THERMAL STABILITY OF FAYALITE SYSTEM FORMATION AT THE INTERFACE BETWEEN STEEL AND MOULD

Bogdan VERDEŞ[1], Ion CHIRA[2], Marian VIRGOLICI[3], Valentin MOISE[4]

Formarea produşilor fayalitici $2FeOSiO_2$; $FeO_2(SiO_2)$ la interfaţa oţel-forma de turnare este un proces ce poate fi controlat şi optimizat utilizând adaosuri suplimentare de oxizi de fier în compoziţia amestecurilor de formare.

Lucrarea de faţă studiază prin analiza termică simultană patru compoziţii de amestec oxizi de fier şi nisip în diferite procente masice cu înregistrarea temperaturii în funcţie de timp atât pe curbele de topire cât şi pe curbele de solidificare caracteristice acestor probe. Analizele termice s-au efectuat atât în atmosfera oxidantă cât şi în atmosfera inertă pentru evidenţierea clară a proceselor de oxidare care apar, dar şi a variaţiilor de masă.

The formation of the $2FeOSiO_2$,$FeO_2(SiO_2)$ fayalite products, at the interface of steel and the casting mold, is a process that can be controlled and optimized by using additional iron oxide additives in the mixture's composition.

This paper studies, by simultaneous thermal analysis, four mixtures compositions consisting in iron oxides and sand mixture, in different mass percentages, by recording the temperature dependence on tine, both on the melting curves and on the solidification curves. Thermal analyses were performed both in oxidant atmosphere and in an inert atmosphere for clear evidence of occurring oxidation processes, but also for the mass variations.

Keywords: casting sand, iron oxides slag, fayalite, thermogravimetry, differential thermal analysis

1. Introduction

Among the oxides that are found in the mold, in steel casting, the liquid oxide FeO presents the greatest importance, as a result of reactions with the components of the mixture, leading to the formation of compounds as

[1] PhD, student, Materials Science & Engineering Faculty Materials Processing & Ecometallurgy Department, University POLITEHNICA of Bucharest, e-mail: verdesbogdan@yahoo.com
[2] Prof., Materials Science & Engineering Faculty Materials Processing & Ecometallurgy Department, University POLITEHNICA of Bucharest, e-mail: iondanchira@gmail.com
[3] PhD, IRASM Center, Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering, Bucharest, Romania, e-mail: mvirgolici@nipne.ro
[4] PhD, student, eng., IRASM Center, Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering, Bucharest, Romania, e-mail: vmoise@nipne.ro

Fe_xO_y/SiO_2. In the iron silicates system, the product with important implications in the quality of parts obtained by molding is the ferrous orthosilicate also known as fayalite, $2FeO \cdot SiO_2$ or $Fe_2(SiO_4)$, which crystallizes in the rhombic system and has a congruent melting at 1205°C as compared to 1377°C (melting temperature of FeO), and 1723°C (melting temperature of SiO_2) and 1538°C (melting temperature of iron) [1.2]:

$$2\ FeO + SiO_2 = 2\ FeO \cdot SiO_2 \qquad (1)$$

These products are the base of adhesions formation, some of the most common defects that occur on the surfaces of alloys cast parts with high casting temperature. According to literature statistics [3], the time required to manufacture cast parts, consuming on average 12-15%, for the procedures to remove adhesions.

The required oxygen for the oxidation of iron comes from the steel's contact with the atmosphere during casting, from the contact with air in the cavity shape and the forming mixture pores, and from the dissociation of water vapors when heating the mould.

The produced silicates, with small wetting angle, are easily penetrating by inter-granular capillary spaces. The fayalite formed in liquid state dissolves the silica in the forming mixture, extending this way the capillary channels which facilitate the penetration of liquid alloy into the pores of the mixture.

According to the literature data [1,4,5], fayalite forms approx. 1180°C, the equilibrium relations dividing this system into two binary systems, each with one eutectic.

This paper aims to investigate the thermal stability of fayalite compounds, using different compositions between sand and iron oxides, watching the phase transformations that occur. The results interpretation will bring additional information on the equilibrium diagram FeO-SiO_2 in terms of materials currently used in the foundry and implicit ways of improving the casting process parameters.

The thermal stability of fayalite formed from the silica sand and iron oxides was studied by simultaneous thermal analysis (STA), thermogravimetry and differential thermal analysis (TG/DTA).

