A NEW APPROACH FOR HEAT YIELD MEASUREMENT OF THE ALUMINOTHERMIC TESTS CARRIED ON IRON BEARING POWDERED WASTES

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Recovery of historical metallurgical waste is a demanded action for strengthening the EU raw material resilience. New technologies for efficient waste recovery in Romania are highly demanding. The aluminothermy is an emerging technology we advance for metallurgical dumps valorization. The aluminothermic reactions give rise to a great amount of heat that control the steel yields and the formation of secondary products as Al_2O_3, Fe_3Al, FeO_4S etc. A proper design of the aluminothermic technology needs the measurement of reaction heat. The commercial calorimetric bombs are unfitted for aluminothermy, therefore a new one which works up to 3000 ^oC is addressed in this paper.

Keywords: heat yield measurement, aluminothermy, calorimetry, waste recovery

1. Introduction

Solid waste should be treated as one of the potential resources in the steel industry to keep up with Environmental Legislation and Regulations and The Economies of Disposal in the present scenario of the Green Deal on Steel [1,2]. Solid waste management in steel industry implies four actions i.e., reduce, reuse, recycle and restore aka “4 Rs” [3-5]. In this view, the European Steel Association

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(EUROFER) promotes technologies that are developed not only for gainful utilization of solid wastes in manufacture of conventional products but also for conversion of same into completely new products. EUROFER points out that a Green Deal on Steel should be agreed between EU steel industry and the EU institutions and governments, with a clear action plan establishing a market for *green steel* in the period 2021 to 2030. This plan can help to promote new efficient technology for reducing CO_2 emission and for advanced utilization of solid wastes in manufacture of conventional products but also for conversion of same into completely new products [2]. Fortunately, considerable research work has been carried out in the iron and steel industry with the objective of finding solutions to the problem of waste material [5-8]. The old metallurgical landfills occupy thousands ha and and generate major environmental problem. Therefore, the waste recycling in Romania represents a priority of the National Strategy for Waste Management (NSWM) [9,10]. Thus, the historical metallurgical dumps as those nearby Galati, Hunedoara, Calan, etc., need being eradicated. In this regard, NSWM recommends the developing of new efficient technologies for waste treatment i.e., "4 Rs". The metallurgical wastes (Table 1) have complex chemical composition as is shown in Tables 1 that depicts the representative contents of such wastes [6].

Table 1

Phase compositions of some representative scale wastes sampled from different locations in Romania [6].

% / Scale waste	SiO_2	CaO	MgO	Al_2O_3	MnO	Fe_xO_y*	Moisture	Oil
Galati slag dump	40.2	0.22	0.01	1.64	0.61	**17.5**	-	-
Hunedoara slag dump	46.0	0.15	-	-	0.86	**18.2**	-	-
Oily scale	0.46	0.15	0.01	-	0.85	**68.38**	12÷15	7÷8
Dry scale	0.39	1.11	0.79	-	0.51	**72.16**	-	-
Coarse sludge G - OLD1	2.57	23.89	2.16	0.19	1.21	**12.9%Fe**; 0.5%Zn; 0.95%C 0%Cr		
Sludge BH	14.06	10.01	2.57	6.44	0.96	**19.35%Fe,** 4.79%Zn, 10.9%C, 1.11%S		
EAF Flue dust	6.06	5.81	1.59	2.04	0.29	**21.9%Fe,** 0.1%Zn, 36.82%C.		
Calan sludge blast furnace	13.93	13.35	2.19	4.5	0.48	**17.9%Fe,** 0.4%Zn, 15.55%C		

Note: *Fe_xO_y denotes a mixture of magnetite, hematite and wüstite.

The iron content of the above-mentioned wastes is the main driving force for applying one of the 4Rs technology as to recover the Fe and other useful substances as abrasive ceramics, ZnO etc. The most used methods for processing of the above-mentioned wastes are mechanical agglomeration, briquetting and pelleting and thermal sintering processes: agglomeration and sintering, chlorinating frying and pelleting etc. [6-9]. Recently, some recycling techniques

have been developed, which include different thermal and chemical processes [6,8]. Among them, the exploitation of termite reactions for environmental protection has received renewed attention [12-19].

The aluminothermy method for producing liquid cast iron or liquid steel from iron bearing dust is based on oxidation-reduction reactions between iron oxides and aluminum or magnesium. [13-16]. This type of reaction occurs in the mixture which is called "thermite" [16].

