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NOVEL TECHNOLOGIES OF SYNTHESIZINGNIHARD BY METALLOTHERMIC METHODS

The lack of materials with required complex of physical, technological and auxiliary properties for the relevant functional purposes has raised a problem of synthesizing corresponding alloys and developing technologies of their production. Synthesis of materials with specific properties will allow not only the new areas of their application to be opened, but also the new trends in further scientific research to be formulated. Combined methods of material synthesis are based on the use of the two types of reactions, namely, the metallothermic ones and the self-propagating high-temperature synthesis (SHS). Combined processes versatility is related to the possibility of synthesizing almost any cast material.
Keywords: *metallothermy, SHS, materials, technologies, synthesis.*

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НОВІ ТЕХНОЛОГІЇ СИНТЕЗУ НІХАРДІВ МЕТАЛОТЕРМІЧНИМИ МЕТОДАМИ

Відсутність матеріалів з необхідним комплексом фізичних, механічних, технологічних і службових властивостей для відповідного функціонального призначення поставило завдання синтезу відповідних сплавів і розробка технологій їх виготовлення. Синтез матеріалів зі спеціальними властивостями дозволяє відкрити не тільки нові сфери їх застосування, а й нові тенденції в області подальших наукових досліджень. Комбіновані методи синтезу матеріалу засновані на використанні двох типів реакцій, а саме металотермічних і само поширюваного високотемпературного синтезу (СВС). Універсальність їх пов'язана із можливістю синтезу практично будь-якого литого матеріалу.
Ключові слова: *металлотермія, СВС, матеріали, технології, синтез.*

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НОВЫЕ ТЕХНОЛОГИИ СИНТЕЗА НИХАРДОВ МЕТАЛЛОТЕРМИЧНЫМИ МЕТОДАМИ

Отсутствие материалов с необходимым комплексом физических, механических, технологических и служебных свойств для соответствующего функционального назначения поставило задачу синтеза соответствующих сплавов и разработки технологий их изготовления. Синтез материалов со специальными свойствами позволяет открыть не только новые сферы их применения, но и новые тенденции в области дальнейших научных исследований. Комбинированные методы синтеза материала основаны на использовании двух типов реакций, а именно металлотермических и самораспространяющегося высокотемпературного синтеза (СВС). Универсальность их связана с возможностью синтеза практически любого литого материала.
Ключевые слова: *металлотермия, СВС, материалы, технологии, синтез.*

1. Subject relevance. The urgent industrial problem of nowadays is not only creation of new materials but also improvement of traditional material properties and advance development of technologies of their production. Detailed studies of the problem allow us to state that this task could be successfully solved by using specially synthesized alloys produced by combined processes based on the combustion of exothermic powder mixtures.

The above technologies are based on the combined processes and allow the predetermined structure to be synthesized with specified alloy properties at cast formation with the use of synthesized materials for the emergency repairs of products, part surface layer recovery and for the use of the synthesized alloy for the cast saving in the exothermic cast additive technologies.

The synthesis technologies developed in this work differ from traditional ones by a series of obvious advantages: the lack of need in the powerful electric energy power supplies, the possibility to use simple and cheap casting equipment, the high process productivity (alloy synthesis time may vary from 30 seconds to a couple of minutes), the possibility of using secondary production waste – graphite electrode grinding, aluminium or magnesium chips, iron cinder, blue powder, i.e. the dust from the filters of the casting shops producing manganese alloys. All the aforementioned have caused an urgent need in carrying out research described in this paper. The above technologies could be successfully applied to save metal at the high-volume and mass production factories producing casts and instruments. Creating materials on the basis of the self-propagating high-temperature synthesis (SHS) and combined (metallothermy+SHS) processes as well as studying the influence of new technological methods of metal production on the cast microstructure, chemical composition and mechanical properties have gained large practical importance. Their use in the existing casting technologies, e.g. in producing steel casts with thermite cast additives increases considerable process efficiency.