2. Materials and methods

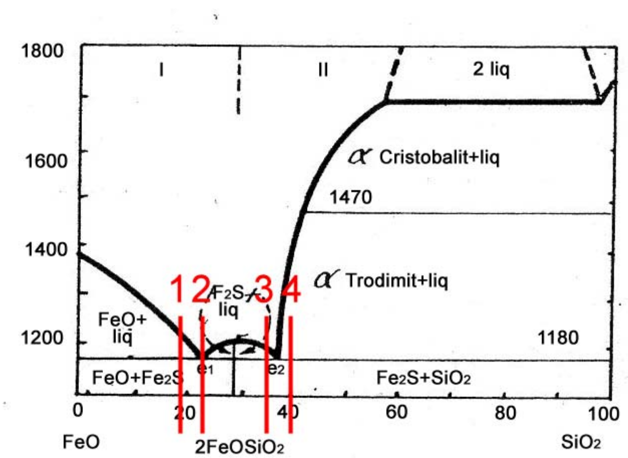
The samples subjected to experimental program were established so that the resulted compound to contain in certain percentages a mixture of iron oxides and SiO_2 used in powder form, corresponding to the concentration of the eutectics indicated in the phase equilibrium diagrams FeO-SiO_2.

Representation in the equilibrium diagram FeO-SiO_2 mixtures was made by concentrations verticals 1,2,3 and 4. (table 1)

Vertical composition 1: the mixture has 82% iron oxides and 18% *SiO_2*;
Vertical composition 2: the mixture has 76% iron oxides and 24% *SiO_2*;
Vertical composition 3: the mixture has 65% iron oxides and 35% *SiO_2*;
Vertical composition 4 the mixture has 60% iron oxides and 40% *SiO_2*.

Table 1

The FeO-SiO_2 diagram indicating the compositions selected for thermal analysis

Diagram with the representation of its own points	Vertical	Iron oxides [%] mass	SiO_2 [%] mass
	1	82	18
	2	76	24
	3	65	35
	4	60	40

The samples were analyzed by thermogravimetry and differential thermal analysis (TG/DTA) with a simultaneous thermal analyzer STA 409 PC Luxx (NETZSCH, Germany), having the following configuration: alumina oven with a type S thermocouple (Pt/Rh), TG/DTA sample carrier with type S thermocouples and Pt/Rh crucibles (200 µl) without lid, dynamic inert (nitrogen) or oxidative (synthetic air) atmosphere (analytical grade gasses, with at least 99,999 % purity) with a constant flow of about 80 ml/min. The applied temperature program consisted in two scans at 10 K/min between 40°C ... 1450°C ... 40°C, with sample weighing at room temperature. The maximum temperature in inert atmosphere was 1500 °C.

Test specimen mass varied between 200 mg ... 300 mg, corresponding to a volume of about 100 µl.

Pt/Rh crucibles were reused between analyses, being conditioned by digestion (24 ... 72 hours, depending on the sample matrix) with hydrofluoric acid (40 %), washed with deionized water and dried in an oven at 130 °C, operation repeated until no significant mass variation could be recorded.

Corrections with empty crucibles were done twice before each analysis, the second being used to correct the sample recorded signal.

The dimensions of the used crucible are shown in figure 1.

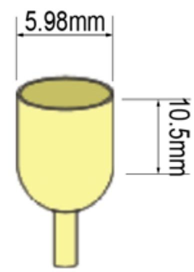


Fig. 1. Crucible dimensions for TG, DTA, DTG analysis.

3. Results

Investigations were conducted on four compositions, consisting in iron oxides and sand, in mass percentages of 60:40, 65:35, 76:24 and 82:18.

TG/DTA diagrams resulted from the simultaneous thermal analysis show in oxidant environment the mass gain processes. Since in an inert environment the mass is constant, we can interpret that any mass gains are due to oxidation. (figures 2 and 5)

Since the mass of the analyzed matrix, the largest share has iron oxides, the processes shown in the TG/DTA diagrams are similar to the processes revealed in the simultaneous thermal analysis on the iron oxide matrix. [6, 7] In figures 3,4 and 6 are given simultaneous thermal analysis for the mixture composition having 60% iron oxide and 40% SiO_2, with representation of two successive sweeps, and sample reweighting after the first sweep.

