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Določanje toplotnih lastnosti eksotermno - izolacijskih materialov

Determination of thermal properties of exothermic-insulating materials

Povzetek

Eksotermno – izolacijski materiali se uporabljajo kot pomožni material v jeklolivarnah, livarnah železovih litin, livarnah neželeznih zlitin in drugod. Materiali z eksotermnim in/ali izolacijskim delovanjem se med seboj razlikujejo po sestavi, eksotermnem učinku, izolacijskih sposobnostih, vžigni temperaturi, načinu izdelave in drugih lastnostih. Za učinkovito uporabo takšnih materialov moramo poznati toplotne lastnosti in eksperimentalne tehnike za doseganje ustreznih lastnosti v procesu izdelave.

Za kontrolo eksotermno - izolacijskih materialov ni predpisanih preiskovalnih metod, ki bi omogočale določanje toplotnih lastnosti, zato tudi ni standardiziranega sistema za njihovo določanje. Načrtovana in izdelana je bila naprava za industrijsko kontrolo preiskovanih materialov. Z diferenčno termično analizo (DTA) podrobno raziskujemo toplotne lastnosti surovin in izdelanih eksotermno - izolacijskih materialov z namenom optimiranja in umeritve industrijske naprave v podjetju Exoterm-IT d.o.o.

Abstract

Exothermic-insulating materials are used as auxiliary materials in steel foundries, cast iron foundries, non-ferrous foundries and elsewhere. Materials with exothermic and/or insulating function differ in composition, exothermic effect, insulating ability, ignition temperature, method of manufacture and other properties. For effective use of such materials, the manufacturer should be familiar with thermal properties and experimental techniques to achieve the appropriate characteristics at the manufacturing process.

To control an exothermic-insulating material no special investigation techniques are prescribed, which allow the determination of thermal properties, so there is no standardized system for their determination. For the industrial control, the device for investigated materials was developed and designed. Using the differential thermal analysis (DTA) the thermal properties of raw materials and manufactured exothermic-insulating materials were investigated, with an aim to optimize and calibrate the industrial device in Exoterm-IT d.o.o.

1 Uvod

Raziskano je bilo področje toplotnih lastnosti eksotermno-izolacijskih materialov, ki se uporabljajo kot pomožni materiali v jeklolivarnah, livarnah železovih litin, livarnah neželeznih zlitin in drugje. Tovrstni materiali imajo lahko eksotermno, izolacijsko ali kombinirano delovanje. Delovanje je odvisno od njihove sestave in eksotermnih reakcij, ki potekajo v materialu ob segrevanju. Za pravilno dimenzioniranje velikosti eksotermnih oziroma izolacijskih oblog, ki omogočajo kontrolirani potek strjevanja, je potrebno določiti sproščeno toploto med eksotermnim delovanjem in izolacijski učinek. Materiali z eksotermno-izolacijskim delovanjem se med seboj razlikujejo po sestavi, eksotermnem učinku, izolacijskih sposobnostih, vžigni temperaturi, načinu izdelave in še v nekaterih drugih lastnostih. Za učinkovito uporabo teh materialov moramo poznati njihove toplotne lastnosti in eksperimentalne tehnike za določanje le-teh. Za doseganje ustreznih toplotnih lastnosti v procesu izdelave je potrebno uvesti procesno kontrolo izdelkov, saj se pri proizvodnji zaradi nehomogenosti in spremembe kakovosti posameznih surovin lahko le-te hitro spremenijo. Za kontrolo eksotermno-izolacijskih materialov ni predpisanih posebnih preiskovalnih metod, ki bi omogočale določitev toplotnih lastnosti, zato tudi ni standardiziranega sistema za njihovo določanje. Z diferenčno termično analizo surovin in izdelanih eksotermno-izolacijskih materialov smo podrobno raziskali toplotne lastnosti materialov in jih med seboj primerjali z namenom umeritve ter optimiranja industrijske kontrolne metode za določanje toplotnih lastnosti v podjetju Exoterm-IT d.o.o.