A challenge in this field represents the historical dump exploitation based on continuous aluminothermic reactions. Some authors have suggested very important technological challenge represented by the development of continuous reactors where self-propagating reactions take place [14] or sequential batch process [19].

The practical exploitation of the aluminothermic technology implies a deeper understanding of kinetics and mechanism of solid–solid and gas–solid self-propagating reactions. This represents a very complicated task due to the unique aspects of complex physico-chemical phenomena simultaneously taking place (melting and diffusion of reactants, chemical reactions with formation of intermediate phases, nucleation, grain growth, etc. [13,16]. Only few techniques are available to perform real-time observation of the aluminothermy process as time resolved XRD analysis, particle-foil experiments, and combustion front quenching, which allow to identify reactions and phase transformations taking place [11,16]. Unfortunately, these investigation techniques do not provide valuable data about released heat during termite reaction which is a very important technological characteristic related to a specific recipe needed to treat a waste. Therefore, the measurement of the heat yield of a termite reaction is a mandatory task when dealing with aluminothermic technology tailoring to a specific iron-bearing waste. In this direction two issues must be addressed in a cooperative manner i.e., the estimation of the heat yields based on a proper knowledge of the reactant and the exactness of the measurement process (accuracy and precision). The comparative analysis of the estimated heat and of the measured one is the key of taking under control the exact heat measurement of the termite kits. In this paper we address the problem of heat measurement, both the design of the first version of a calorimetric bomb and the preliminary results and the correlation between heat yield and the microstructure of the aluminothermic reaction products.

2. Estimation of the heat yields of aluminothermic reactions

The estimation of the heat yields of aluminothermic reactions of the reduction reactions is based on the following reduction reactions [31]:

$$3FeO+2Al=Al_2O_3+3Fe \quad (1)$$

$$Fe_2O_3+2Al=Al_2O_3+2Fe \quad (2)$$
$$3Fe_3O_4+8Al=4Al_2O_3+9Fe \quad (3)$$

The waste recovery practice deals with complex thermite compositions consisting of magnetite (ferrous-ferric oxide), hematite (ferric oxide) and some impurities as corundum, silica, etc. The heat estimation of a complex mixture is very difficult. Therefore, we addressed the binary thermitic compositions made of magnetite and wüstite as follows:

$$Fe_3O_4+7Fe_2O_3+14Al=17Fe+7\ Al_2O_3+2O_2 \quad (4)$$
$$2\ Fe_3O_4+4\ Fe_2O_3+12Al=14Fe+6\ Al_2O_3+O_2 \quad (5)$$
$$2\ Fe_3O_4+3\ Fe_2O_3+10Al=12Fe+5\ Al_2O_3+O_2 \quad (6)$$
$$3\ Fe_3O_4+3\ Fe_2O_3+14Al=15Fe+7\ Al_2O_3 \quad (7)$$
$$3\ Fe_3O_4+\ Fe_2O_3+10Al=11Fe+5\ Al_2O_3 \quad (8)$$
$$6\ Fe_3O_4+\ Fe_2O_3+18Al=20Fe+9\ Al_2O_3 \quad (9)$$

The heat yield of the reaction depicted in equations (4÷9) is assessed as the reaction enthalpies ΔH at different temperatures (K). In this regard, the heat yield depends on magnetite/hematite ratio (wt.%) and on the temperature at which the reaction occurs. The maximum heat yield is achieved in the case where magnetite/hematite ratio is 1/1. An increasing of the proportion of any component, to the detriment of the other oxide, leads to the decreasing of the heat yield.

3. Calorimetric conception and design

These theoretically achievements help us to estimate a heat quantity of approximately 2500 J released by 100 g of magnetite and hematite mixtures at ratios in the (0.4÷0.6) range. Also, we envisaged that locally temperature inside the reactant mass can rich 3000 ^oC and a graphite crucible is needed to avoid local melting of the metallic parts of the calorimeter. The very explosive thermite reaction will produce a thermal shock wave which may melt the very surface inner metallic layer, but the heat amount would be rapidly diffused into calorimeter. The design of the aluminothermic bomb was made for a single-use of the crucible, having walls as thin as possible. The thinner the walls, the smaller the thermal inertia is achieved, also the higher the accuracy of the measurements. The calorimetric variant we design help capturing the gaseous combustion products of the aluminothermic reaction for further analysis, as the reaction proceeds in the absence of oxygen, not being necessary to pressurize the reaction chamber. The calorimetric bomb was designed for a 50÷100g thermit load, considering the se followings parameters: T_{max}. 3000 ^oC in the crucible, max. 3010 KJ/mol i.e., it was established the dimensions of the crucible, outer vessel, the amount of chilling fluid. It worth noting that at such a load, the main solid reaction products are ferrous alloy (approx. 55%) and slag consisting mainly of