By the superimposed curves representation corresponding to each vertical composition of samples analyzed, the transformation corresponding to eutectic points from the diagram represented in table 1, appears different, as follows: In oxidizing atmosphere, the transformation occurs on the cooling curve at temperatures between 1197°C and 1208°C (figures 7,8. a and b) while in an inert atmosphere, the transformation occurs on the heating curve at temperatures between 1149°C and 1188°C (figures 9 and 10). These data indicates that in the oxidizing atmosphere an oxidation processes occurred with mass gain, while in an inert atmosphere, above 570°C the processes of iron oxides reaction with SiO_2 occurs fast and without mass gain.

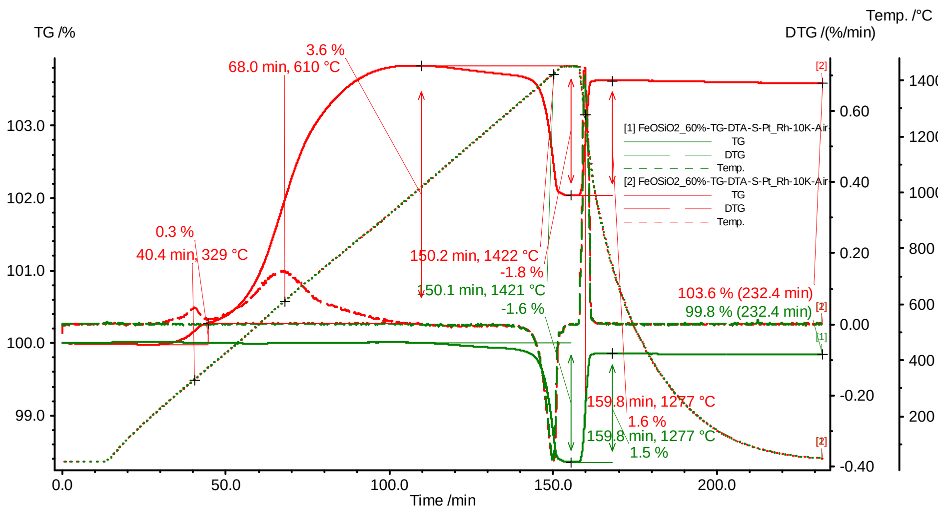


Fig. 2. TG/DTG analysis (in oxidative atmosphere) of iron oxides slag / silica sand mixtures 60%: 40%. Two scans 40°C ... 1450°C ... 40°C with sample weighing at room temperature: First scan in red, second in green

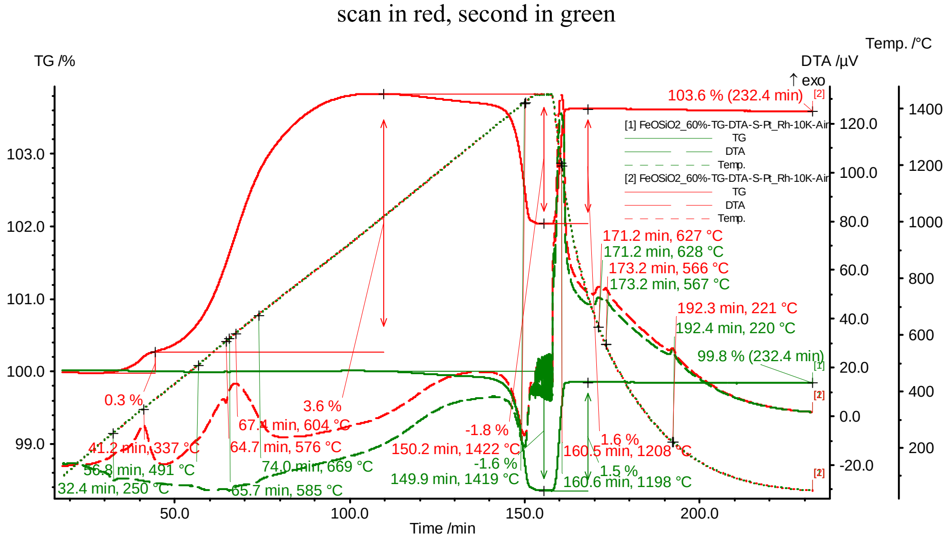


Fig. 3. TG/DTA analysis (in oxidative atmosphere) of iron oxides slag / silica sand mixtures 60%: 40%. Two scans 40°C ... 1450°C ... 40°C with sample weighing at room temperature: First scan in red, second in green