1 Introduction

The thermal properties of exothermic-insulating materials were investigated, which are used as auxiliary materials in steel foundries, cast iron foundries, non-ferrous foundries and elsewhere. These types of materials can have exothermic, insulating function or combination of both. Its function differs regarding their composition and exothermic reactions, which occur during heating. For accurate design of exothermic or insulating lining, that enables controlled solidification, it is necessary to determine the heat released during the exothermic operation, and the insulating effect. Materials with exothermic-insulating function differ in composition, exothermic effect, insulating ability, ignition temperature, method of manufacture and other properties. For effective use of such materials, the manufacturer should be familiar with thermal properties and experimental techniques to achieve the appropriate characteristics at the manufacturing process. To achieve adequate thermal properties during the manufacturing process the introduction of process control of the products is required due to inhomogeneities and changes in the quality of individual raw material that can quickly change the thermal properties at the manufacture. To control the exothermic-insulating materials no special investigative technique that would allow the determination of thermal properties is prescribed, so there is no standardized system for their determination. Using the differential thermal analysis of raw materials and manufactured exothermic-insulating materials the thermal properties of materials were investigated in depth and compared with each other with the purpose of calibration and optimization of industrial control methods for determining the thermal properties in the company Exoterm-IT d.o.o.

2 Teoretični del

Eksotermno-izolacijski materiali se že dolgo uporabljajo v jeklolivarnah, livarnah železovih litin in drugod. Kombinacija materialov, ki se uporablja za izdelavo eksotermno-izolacijskih materialov lahko deluje eksotermno, izolacijsko ali kombinirano. Toplota, ki se sprošča pri eksotermni reakciji, in izolacijska sposobnost teh materialov zmanjšujeta oziroma upočasnjujeta odvajanje toplote iz taline v okolico in s tem zmanjšujeta hitrost ohlajanja oziroma podaljšujeta čas strjevanja taline. Pri klasičnem litju jekla v ingote tako z uporabo tovrstnih materialov za ogrevanje glav ingotov dosežemo manjšo krčilno poroznost v ingotu. V livarnah se eksotermno-izolacijske materiale uporablja za napajalnike, ki so zaradi večjega izkoristka taline lahko manjši. Eksotermno-izolacijski materiali morajo zadostiti zahtevam na področju eksotermnega učinka, izolacijskih sposobnosti, trdnostnih lastnosti, ognjevzdržnosti in oblike končnih izdelkov. Za kakovost materiala je potrebno spremljati tudi produkte eksotermnih reakcij kot so: prašni ostanek, nastali plini s prašnimi delci in pripekanje. (1; 2)

Večina eksotermno-izolacijskih materialov je izdelanih iz več sklopov mešanic (3):

- aktivnih komponent (aluminija, fluoridov, nitridov, oksidov),
- veziv (smole, gline, škroba, vodnega stekla),
- različnih polnil (kremenčevega peska, riževih plev, celuloznih vlaken),
- izolacijskih vlaken (tervolnih vlaken, isofax vlaken, mineralna volna).

Eksotermni materiali so sestavljeni iz materialov, ki ob določenih pogojih eksotermno reagirajo. Eksotermni reaktant, običajno aluminij ali magnezij, zgorita delno

2 Theoretical

Exothermic-insulating materials are being used in steel foundries, cast iron foundries, and elsewhere. The combination of various materials that are being used for exothermic-insulating materials can have exothermic or insulating function or combination of both. The heat released at the exothermic reaction and the insulating ability of these materials reduce or slower heat release from the melt to the surroundings, and thereby reduce the cooling rate and prolong the solidification time of the melt. At the traditional casting of steel ingots the use of such materials for heating of ingot heads, lower shrinkage porosity in the ingot is achieved. In the foundry the exothermic-insulating materials are used for power supplies, which can be reduced, due to increased utilization of the melt. Exothermic-insulating materials must meet requirements in the field of exothermic effect, the insulating ability, strength properties, refractory properties and to form a finished product. The quality of the material must be accompanied by an exothermic reaction product such as powder residue, resulting gases with dust particles. (1; 2)

Most of the exothermic-insulating materials is produced from more multi-component mixtures: (3)

- active component (aluminium, fluoride, nitrides, oxides),
- binders (resins, clay, starch, water glass),
- different fillers (silica sand, rice husks, cellulose fibres),
- insulating fibres (tervol fibres, isofax fibres, mineral wool).