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2. Research goal. The main goal of the present research was to predict the structure and the phase composition of the synthesized alloys, to elucidate the influence of combined technologies on the material properties and to determine the most optimal areas of the above alloys application. In addition, this work is intended to study the synthesized materials, namely the thermite cast irontype nihard etc.

3. Materials and research technique. The following materials were used in this work: the smoke black, the aluminium powder "ПА-3" – "ПА-4", the iron cinder (rolling made) with the following average chemical composition (in mass %): 0.05 C; 0.10–0.35 Si; 0.10–0.35 Mn; 0.01–0.03 S; 0.01–0.03 P; 40–50 Fe_2O_3; 50–60 FeO and others. The powder burden was dried, mixed, consolidated and placed into the metallothermic reactor, in the simplest variant – into the metallothermic pot.

The essence of the metallothermic and combined syntheses is quite simple, i.e. the powder-like burden ingredients are loaded into the metallothermic reactor and then are burnt up using a special igniter. After combustion completion, in the bottom part of reactor the cast is formed, whereas the slag is collected in the upper part due to a considerable difference in the specific masses of the reaction products.

To determine the cast mass and alloy yield, at the first stage of our studies the microsmeltings were carried out in the metallothermic pot at the burden mass of 100–150 g. Combustion process was initiated by a special titanium powder (ПХ-2)made igniter.

After determining the burden composition by the chemical reaction stoichiometric coefficients and its correcting by the component fixation coefficients, the adiabatic combustion temperature of the metallothermic reaction was calculated to find the possibility to separate the alloy from the slag.

The technique developed allows the metallothermic burden composition to be found and its adiabatic combustion temperature to be calculated. The principal condition of the synthesis process is the necessity to keep the actual burden combustion temperature above the slag melting temperature (for Al_2O_3 – 2400 K).

To minimize the high temperature influence on the thermite metal, as well as to eliminate the related high porosity and cast shrinkage, the inert additions were introduced into the burden in a form of the relevant alloy chips and ferrous alloys. To increase the combustion stability and to improve the kinetic characteristics of reaction, 1–2% (of the burden mass) of fluorspar CaF_2 were added to the burden. This addition not only reduces the ignition temperature of the exothermic powder mixture but also increases the metal yield from it.

4. Theoretical part. Taking into account the necessity to predict the alloy structure, phase composition and properties, the authors have developed the principles of the synthesized alloy formation. The techniques based on the above principles allowed the exothermic burden adiabatic combustion temperatures to be determined. The methods of geometric thermodynamics for the structure optimization and prediction were modified as well.

Theoretical grounds of synthesis reaction. When organizing the ferrous alloy synthesis process, we used the thermite reactions based on the aluminium acidification and iron reduction: $\mathrm{Fe_3O_4 + Al \rightarrow Fe + Al_2O_3}$, or the metallothermic metal oxide reactions with oxidizer and the classical "oxygen-free" combustion SHS reactions.Microsmeltings carried out by us have shown the regularities of the carbon (in a form of silver graphite) and other doping elements fixation by the thermite metal that is necessary to synthesize the desired thermite steel chemical composition when calculating the exothermic burdens.

Method of recovering the exothermic mixture adiabatic combustion temperature and selecting reactions suitable for the alloy synthesis. To find the boundary conditions of the alloy synthesis the authors have developed a method on the basis of adiabatic temperature dependence on the molar composition of synthesized compounds. This allowed the synthesis reactions to be divided into two principal groups. The first of them includes those reactions, the adiabatic temperature of which is higher than the temperature of separation of the synthesized alloy and slag. These reactions are applicable for the alloy formation. The second group of reactions occurring at the ingredient interaction results in the formation of an alloy in a form of separate "grains" in the slag or leads to the slag part non-separation from the alloy itself. These reactions are not acceptable for further experimental use.