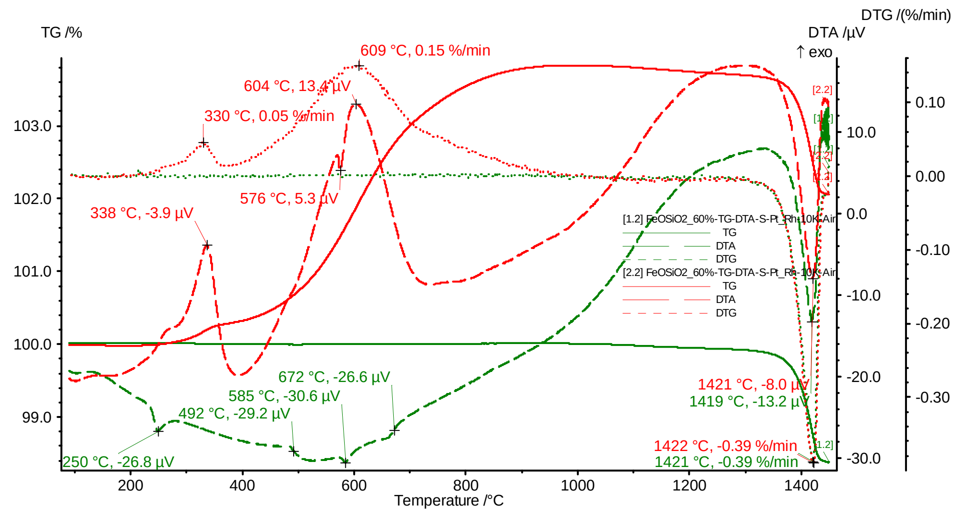


Fig. 4. TG, DTG and DTA analysis (in oxidative atmosphere) of iron oxides slag / silica sand mixtures 60%: 40%. Two scans 40°C ... 1450°C ... 40°C with sample weighing at room temperature: First scan in red, second in green

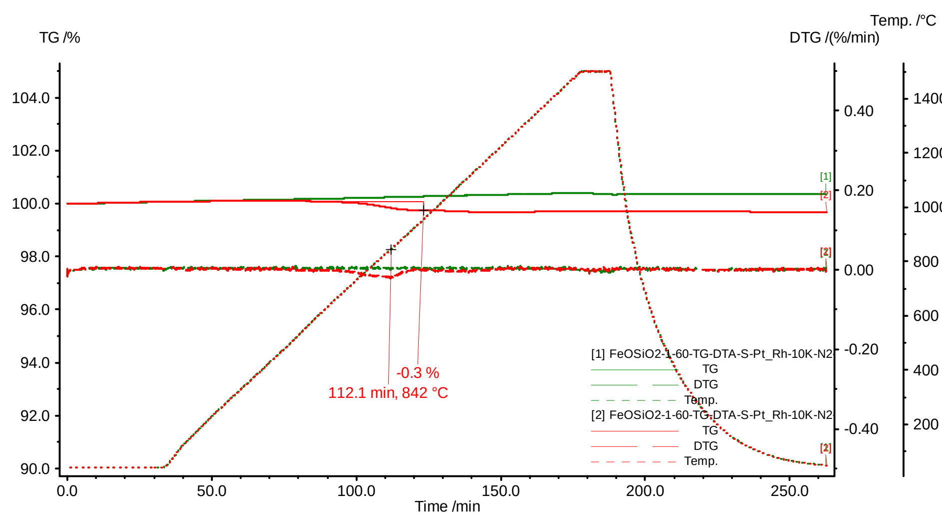


Fig. 5. TG/DTG analysis (in inert atmosphere) of iron oxides slag / silica sand mixtures 60%: 40%. Two scans 40°C ... 1450°C ... 40°C with sample weighing at room temperature: First scan in red, second in green