corundum (approx. 45%). The reaction crucible was designed being made of graphite, because this material withstands such higher temperatures and thermal shocks. Also, graphite has proper parameters: thermal conductivity of max. 470 W/mK; specific heat of 710÷830 J/kgK; compression strength of up to 200 MPa in case of a porosity of approx. 53%, at which it reaches a density of 1950 Kg/m^3. Graphite is easily machined by turning, resulting in a smooth surface. It also has a very good thermal accumulation coefficient, as well as a high thermal diffusivity, being from these points of view, at the same time, a heat "accumulator", but also a "transporter". The wall thickness was chosen so that there is a drop in temperature on its section from approx. 2800 ^{o}C to 1500 ^{o}C, enabling the temperature measurement using commercial thermocouples. The crucibles made of refractory materials based on silica, magnesium and zirconia was also approached.

The material of the reaction chamber, of the fluid vessel, of the insulating vessel, as well as of the lids, was chosen to be pipe steel, because it has a sufficient mechanical resistance, being also versatile in terms of processing: mechanical, welding, cutting, deformation; it also has an affordable price.

Regarding the fluid in which the actual reaction chamber is immersed, heat treatment oil was chosen, because it has two characteristics that favor its use: i) high ignition temperature, up to 300 ^{o}C; ii) ensures a fast heat transfer, increasing from 290 W/m^{2}K at 1000 ^{o}C, to 1390 W/m^{2}K at 600 ^{o}C, and then decreasing again to 230 W/m^{2}K at 100 ^{o}C. As a thermal insulator, the fire-retardant polyurethane foam was chosen, which has a thermal conductivity of 0.024 W/mK, being one of the most efficient insulating materials at present. It is also very easy to operate with it, contributing after strengthening to the stiffening the walls of the aluminothermic bomb.

a) b)

Fig. 1 Schematically representation of the calorimeter parts.

The assembly of all components is done with the help of screws with nut, and the sealing with the help of heat-resistant mastic (up to 1200 ^{o}C).

Accordingly, a robust cylindrical camera was designed for the reactor camera as is shown in Fig. 1. The reactor camera is immersed in another cylindrical vessel which is thermally isolated against heat leakage to surrounding environment, denoted as calorimetric bath. The inner space between the reactor camera and the metallic wall of the engulfing vessel is filled with distilled water.

The temperatures of the reactor camera, of the outer metallic wall, of the fluid and of the exterior wall of the calorimeter were foreseen to be measure using a system of thermocouples of commercial type. The temperature inside the walls of the crucible will be measured, at two different distances from the inner surface. Since the material of the crucible is homogeneous in terms of thermal conductivity, the temperature distribution in the material is linear. Knowing the temperature in two points and their distance from the inner surface, we can calculate the temperature on the inner face.

Indirect temperature measurement was necessary, as we expect temperatures in the range of 2500-3000 ^{o}C, and the sensors used (thermocouple type) withstand up to 1500 ^{o}C. To reduce the measurement errors due to the uneven temperature distribution inside the reaction chamber, two sensors were used to determine the temperature at the same distance from the inner surface (A and B), the sensors being placed diametrically opposite the walls of the crucible. The temperature at a distance A and B from the inner surface of the crucible will be the arithmetic mean of the values recorded by the two pairs of sensors.

If T_{A1} and T_{A2} are the temperatures measured at points *A1* and *A2*, points located at a distance *A* from the inner surface, and T_{B1} and T_{B2} are the temperatures measured at points *B1* and *B2*, points located at a distance *B* from the inner surface then the respective average temperatures at distance *A* and B from the inner surface are:

$$T_A=(T_{A1}+T_{A2})/2 \quad (10)$$

$$T_B=(T_{B1}+T_{B2})/2 \quad (11)$$

The variation of temperature with distance inside the walls of the crucible is:

$$(T_B-T_A) / (B-A) \ [^{o}C/mm] \quad (12)$$

The temperature inside the reaction medium is calculated as:

$$T_{Ra}=T_A+A*(T_B-T_A)/(B-A) \quad (13)$$

$$T_{Rb}=T_B+B*(T_B-T_A)/(B-A) \quad (13)$$

The temperature inside the reaction chamber is calculated as the arithmetic mean of TRa and TRb as to reduce the measurement uncertainty:

$$T_R=(T_{Ra}+T_{Rb})/2 \quad (15)$$

Each thermocouple was connected to a voltage amplifier, having a high amplification factor, so that the voltage provided by amplifier chain for each thermocouple ranges 0÷10V, for a temperature variation from 0 to 1700 ^{o}C.