Exothermic materials are made of materials which under certain conditions react exothermically. Exothermic reactant, usually aluminium or magnesium, burn

s kisikom iz zraka, delno pa s trdimi nosilci kisika, kot so: Fe_3O_4, Mn_3O_4, Fe_2O_3, Ba_2O, itn. V takem sistemu nastopajo naslednje reakcije:

$$8Al + 3Fe_3O_4 = 4Al_2O_3 + 9Fe + 3396\,kJ, \quad (1)$$

$$4Al + 3MnO_2 = 2Al_2O_3 + 3Mn + 11300\,kJ \quad (2)$$

$$8Al + 3Mn_3O_4 = 4Al_2O_3 + 9Mn + 2347\,kJ \quad (3)$$

$$4Mg + Fe_3O_4 = 4MgO + 3Fe + 1328\,kJ \quad (4)$$

V primerih, ko mešanica vsebuje večji delež aluminija, ga nekaj reagira tudi s kisikom iz zraka:

$$2Al + 3/2O_2 = Al_2O_3 + 1676\,kJ \quad (5)$$

Za aktivacijo zgornjih reakcij je potrebno dodati dodatke, ki delujejo katalitično in v sistem dovedejo potrebno aktivacijsko energijo. Za ta namen se v mešanico dodaja zmesi nitridov ($NaNO_3$ in KNO_3) in fluoridov (Na_3AlF_6, NaF, KF in CaF_2). V temperaturnem območju med 300 – 600 °C nitridi reagirajo z aluminijem in zaradi sproščanja toplote aktivirajo preostalo zmes v skladu z naslednjo reakcijo (3):

$$10Al + 6NaNO_3 = \\ = 5Al_2O_3 + 3Na_2O + 3N_2 + 25100\,kJ \quad (6)$$

Prisotnost fluoridov pospeši potek reakcij in nekoliko poveča eksotermni učinek mešanice. Ob tem pa potečejo naslednje reakcije (1):

$$Na_3AlF_6 = 3NaF + AlF_3 \quad (7)$$

$$Na_3AlF_6 + 2Al_2O_3 = 3/2Na_2O \cdot Al_2O_3 + 2AlF_3 \quad (8)$$

$$2/3Na_3AlF_6 + 1/2O_2 = 1/3Al_2O_3 + 2NaIF + F_2 \quad (9)$$

$$2Al + AlF_3 = 3AlF \quad (10)$$

Osnovni namen toplotno izolacijskih materialov je zmanjšanje prehoda toplote iz taline v okolico. To dosežemo z izolacijskimi materiali, ki imajo čim nižjo toplotno prevodnost in so odporni do temperatur, pri katerih se uporabljajo. V mešanice eksotermno-izolacijskih materialov se dodaja različna izolacijska vlakna, kot so

partially with oxygen from the air, and partially with solid carriers of oxygen, such as Fe_3O_4, Mn_3O_4, Fe_2O_3, Ba_2O, etc. In such a system, the following reactions perform:

$$8Al + 3Fe_3O_4 = 4Al_2O_3 + 9Fe + 3396\,kJ, \quad (1)$$

$$4Al + 3MnO_2 = 2Al_2O_3 + 3Mn + 11300\,kJ \quad (2)$$

$$8Al + 3Mn_3O_4 = 4Al_2O_3 + 9Mn + 2347\,kJ \quad (3)$$

$$4Mg + Fe_3O_4 = 4MgO + 3Fe + 1328\,kJ \quad (4)$$

In cases where the mixture contains a major proportion of aluminium, it also reacts with the oxygen from the air:

$$2Al + 3/2O_2 = Al_2O_3 + 1676\,kJ \quad (5)$$

To activate the above reactions, it is necessary to add additives which act catalytically and supply required activation energy to the system. For this purpose, a mixture of nitrides ($NaNO_3$ and KNO_3) and fluorides (Na_3AlF_6, NaF, KF and CaF_2) are added to the mixture. In the temperature range 300–600 °C nitrides react with the aluminium and, due to release of heat, activate the remaining mixture in accordance with the following reaction (3):

$$10Al + 6NaNO_3 = \\ = 5Al_2O_3 + 3Na_2O + 3N_2 + 25100\,kJ \quad (6)$$

The presence of fluoride accelerate the reactions and slightly increases exothermic effect of the mixture. At the same time the following reactions take place (1):

