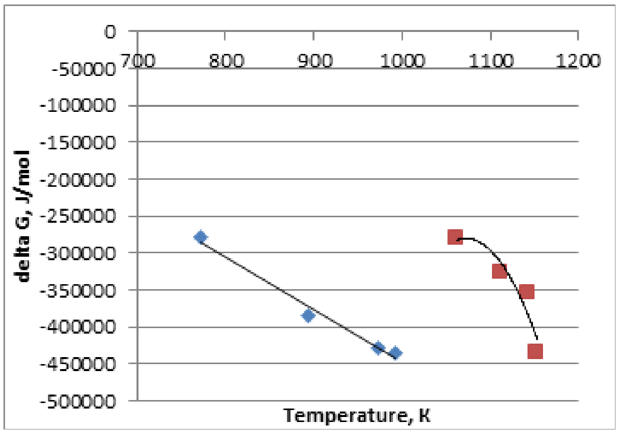

Fig. 8. Gibbs energy as a function of temperature, for fayalite/CaC_2 in 1:10 ratio.

(7) for the same mixture 2 describes the possibility of a new phase calcium train-silicate formation.

The thermodynamic calculations of reaction (2) and the carried out analyses show that the products as FeO and Ca_2SiO_4 were not obtained.

$$\Delta G_{exp.} = -406150+234,54.\ T,\ J/mol$$
$$R^2 = 0,9416 \qquad (6)$$

$$\Delta G_{exp.} = 269021 - 716,45\ .\ T,\ J/mol$$
$$R^2 = 0,9814 \ \text{at}\ T = 773 - 993\ K \qquad (7)$$

$$\Delta G = -586770 + 340,20.T,\ J/mol\ [19]$$
$$\Delta G_{exp} = -\ 2.107+44887.\ T - 20,927.\ T^2$$
$$R^2 = 0,8829\ \text{at}\ T=1063 - 1153\ K \qquad (8)$$

Briquettes obtained from fayalite/ calcium carbide mixtures

The toughness indexes of raw and heated briquettes were examined. The raw briquettes do not have sufficient mechanical strength. The heated briquettes exhibit higher strength characteristics mainly for 1:1 ratio.

The photos of the products, obtained after thermal processing of the briquettes of both mixtures to a temperature up to 1423 K, are shown in Figs. 9 and 10.

For mixture 2, containing a higher quantity of calcium carbide, the interval between the softening and meltdown was smaller, than that for mixture 1. Briquettes (Fig. 9), obtained at a ratio of 1:1 were sintered at a temperature about 1423 K and had linear elongation. The obtained melts were less than 20 %. The briquettes heated to the same temperature in ratio 1:10 (mixture 2) was smelted.

Fig. 9. Briquettes heated at T = 1150^0C in 1:1 ratio.

Fig. 10. Briquettes heated at T = 1150^0C in 1:10 ratio.

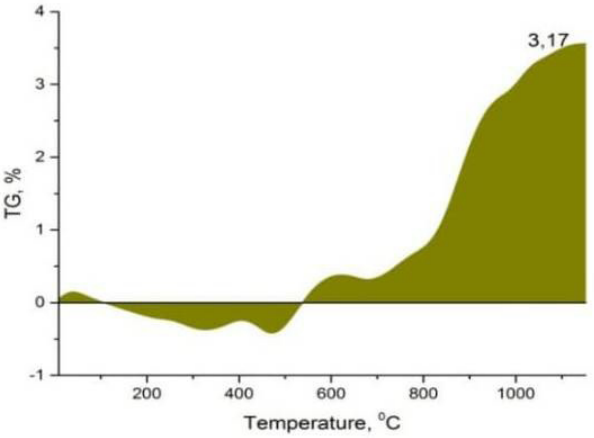

Fig. 11. Temperature vs weigh changes (TG) for mixture 1(1:1 ratio).

A change in the weight during the briquettes heating was observed. The obtained results are shown as the dependence of temperature on weight change in Figs. 11 and 12. Two stages were registered - of reducing and increasing of the weight. The increase of weight started at different temperatures for both mixtures. The higher amount of CaC_2 moves this stage to higher temperatures - from 853 K (mixture 1) to 1073 K (mixture 2).