The 4 voltages provided by amplifier were connected to the analogous inputs of a programmable controller (PLC model EATON EASY 822 DC TC), which could read the 4 values simultaneously, perform real-time mathematical operations and display their results in real time (see Fig. 2a). This apparatus has 4 0÷10V analog inputs, 6 digital inputs, 6 relay outputs, a 0÷10V proportional output and a display with 4 lines or 14 alphanumeric characters.

a) b) c)

Fig. 2 Setup temperature measurements: a) programmable controller - PLC model EATON EASY 822 DC TC; b) resistive nickel wire (nickeline); c) crucible equipped with the ignition system.

A manometer with a maximum scale of 10 bar was installed for measuring the pressure inside the calorimetric bomb during the aluminothermic reaction.

The ignition of the aluminothermic reaction was designed to occur indirectly, by an output of the PLC, by means of a "soft-start" button, coupled to one of the digital inputs of the same PLC. This order can be given instantly or with a scheduled delay, depending on the needs of the experiment. Activation of the ignition control can be repeated at a second output of the PLC, where an optical indicator will be connected. A resistive nickel wire (nickeline), with a specific resistance of 20 ohms/m, with a length of 15 cm, was used to ignite the powder mixture (see Fig. 2b). When a voltage of 12 Vdc is applied, the wire heats up to the melting point, causing the reaction to start. The nickel wire passes through two holes made in the crucible, so that the connector remains outside, only the wire is inside the crucible, as it is shown in Fig. 2c.

Once the ignition control is activated, the PLC starts a time counter, which is displayed on its screen. Stopping the experiment (stopwatch) has been set to reach a certain lower temperature threshold, which can be adjustable.

The outside temperature of the crucible is practically the temperature of the heat treatment oil, which is measured with a digital thermometer capable of measuring temperatures up to 125 ^{o}C.

Since the crucible is made of graphite, we can consider that the temperature is distributed almost linearly inside the walls. Thus, if we note with

T_R the temperature in the reaction chamber, with T_T the temperature measured by the thermocouple inside the crucible walls and respectively with T_E the temperature measured outside the crucible (heat treatment oil temperature) and we consider the uniform temperature distribution inside the crucible walls, the thermocouples being positioned at an equal distance from the two walls of the crucible (inside and outside respectively), then T_R can be estimated as:

$$T_R=2T_T-T_E \quad (16)$$

The thermal capacity (C) of the calorimetric ensemble is calibrated by powering heat treatment oil into the calorimetric chamber and recording the temperatures until all the temperatures reach the plateau state. The (C) calibrated values are checked through a theoretical evaluation based on the masses of the parts; the specific thermal capacity of each material used for part manufacturing. The (C) value is validated if difference between measured (C) value and the estimated value are less than 1% of the (C) value.

4. Results and Discussion

The iron thermite sample is placed in a graphite crucible. After charging the sample, connecting the igniter, and sealing the reactor, the entire ensemble is introduced in the thermal isolated bath and four thermocouples are connected to the main measurement points, as already mentioned. The temperatures values are recorded through the PLC-EATON controller.

The main difficulty of the thermite reaction heat yield measurement consists of the cautions that must be taken to prevent the accidents that can happen if the fluid leaks into reactor during reaction. Thermite reaction is hazardous due to the extremely high temperatures produced during its occurrence and the extreme difficulty in smoothing a reaction once initiated. Thus, the procedure of heat measurement must be followed very carefully i.e., the reactor chamber sealing must be checked weighing it before and after two hours dipping in calorimetric bath. Also, the temperature recording must be started with about 15 minutes before the ignition is triggered.

Table 2

The ΔH values obtained undertaken iron thermite reaction on six different compositions.