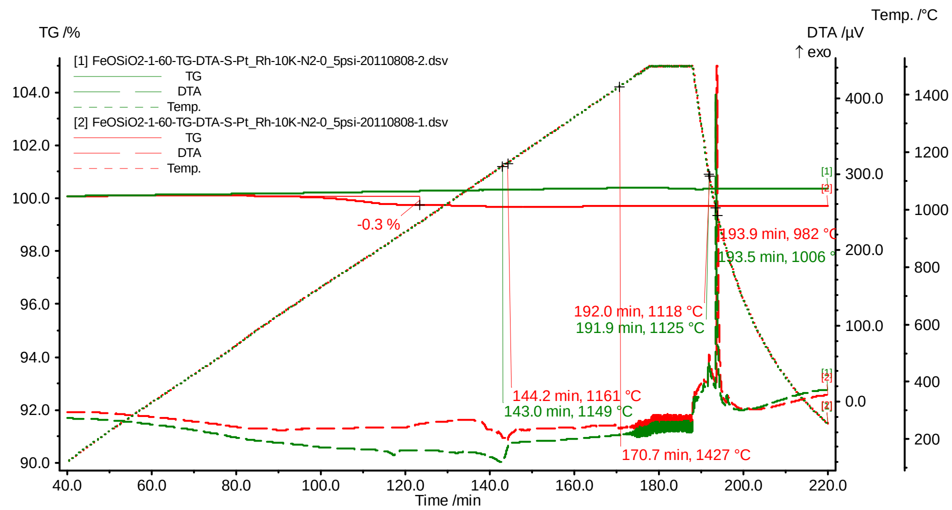


Fig. 6. TG/DTA analysis (in inert atmosphere) of iron oxides slag / silica sand mixtures 60%: 40%. Two scans 40°C ... 1450°C ... 40°C with sample weighing at room temperature: First scan in red, second in green

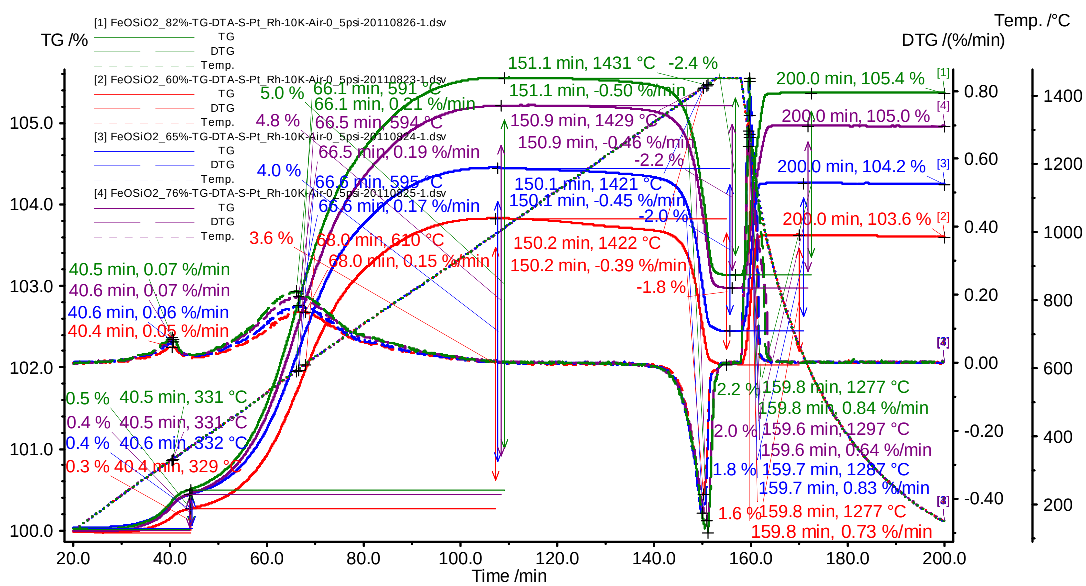
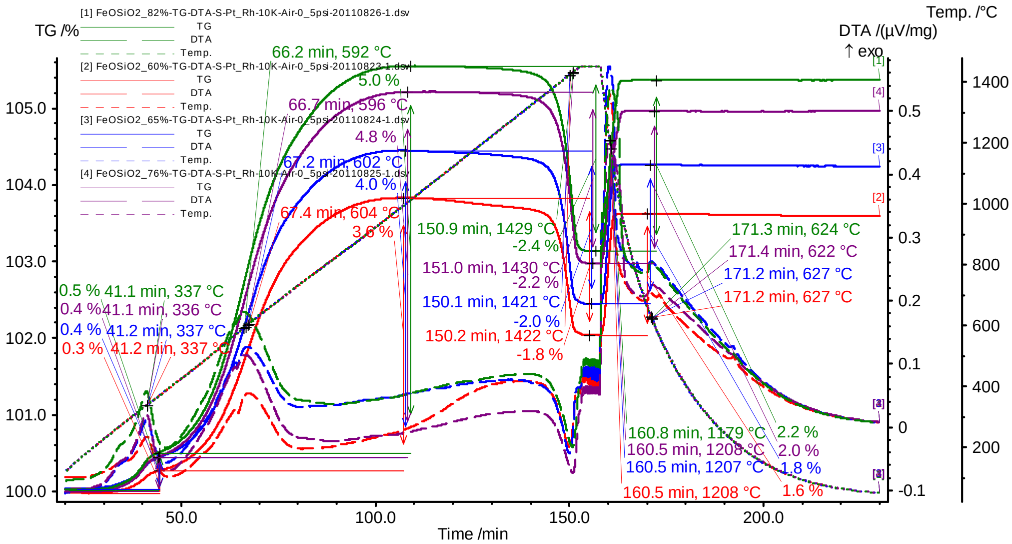
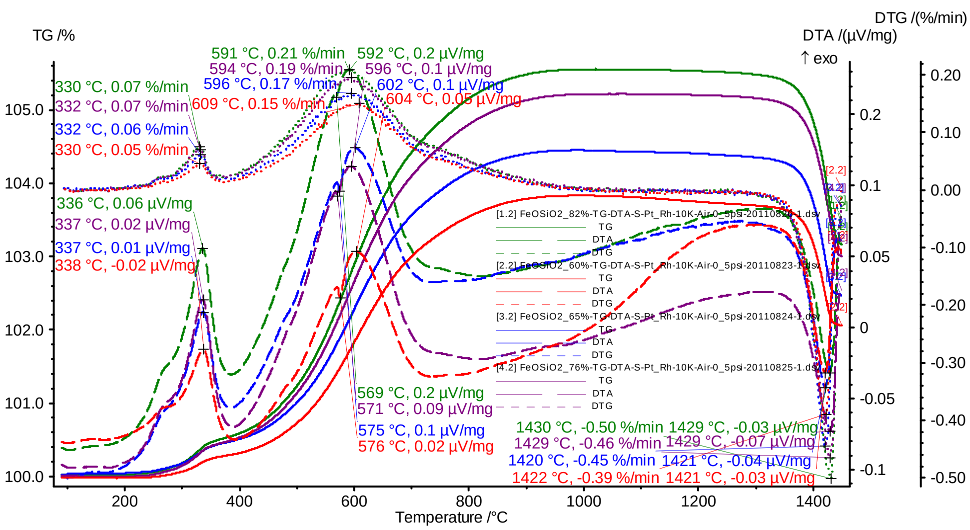