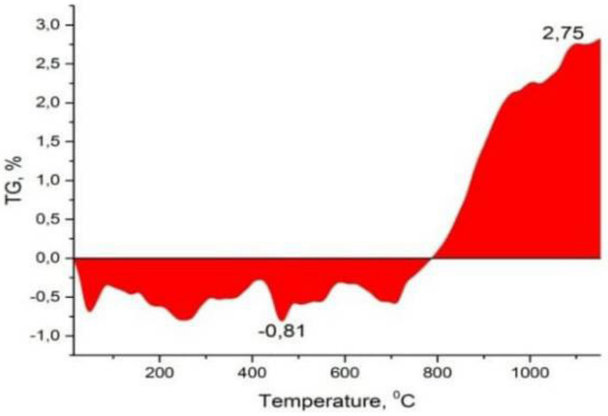

Fig. 12. Temperature vs weigh changes (TG) for mixture 2 (1:10 ratio).

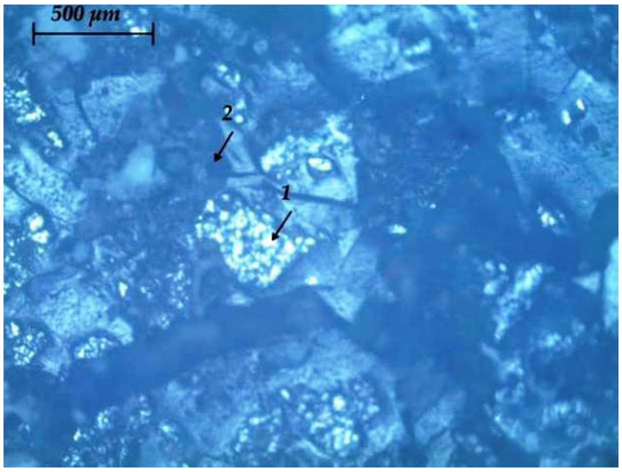

Fig. 13. Microstructure of the obtained briquettes for Mixture 1 (1:1 ratio); 1- Fe_3O_4, Fe_2O_3, FeO; 2 - silicate connection (Olivine).

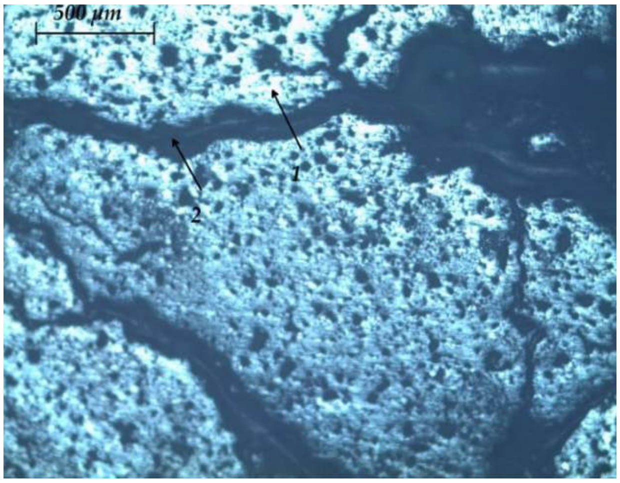

Fig. 14. Microstructure of the obtained briquettes for Mixture 2 (1:10 ratio); 1- Fe_3O_4, Fe_2O_3, FeO; 2- silicate connection (Olivine).

The reducing of the weight is related to the dissociation of Fe_2O_3 to Fe_3O_4 through the reversible reaction $3Fe_2O_3 \leftrightarrow 2Fe_3O_4 + ½\ O_2$. The weight increase was due to the hedenbergit and calcium silicate phase formation, and that decreases the melting temperature.

The microstructure of the obtained briquettes is shown in Figs. 13 and 14. It is obvious that in mixture 2 the amount of iron oxides is higher than that in mixture 1.

CONCLUSIONS

- Equations for $DeltaG_T = f\ (T)$ for different temperature ranges, based on the experimental data for fayalite/CaC_2 mixtures have been found. Two equations for a mixture in 1:10 ratio, corresponding to the Gibbs energy of reversible reaction $Fe_2O_3 \leftrightarrow Fe_3O_4$ and Gibbs energy of formation for a new calcium ferrous silicate phase were received.
- It was found out that by increasing the amount of calcium carbide the strength parameters of the raw briquettes were reduced and the melting temperature of the test mixtures is decreased.
- The results of the experiment show that the usage of calcium carbide as a reducing agent and as a binder was unsuccessful. There is a partial regulation of basicity, but low mechanical properties of the raw briquettes and some specifics at work show that calcium carbide is not suitable for briquetting charge material. Calcium carbide could be successfully used in the metallurgical bath.

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