Thermite	Al, [g]	Fe_3O_4, [g]	Fe_2O_3, [g]	Fe_3O_4 / Fe_2O_3	Mass, [g]	T_{max}, [°C]	ΔH, [kJ]
TK 1	20	10	70	1/7	100	**1920**	**285.2**
TK 2	20	27	53	2/4	100	**2110**	**358.7**
TK 3	20	32	48	2/3	100	**2341**	**341.9**
TK 4	20	40	40	1/1	100	**2431**	**451.2**
TK 5	20	60	20	3/1	100	**2402**	**447.3**
TK 6	20	69	11	6/1	100	**2397**	**441.8**

Six experiments were performed, the composition of the thermitic composition mixture being 100 grams. The receipts of the 6 charges are shown in Table 2. These compositions considered the ratio between the two oxides, so that the results obtained can be compared with those obtained by using specialized software [30]. The values of the maximum temperatures registered during the aluminothermic reaction, as well as of the reaction enthalpies, are also presented in Table 2.

Following the separation of the reaction products (solidified ferrous alloy and slag composed mainly of corundum), TK 1, TK 4 and TK 6, were selected as representative cases. The macroscopic aspects of metal outcomes of the selected reactions are shown in Fig. 3.

a) TK 1 b) TK 4 c) TK 6 d) mounted samples

Fig. 3 Macroscopic aspects of the as cast samples (a, b, c), and compression mounted samples after cutting, in EpoMet G compound (d).

The stereomicroscopy images of the three samples are shown in Fig. 4. The internal shrinkages and pores occurring in all three samples can be easily observed. However, the TK 1 sample has the highest proportion of pores, which are much larger in size compared to the other samples. The TK 4 sample shows the smallest proportion of internal shrinkages and pores. No exogenous inclusions are observed in any sample.

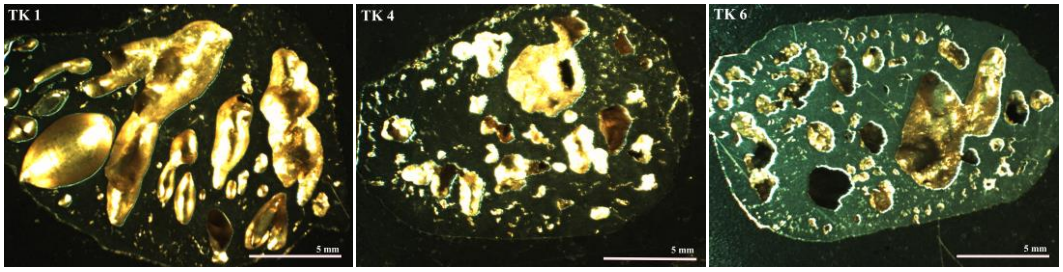

Fig. 4 The stereomicroscopy aspects of the three samples.

This type of structure resulting from solidification is typical when the melting, overheating and solidification process takes place in the same crucible.

Even in these conditions, the process of separating the slag from the ferrous alloy occurred almost completely. This aspect can be easily observed in the micrographs presented in Fig. 5 for the three representative thermitic compositions (TK 1, TK 4, and TK 6).