Fig. 7. TG/DTG analysis (in oxidative atmosphere) of iron oxides slag / silica sand mixtures: 60% : 40% in red, 65% : 35% in blue, 76% : 24% in purple, 82% : 18% in green. First scan: 40°C ... 1450°C ... 40°C in time scale



a)



b)

Fig. 8. TG/DTA analysis (in oxidative atmosphere) of iron oxides slag / silica sand mixtures: 60% : 40% in red, 65% : 35% in blue, 76% : 24% in purple, and 82% : 18% in green. First scan: a) 40°C ... 1450°C ... 40°C in time scale; b) 40°C ... 1450°C in temperature scale.

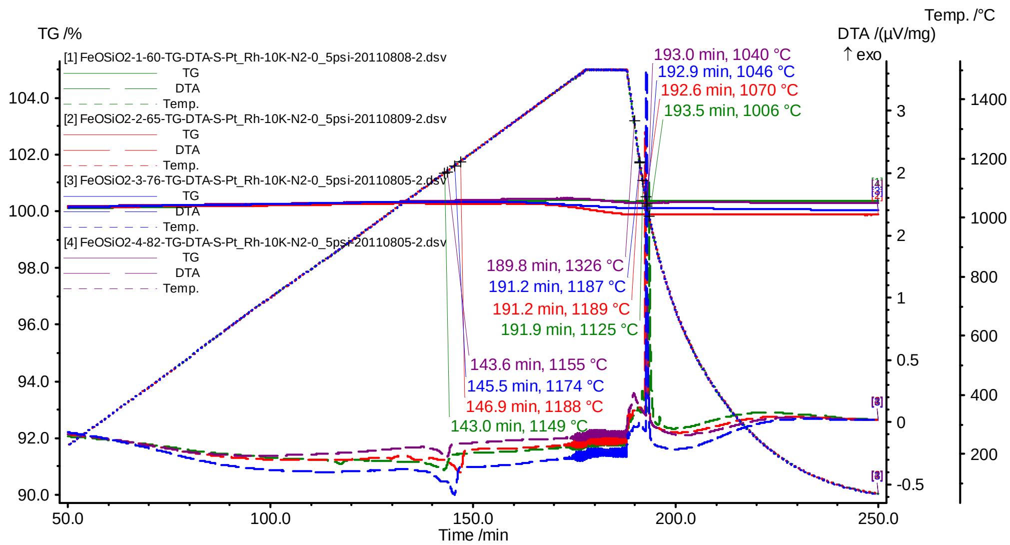


Fig. 9. TG/DTA analysis (in inert atmosphere) of iron oxides slag / silica sand mixtures: 60% : 40% in green, 65% : 35% in red, 76% : 24% in blue, and 82% : 18% in purple. Second scan: 40°C ... 1450°C ... 40°C in time scale, with sample weighing at room temperature after first scan. The second sweep of the temperature program, after opening the oven at room temperature and reweighting the sample.