$$Na_3AlF_6 = 3NaF + AlF_3 \quad (7)$$

$$Na_3AlF_6 + 2Al_2O_3 = 3/2Na_2O \cdot Al_2O_3 + 2AlF_3 \quad (8)$$

$$2/3Na_3AlF_6 + 1/2O_2 = 1/3Al_2O_3 + 2NaIF + F_2 \quad (9)$$

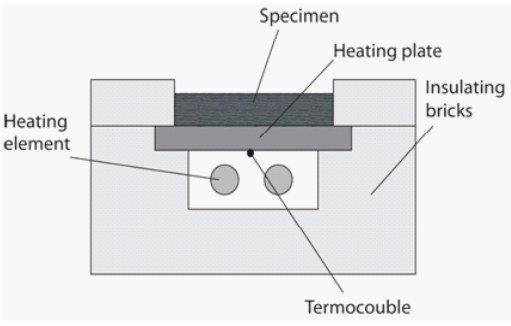
$$2Al + AlF_3 = 3AlF \quad (10)$$

The basic purpose of the thermal insulation material is to reduce heat transfer from the melt to the surroundings. This is achieved by insulating materials having the lowest possible thermal conductivity and by being resistant to the temperatures at which they are used. In a mixture of an exothermic-

tervolna in isofax vlakna. Izolacijska vlakna materialu poleg boljših izolacijskih lastnosti zaradi svoje strukture izboljšajo žilavost in znižajo gostoto izdelkov (4).

3 Opis naprave in meritev

Za doseganje ustreznih toplotnih lastnosti je potrebna kontrola izdelkov, saj se pri proizvodnji zaradi nehomogenosti in spremembe kakovosti posameznih surovin lahko toplotne lastnosti hitro spremenijo. Za kontrolo eksotermno-izolacijskih materialov ni predpisanih posebnih preiskovalnih metod, ki bi omogočale določitev toplotnih lastnosti, zato tudi ni standardiziranega sistema za njihovo določevanje. Namen dela je bil izdelati industrijsko kontrolno metodo EXOPROBE, ki omogoča načrtovanje in razvoj eksotermno-izolacijskih materialov, ter procesno kontrolo izdelkov (slika 1 in 2). Kontrolna metoda deluje na principu vzdrževanja stacionarnega temperaturnega stanja z meritvijo in kontrolo moči grelnih elementov. Iz pridobljenih rezultatov nato izračunamo toplotne lastnosti materialov.



Slika 1: Shema kontrolne metode EXOPROBE

Figure 1: Scheme of control method EXOPROBE

Na sliki 1 je prikazana shema naprave, ki jo sestavljajo grelni elementi, grelna plošča, izolacijske opeke in termoelementa.

insulating material different insulating fibres are added, such as tervol and isofax fibres. Insulating fibres, in addition to the improved insulation properties due to its structure, improve toughness of the material and reduce the density of the product (4).

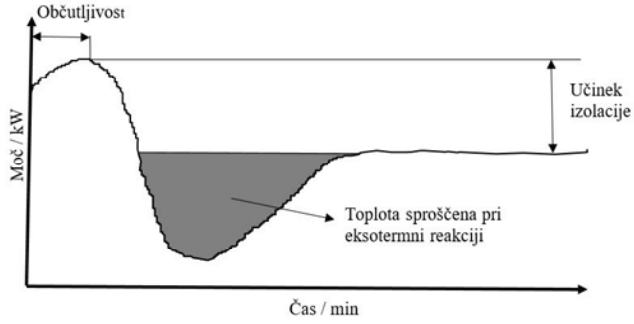
3 Device and measurement description

To achieve adequate thermal properties a product control is needed. During the manufacture, changes in the quality of individual properties can quickly change the thermal properties due to inhomogeneities of the material. To control the exothermic-insulating materials no special investigative technique, which would allow the determination of thermal properties, is prescribed, whereas no standardized system for their determination exists. The purpose of this work was to create an industrial control method EXOPROBE, allowing the design and development of an exothermic-insulating materials and process control of the products (Figure 1 and 2). The control method operates on the principle of maintaining the stationary state of the temperature measurement and the power control of the heating elements. From the obtained results the thermal properties of the materials are calculated.

Figure 1 shows the scheme of the device, consisted of heating elements, a heating plate, insulating brick, and a thermocouple. The temperature of the heating plate and the power of the heating elements are measured. Measurements are captured and processed by a EXOPRO computer program. For the calculation of the test results the most important is the diagram of power regarding the time (Figure 3).