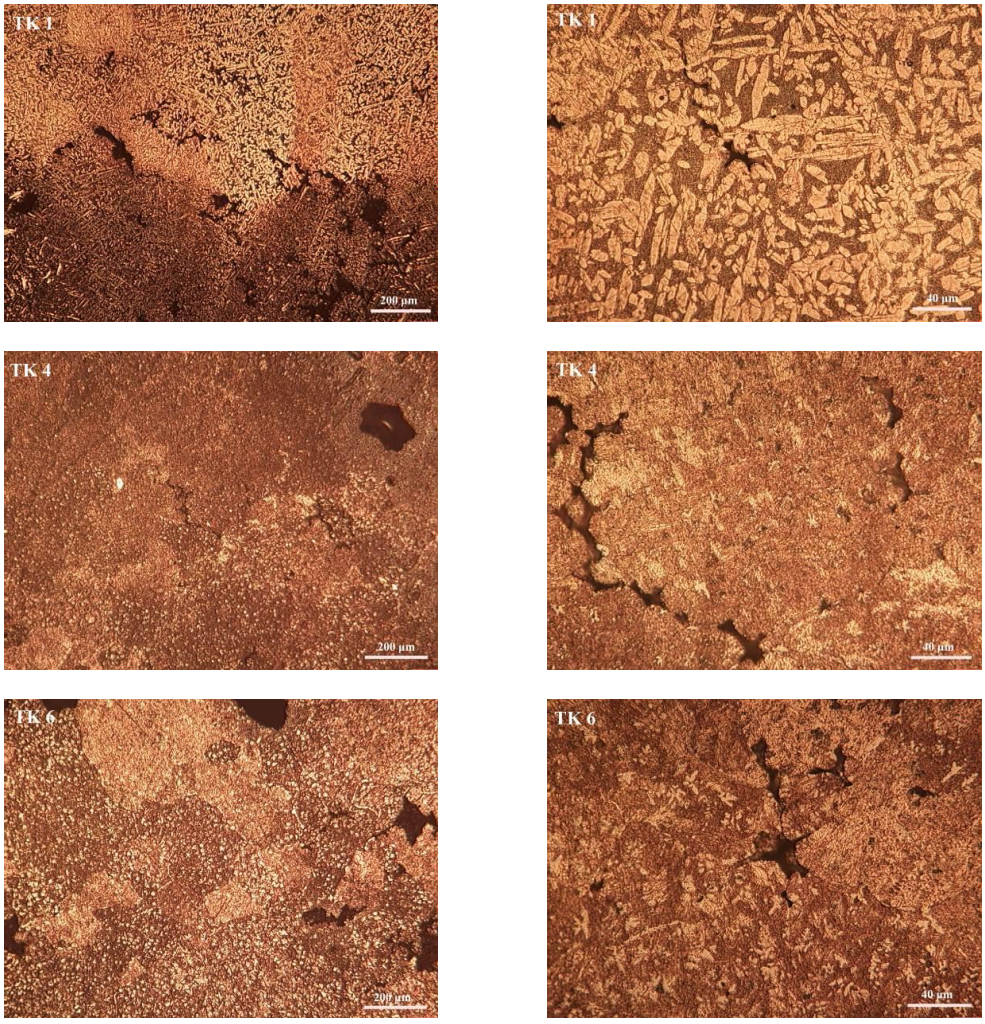

Fig. 5 Optical microscopy of the TK 1, TK 4 and TK 6 thermal kits samples.

From the comparative analysis of the optical microscopy images presented in Fig. 5, some observations are highlighted: a) micro-segregation of all samples is obvious, due to the differentiated chemical etching (NITAL 2% reagent), which is easy to observe at small magnification (100x), where the field is large; b) random distributed micro-shrinkages occur into all three samples; c)the micro-shrinkage size is maximum for TK 6 and minimum for TK 1; d) there are

inclusions of micrometric dimensions (most likely endogenous inclusions), dimensionally comparable to the structural phases, the proportion of which increasing from sample TK 1 to TK 6; e) The formation of these inclusions is due to excess oxygen and other reaction gases, during the aluminothermic reaction, which are solubilized in the melting bath, and combined with existing chemical elements, with which they have high affinity (for example, C, Mn, Si, S, P), some of them becoming crystal nuclei; f) from the microstructural point of view, the distribution of the constituents is totally uneven, first due to the unidirectional solidification; g) the constituents are typical of steels, respectively ferrite and perlite, the proportion of ferrite decreasing from sample TK 1 to TK 6, this being the effect of the compositional variation of the thermitic kit; h) the grain size also differs, observing a medium uniform and a minimum size at the TK 4 sample; i) the sample TK 4 presents the highest needle-like tendency of the microstructure, along with the increase of the proportion of perlite; j) for a totally uncontrolled solidification, in which practically no specific rule of the cake ingots was observed, the obtained steel is relatively free of major inclusions, but it has multiple closed shrinkages and macropores.

4. Conclusions

In binary thermal compositions, which contain ferro-ferric oxide and ferric oxide (magnetite and hematite), the maximum thermal effect of the metal-thermal reaction is ensured for equal proportions of the two types of oxide (451.2 KJ and 2431 ^{o}C); an increase in the proportion of any component of the oxide mixture, leads to a decrease in the thermal effect of the reaction, the stronger the proportion of ferric oxide (285.2 KJ and 1920 ^{o}C). The tested calorimeter can deal with temperature of the inner atmosphere up to about 2200 ^{o}C, hence the calorimetric walls have a higher thermal inertia due to which inner wall surface do not overpass 400 ^{o}C during all performed tests.

The obtained results were verified by comparison to the reported ones. The outcomes variability is assigned to the Al powder previous oxidation and to the impurities occurring in the aluminothermic precursors.

Further work must be done to improve the exactness of the temperature and heat measurements.

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