After determining the burden composition according to the stoichiometric coefficients and after correcting them by the burden component fixation coefficients, it is recommended to calculate the metallothermic reaction adiabatic combustion temperature T_a [1-3]. In these calculations of the burden adiabatic combustion temperature according to the methods developed, the aluminium sublimation was not taken into account giving the error of finding T_a and the reaction heat Q_r. That is, the principal criterion of the cast production is that T_a for all reactions must exceed the reaction product temperature

T_{mel}. The T_a value calculation, obviously, does not take into account the heat losses during combustion and the completeness of reactants transformation into reaction products.

5. Experimental part. The experimental studies carried out by the authors were stimulated by the necessity to confirm the development of a complex of theoretical notions. This work was carried out to synthesize the different thermite cast irons.

Taking into account the data of the studies we have developed and realized the production of the different carbon steels as a result of the aluminothermic reduction of the iron cinder with introduction of carbon and ferrous alloys into the thermite. It has been found that introduction of more than 20% dopants to the thermite mixture results in the termite alloy and slag separation termination in the conditions of the laboratory thermite microsmeltings at the burden mass below 300 g. In case of the exothermic burden mass from 0.3 to 5 kg, the dopant content in it could reach 25%, while for the 5–50 kg masses it is 30%.

Thermite steel adding to the conventional one decreases essentially the grain size in the casting condition. For the same reason the alloy in the subadditional zone of the steel casts synthesized with the use of the high temperature gradient thermite cast addition technology is more fine-grained then that in the case of using the ordinary technology [4].

High percentage content of impurities and ferrous alloys excessively "cools" the exothermic reaction, and then the calculated burden composition for the high alloy steel does not ensure the optimal combustion temperature of the exothermic mixture. In this case it is necessary to use the other, different from the above one, direction of the alloy steel synthesis. It is related to the synthesis of a preset alloy chemical composition not by adding a certain quantity of ferrous alloys but by composing a special exothermic burden comprising the alloying oxides (e.g., Cr_2O_3, CrO_3, NiO, CuO, V_2O_5 and others) and the iron cinder reduced by aluminium in the course of the aluminothermic process. The technique of the relevant calculations and the synthesis technology have been developed to obtain the thermite high alloys.

When carrying out the thermite smelting according to the suggested method, one has to take into account the "activity" of the elements that compose the metallothermic burden. Speaking about the inhomogeneity of the element distribution in the casts synthesized by the aluminothermic reduction of oxides, one must indicate the sequence of the above oxides reaction with aluminium. First the most easily reducible elements (Fe, Ni, etc.) are reduced, whereas hardly reducible oxides move to the slag melt. Afterwards the thermite metal that contains the excessive aluminium, while passing the slag layer, reduces the hardly reducible oxides as well.

The further experimental microsmeltings were directed to synthesize the four types of the high alloy cast irons – the nihards, i.e. the analogues of the industrial cast irons (the types I, II, III ones and a special one). The chemical composition of the above alloys shown in table 1 confirms the correctness of the burden calculation results. In this case the synthesis reaction was carried out both in the chill mold-type reactor and in that with the graphite lining to find the influence of the heat removal regime on the nihard mechanical properties (table 2).

Table 1.

Chemical composition of the thermite nihards (mass %)

Synthesized nihard	Alloying element content							
	C	Si	Mn	Ni	Cr	Mo	S	P
Type I	3.2–3.5	0.4–0.7	0.3–0.5	4–4.5	2–2.5	–	≤0.05	≤0.05
Type II	2.7–3.2	0.4–0.7	0.3–0.5	4–4.7	2–2.5	–	≤0.05	≤0.05
Type III	1–1.5	0.4–0.7	0.3–0.5	4–4.5	1.4–1.6	–	≤0.05	≤0.05
Alloy 3-2-1	3.2–3.5	0.4–0.7	1.2–2.0	3–3.5	1.5–2.0	0.8–1.0	≤0.15	≤0.40

The use of the graphite pot leads to a slight nihard strength increase. In general, the microsmelting conditions establish such intense melt cooling regime that the influence of the reactor lining stops dominating. All the casts made of the nihards had no external signs of shrink holes and cast cutting and macroanalysing confirmed these conclusions. No chemical composition liquation over the cast volume was found.