Slika 2: a) Kontrolna metoda za eksotermno-izolacijske materiale EXOPROBE b) s postavitvijo vzorca

Figure 2: a) The control method for the exothermic-insulating materials EXOPROBE b) and the specimen



Slika 3: Shema prikaza grafa odvisnosti moči grelnih elementov od časa

Figure 3: The graphic presentation of the correlation between the power of heating elements and time

Merimo temperaturo grelne plošče in moč grelnih elementov. Meritve zajemamo in obdelamo z računalniškim programom EXOPRO. Za izračune rezultatov preizkusa je najpomembnejši graf odvisnosti moči od časa (slika 3).

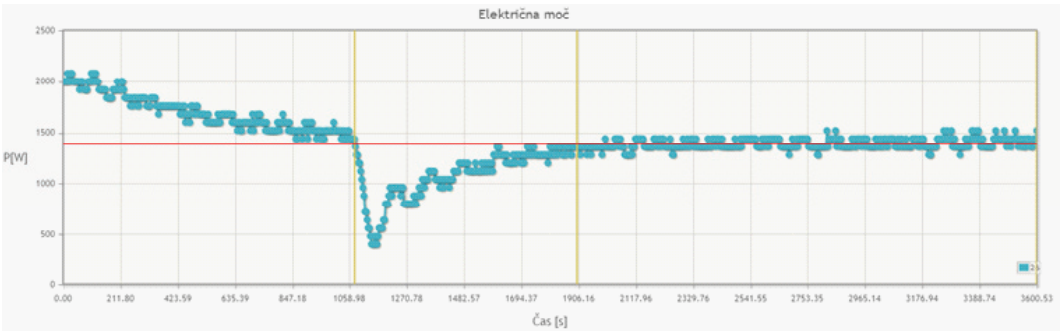
4 Rezultati meritev

Najpomembnejši rezultat analize eksotermno-izolacijskega materiala s kontrolno metodo EXOPROBE in programskim paketom EXOPRO je graf odvisnosti moči od časa (slika 4).

4 Results

The main result of an exothermic-insulating material analysis with the control method EXOPROBE and EXOPRO programme package is a plot of power as a function of time (Figure 4). From the measured results the sensitivity of the exothermic reaction, the burning time, the insulating capability and the energy value of the sample is calculated.

In the diagram (Figure 4) three time zones are shown. The area up to 1060 s (first yellow line) represents heating of the sample and the time until the beginning of



Slika 4: Graf odvisnosti električne moči od časa za analizo eksotermno-izolacijskega materiala EXIPP

Figure 4: The diagram shows the correlation between electrical power and time for the analysis of an exothermic-insulating material EXIPP.

Iz izmerjenih rezultatov izračunamo občutljivost na eksotermno reakcijo, čas gorenja, izolacijsko sposobnost in energijsko vrednost vzorca.

Iz zgornjega grafa so razvidna tri časovna območja. Območje do 1060 s (prva rumena črta) predstavlja ogrevanje vzorca in čas do začetka eksotermnih reakcij. V drugem območju, med 1060 s in 1900 s (med rumenima črtama), potekajo eksotermne reakcije. V tem območju se med krivuljo in rdečo črto izračuna površino eksotermnega vrha in sproščeno toploto vzorca. Zadnje območje v primerjavi z začetnimi pogoji predstavlja učinkovitost izolacije vzorca.