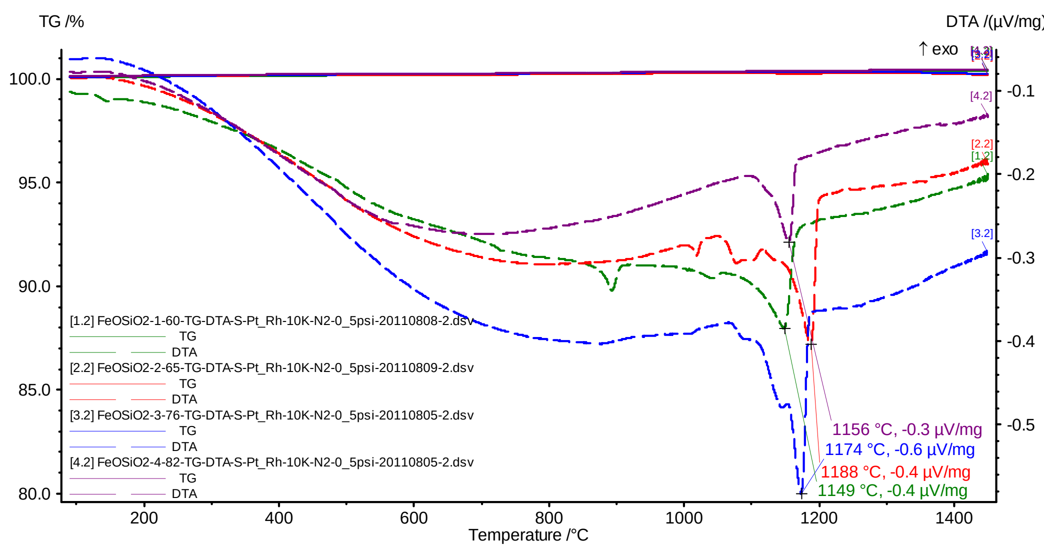


Fig. 10. TG/DTA analysis (in inert atmosphere) of iron oxides slag / silica sand mixtures: 60% : 40% in green, 65% : 35% in red, 76% : 24% in blue, 82% : 18% in purple. Second scan: 40°C ... 1500°C.

4. Discussion and conclusions

Comparative analysis of the four formulas of iron oxides/foundry sand experimentally tested (60:40, 65:35, 76:24 and 82:18), shows the largest amount of fayalite resulting for the percentage composition 65:35.

At a careful analysis of the TG/DTA curves for the mixed iron oxides: sand=60:40 (figures 2-6) the following changes and phase transitions were observed:

a. 3 steps (processes) as follows:
  - first oxidation process, the mass gain 0.3% (measured experimentally), compared to 0.36% calculated at the rate of 60% iron oxides in the mixture), with a top speed reaction at a temperature of 329°C, confirmed in the DTA curve with an exothermic peak at temperature 337°C;
  - the second oxidation process, the mass gain 3.6% (measured experimentally), compared to 3.66% calculated on the percentage of 60% iron oxides in the mixture), with a top speed of reaction at a temperature of 610°C, confirmed in the DTA curve with a exothermic peak at maximum temperature of 604°C;
  - a reversible process of iron oxide disproportion (-1.8% experimentally measured, compared with 1.8% calculated on the percentage of 60% iron oxides in the mixture), with mass loss (perhaps oxygen elimination), with a top speed of reaction at a temperature of 1422°C, confirmed by the DTA curve with an endothermic peak at the same temperature. At lower temperature (cooling the sample with ballistic speed) process occurs in reverse through the oxidation reaction step as evidenced by a mass gain (1.6%), with a top speed of reaction at a temperature of 1277°C, confirmed by the DTA curve with an exothermic temperature around 1198°C;