Synthesized thermite wear-proof cast irons, i.e. nihards, relate to the chromium-nickel martensitic cast irons, graphitizing probability of which at the alloy synthesis using the aluminothermic method decreases significantly due to the large temperature gradient and high rates of heat removal. The microstructural analysis has shown that in the thermite cast irons the cementite content is not less than 50% that results in the 1000 – 1050 HV hardness.

Table 2.

Mechanical properties of the thermite nihard

Cast iron type	Casting method	σ_b	HB	σ_u
		MPa		
I	Chill reactor	270–320	570–640	470–890
	Graphite pot	280–320	600–670	490–710
II	Chill reactor	380–450	590–630	560–770
III	Graphite pot	–	370–410	–
Alloy 3-2-1	Graphite pot	–	490–560	–

Cast iron wear-resistance at the abrasive wear is known to depend on the structural components microhardness, shape, location and number. The principal phases in the nihard structure (as the X-ray spectral analysis has shown) that influence most intensively the wear-resistance are cementite and the more wear-proof Cr, Mo etc. carbides. The X-ray spectral analysis has found in these cast iron structures, besides the Fe_3C, $(Fe,Cr)_3C$ and carbides, the $(Fe,Cr)_7C_3$ carbides that provided the 15 GPa HV microhardness. That of the $(Fe,Cr)_3C$ carbides is 10.0-10.5 GPa, while for $(Fe,Cr)_7C_3$ and $(Fe,Cr)_{23}C_6$ it is 14.5–17.5 GPa.

At the same time, the alloyed thermite cast irons at the manganese content increase [4-12] demonstrate, despite high synthesis temperatures, the castability worsening with the shrink-off conservation within 1.6–2.2 %. To improve the casting properties and the quality of the cast made from the thermite nihard, the metallothermic reactor was heated up to 420–520 K.

The synthesized cast irons are badly processed by cutting [4, 13-16]. The nihards are ready to produce microcracks even at grinding. This results in the necessity to use the low-temperature cast softening with the 4–6 hr exposure or normalization with subsequent softening.

6. Conclusions. The results of the theoretical and experimental studies presented above are related to the synthesis of materials by combined technologies based on the metallothermy and SHS. On the basis of developed methods of calculations the compositions of burdens have been found and a wide spectrum of different-type alloys have been synthesized.

The specific features of smelting using combined methods have been found, the mechanical properties and the structure of alloys produced have been studied, the recovery coefficients for the alloy elements in the metallothermic and combined processes have been found. In addition, the technologies of the thermite welding and smelting onto the super-hard surfaces have been developed, while combining the LSH and SHS processes in one operation allowed one to solve a complex of technical problems of production of the carbide steel-like materials and hard alloys on the metal surface.

7. Outlooks of the further use of the combined technologies and synthesized cast alloys. Theoretical, experimental and research-industrial works carried out by the authors allow a series of problems to be solved being related to the production of the materials for certain functional purposes and the novel synthesis technologies to be applied in the non-traditional conditions. This allows a number of the most serious technical problems that retard development and use of combined processes in the industrial production practice to be removed.

It is necessary in the closest future to:

1. Develop typical technologies based on the combined processes of material synthesis.

2. Extend the practice of the developed technologies application for the casting and welding productions, etc.

3. Develop typical equipment for synthesizing the above materials.

4. Develop the method of using the synthesized alloys to liquidate the emergency situations due to repairing at the movable railway platforms; marine objects both on the water surface and under water; for spacecraft's that underwent microdestruction during space flight; in case of necessity of repairs at the drilling units and on the transpolar territories or in other places away from the energy power supplies.

5. Extend a spectrum of synthesized alloys and determine their structure and phase composition for the optimal use.

6. Increase the efficiency of the use of the laser surface hardening and combined processes of alloy synthesis.

7. Define the most expedient areas of the use of the above synthesized materials.

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