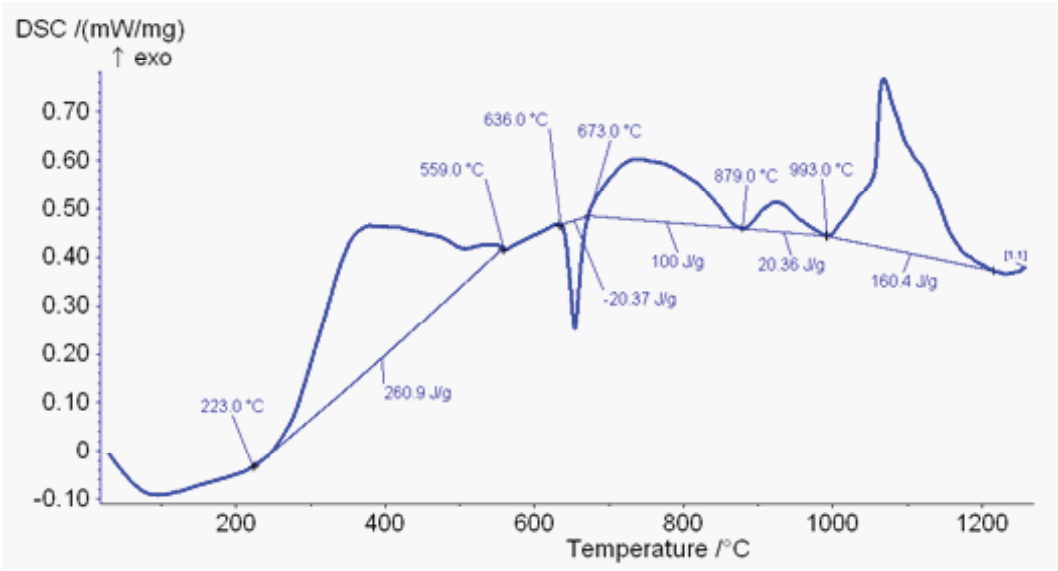
Z diferenčno termično analizo (DTA) smo raziskali toplotne lastnosti surovin in izdelanih eksotermno-izolacijskih materialov. Na sliki 5 je prikazana ogrevna DTA krivulja eksotermno-izolacijskega materiala EXIPP, ki smo jo opravili na aparaturi STA 449 Jupiter podjetja NETZSCH.

Iz krivulje je razvidno, da v temperaturnem območju med 223 in 559 °C potekajo eksotermne reakcije nitridov in fluoridov ter zgorevanje veziva. Sproščena toplota teh reakcij znaša 260,9 J/g. Pri 636

exothermic reactions. In the second area, from 1060 s to 1900 s (between the yellow lines), the exothermic reaction is taking place. In this area, between the curve and the red line, the surface of exothermic peak and the heat released of the sample is calculated. The last field regarding the initial conditions represents the insulating effect of the sample.

Using the differential thermal analysis (DTA) thermal properties of raw materials and manufactured exothermic-insulating materials were studied. Figure 5 shows the heating DTA curve of exothermic-insulating material EXIPP, which was made on the apparatus STA 449 Jupiter from NETZSCH Company.

From this curve in Figure 5 it is evident that in the temperature range between 223 and 559 °C the exothermic reaction of nitrides, fluorides, and the combustion of the binder are taking place. The released heat of these reactions is 260.9 J/g. At 636 °C the aluminium begins to melt and then at 673 °C reacts with the oxygen from the solid carriers of oxygen and atmosphere. The exothermic reactions of aluminium release 280.8 J/g of heat.



Slika 5: Diferenčna termična analiza eksotermno-izolacijskega materiala EXIPP

Figure 5: Differential thermal analysis of exothermic-insulating material EXIPP

°C se začne taliti aluminij, ki nato pri 673 °C reagira s kisikom iz trdnih nosilcev kisika in atmosfere. Eksotermne reakcije aluminija sprostijo 280,8 J/g toplote.

5 Zaključki

Namen je bil izdelati industrijsko kontrolno metodo, ki omogoča načrtovanje in razvoj eksotermno-izolacijskih materialov ter procesno kontrolo izdelkov. Kontrolna metoda EXOPROBE deluje na principu vzdrževanja stacionarnega temperaturnega stanja grelne plošče z meritvijo in kontrolo moči grelnih elementov. Iz pridobljenih rezultatov nato izračunamo toplotne lastnosti materialov.

Eksotermno-izolacijske materiale smo podrobno raziskali z diferenčno termično analizo (DTA). Pri tem smo določili toplotne lastnosti eksotermno-izolacijskih materialov in jih uporabili za umerjanje

5 Conclusions

The purpose of the work was to develop industrial control method that allows planning and development of the exothermic-insulating materials, and the process control of the products. EXOPROBE control method works on the principle of maintaining the fixed temperature state of the heating plate by measuring and controlling the power of the heating elements. From the obtained results the thermal properties of materials are calculated.

Using the differential thermal analysis (DTA) the thermal properties of the exothermic-insulating materials were investigated. The results obtained with the DSC analysis were used for the calibration of the industrial control methods EXOPROBE, which already experimentally runs in the Exoterm-IT d.o.o. company.

industrijske kontrolne metode EXOPROBE, ki že poskusno deluje v podjetju Exoterm-IT d.o.o.

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