b. other phases transitions, as follows:
  - a process with changing baseline at a temperature of 250°C, shown in the second sweep of the program of temperature in oxidizing atmosphere (after cooling and reweighting the sample), found also in casting sand at temperature of 239°C [literature], which may be a reversible allotropic transformation of SiO_2;
  - a complex process (assuming two different processes of the mixture components overlaid as temperature range) by changing baseline at temperature of 492°C, visible only in the second sweep of the program of temperature in oxidizing atmosphere, met both casting sand at temperature of 485°C as well as iron oxides at a temperature of 486°C [bibliography];
  - an endothermic process met at a temperature of 576°C at first heating (a process competing with the second oxidation of iron oxides), and then the temperature of 585°C in the second heat, with a corresponding exothermic

peak on cooling at a temperature of 567° C, met also in foundry sand [the same literature as for the sand], which could be a reversible allotropic transformation of SiO_2, type β → α;
- a changing process of the baseline in the DTA curve at temperature of 672°C (process probably reversible, with a corresponding exothermic peak on cooling at temperature of approximately 628ºC);

c. an endothermic process revealed only in an inert atmosphere at a temperature of 1149°C, probably corresponding to the melting fayalite (formed between the FeO from the iron oxides and SiO_2 from the foundry sand). Phase transition at the second swap of the temperature program in oxidizing atmosphere may be due to formation of some iron oxides species with melting temperature higher to those available in the program temperature, thus preventing the formation and monitoring the fayalite melting temperature.

Comparative analysis of the TG/DTA curves for the four mixtures of iron oxides/foundry sand (figures 7-10) revealed the following trends with respect of increasing concentrations of iron oxides in combination:
- the amount of oxygen consumed (mass gain) in oxidizing atmosphere, the speed of reaction and the corresponding temperature of the first oxidation process maximum increase proportionally with increasing concentration of iron oxides;
- the amount of oxygen consumed (mass gain) in the oxidizing atmosphere and speed of reaction of the second oxidation process increases proportionally with increasing concentration of iron oxides on the temperature corresponding to maximum rate of reaction decreases to 610°C for mixing oxides iron/sand 60:40, at 591ºC for 82:18 mixture;
- in the case of the reversible process of a iron oxide disproportion from iron oxides composition, the disproportion temperature increases with the concentration of iron oxides in the mixture;
- in an inert atmosphere (figure 10) the composition of 65:35 has the largest amplitude fayalite melting peak, this amplitude decreasing for the other two concentrations of 76% and 82% iron oxides in the mixture. This behavior suggests that the largest amount of fayalite was formed for the mixture 65:35 among the formulas iron oxide/foundry sand experimentally tested.

A possible casting problem when using an iron oxide/foundry sand mould would be the disproportion of a iron oxide from the composition iron oxides with oxygen elimination in a gas form, which can lead to surface alterations by the appearance of gas bubbles and on the other hand of secondary oxidation processes. Therefore, future studies should be conducted to optimize the composition of iron oxides/foundry sand so as to minimize the formation of fayalite at the interaction of the casted alloy with SiO_2, and gas formation of iron oxides at a temperature of 1422°C ... 1431°C.

REFERENCES

[1] *I. Dragomir*, The theory of steel processes, Didactic and Pedagogical Publishing House, Bucharest, 1985

[2] *Bogdan Alexandru Verdes, Ion Chira*, Remarks on the $FeOSiO_2$ system regarding the adherence of casted parts, Materials Science and Engineering Congress, MSE 2010, Darmstad, Germany, 24-26 Aug., 2010, conference poster no. E2-825

[3] *C. Cosneanu , Cl. Stefãnescu*, Mixtures of training systems for foundries, Technical Publishing House, Bucharest, 1989, pp. 236

[4] *M. Ishikawa, H.Nanri, M.Wakamatsu, K.Watanabe,* High temperature oxidation of SiC and SiC based monolithic refractories by FeO, Taikabutsu overseas, **vol.16**, no.1, 1996, pp. 3-7

[5] ***http://baike.sososteel.com/doc/view/47077.html

[6] *G. Ennas, G.Marongiu, A. Musinu*, Characterization of nanocrystalline γ-Fe_2O_3, prepared by wet chemical method, Journal of Matreials research, **vol.14**, no.4, 1999, pp.1570-1575

[7] *J-P. Kolivet, E.Tronc and C.Chaneac*, Iron oxides: From molecular clusters to solid. A nice example of chemical versatility. Comptes Rendue Geoscience, no.338, 2006, pp.488-497