Composite material for surfacing, obtained by self-propagating high-temperature synthesis

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This paper presents the results of theoretical and experimental studies of the development of a composite material obtained by self-propagating high-temperature synthesis (SHS), which is used to modify a deposited alloy of the NiCrBSi system (self-fluxing alloy PG-10N-01). The source components of the composite material are powders of titanium Ti, technical carbon C, aluminum powder Al, iron oxide Fe₂O₃, thermosetting powder PT-NA-01, and refractory clay PGOSA-0. The mechanical activation of the charge was performed in a ball mill for 15 minutes at 130 rpm and the ratio of the mass of the charge to the mass of the grinding media was 1:40. The SHS process was initiated by heating a nichrome spiral with a diameter of 0.8 mm in an argon Ar environment. As a result of deposition, the layers with a dense and multiphase structure are formed. The deposited layer of PG-10N-01 alloy consists of a solid solution of nickel (Y-Ni), boride phase Ni_{B} and inclusions of chromium carbide $Cr_{3}C_{2}$ and boron carbide $B_{4}C$. When the synthesized composite material was added to the PG-10N-01 alloy, titanium carbide TiC and silicon carbide SiC were additionally detected in the deposited layer, which lead to an increase in the layer microhardness. The phase composition of the layer deposited from a mechanical mixture of 10~%(Ti-C-Al-SiO₂-Fe₂O₂-PT-NA-01) + 90 % PG-10N-01 is a solid solution of y-Ni nickel, nickel boride Ni B, titanium nitride TiN, chromium silicate CrSi, and intermetallic FeAI. The microhardness of this layer is 20 % lower than that of the PG-10N-01 alloy layer.

Keywords: composite material, SHS process, deposition, structure, phase composition, microhardness.

Композиційний матеріал для наплавлення, одержаний самопоширюваним високотемпературним синтезом. С.О. Лузан, П.А. Ситников

В роботі наведено результати теоретичних та експериментальних досліджень розробки композиційного матеріалу, одержаного самопоширюваним високотемпературним синтезом (CBC), який використовується для модифікування наплавленого сплаву системи Ni-Cr-B-Si (самофлюсівного сплаву ПГ-10Н-01). В якості вихідних компонентів композиційного матеріалу використано порошки титану Ті, технічного вуглецю С, алюмінієвої пудри АІ, оксиду заліза Fe₂O₃, термореагуючого порошку ПТ-НА-01 та вогнетривкої глини ПГОСА-0. Механічна активація шихти виконувалося у кульовому млині протягом 15 хв, при 130 об/хв та співвідношенні як 1 до 40 маси шихти до маси тіл подрібнення. Ініціювання СВС-процесу здійснювалося теплотою нагрітої ніхромової спіралі діаметром 0,8 мм, в середовищі аргону Аг. В результаті наплавлення формуються шари, які мають щільну та багатофазну структуру. Наплавлений шар сплаву ПГ-10Н-01 складається з твердого розчину нікелю (у-Ni), боридної фази Ni₃B, включень карбідів хрому Cr₂C₃ та бору B₄C. При додаванні до сплаву ПГ-10Н-01 синтезованого композиційного матеріалу в наплавленому шарі додатково виявлені карбіди титану ТіС та кремнію SiC, які призводять до підвищення мікротвердості шару. Фазовий склад шару, наплавленого механічною сумішшю складу 10 % (Ti-C-Al-SiO₂-Al₂O₂-Fe₂O₃-ПТ-НА-01) + 90 % ПГ-10Н-01, є твердим розчином нікелю γ-Ni, боридів нікелю Ni₄B, нітридів титану ТіN, силіцидів хрому CrSi та інтерметалідів FeAl. Мікротвердість цього шару у порівнянні з шаром зі сплаву ПГ-10Н-01 на 20 % нижче.

1. Introduction

Composite materials based on titanium carbide TiC and silicon carbide SiC are among the most promising materials because they combine high hardness, heat resistance and thermal conductivity at a low cost. Due to these properties, TiC and SiC are widely used as abrasives and cutting materials, and also form the basis of metal-ceramic materials for various purposes [1, 2]. At the same time, the cost of traditional methods of producing such carbides, including powder metallurgy, remains an energy- and cost-intensive process, which prompts the search for more efficient methods of their production.

The method of self-propagating high-temperature synthesis (SHS) is one of the most advanced methods for obtaining composite materials. The physical essence of the SHS process lies in the local initiation of exothermic reactions between the source reagents; they make it possible to generate a significant amount of heat for the propagation of the front of physical and chemical transformations necessary for the formation of materials of the predicted structure and phase composition. The SHS process is one of the energy-saving technologies for obtaining materials with specified properties and the possibility of repeated regeneration of the resulting materials. [3 -5]. Products obtained using the SHS process can be used both as finished products and as raw materials for powder mixtures used in various deposition and thermal coating processes.

The aim of the paper is to research the structure and mechanical properties of the composite material obtained by self-propagating high-temperature synthesis for deposition wear-resistant coatings of machine parts.

2. Experimental

The source components used to produce the composite material (CM) were powders of titanium Ti of PTM-1 grade, technical carbon C of P-803 grade, silicon oxides SiO_2 and aluminum Al_2O_3 , which were added in the form of refractory clay of PGOSA-0 grade. In order to enhance the thermal effect of the reaction, aluminum (Al) powder of PAP-1 grade, iron oxide Fe_2O_3 , and thermosetting powder of PT-NA-01 grade were added to the source charge. The granulometric size of the source powders did not exceed 100 microns. The ratio of the source components of the charge was equimolar, so that during the SHS process the synthesis of titanium carbide





Fig. 1. Stages of SHS process initiation: a) – sample from the charge (1) with a supplied spiral (2); b) – beginning of sample heating; c) – SHS process; d) – cooled spike.

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Fig. 2. Microstructure and diffraction patterns of deposited layers: a) - PG-10N-01; b) - 10 % CM + 90 % PG-10N-01; c) - 10 % MM + 90 % PG-10N-01.

 ${\rm TiC}$ and silicon carbide ${\rm SiC}$ of the stoichiometric composition occurred.

Mixing and mechanical activation of the charge was carried out in a ball mill for 15 min at 130 rpm and the ratio of the mass of the

charge to the mass of the grinding bodies (steel balls with a diameter of 6 mm) was 1: 40. After mechanical activation, the maximum particle size of the charge did not exceed 40 μ m [6]. Metylan adhesive was added to the mechanically



Fig. 3. Change in microhardness (HV) of the deposited layer in the direction from the surface of the deposited layer to the surface of the base: a) - PG-10N-01; b) - 10 % CM + 90 % PG-10N-01; c) - 30 % CM + 70 % PG-10N-01; d) - 10 % MM + 90 % PG-10N-01.

activated charge as a binder, after which it was mixed and a cylindrical sample with a diameter of 16 mm and a height of 20 mm was formed and dried for 72 hours.

For initiating the SHS process, a special device that provides heating of the sample *1* with a nichrome coil *2* was made (Fig. 1, a) [7]. Fig. 1, b shows the stage of the beginning of the sample heating, which, after the beginning of the SHS process (Fig. 2, c), turns into a sinter (Fig. 2, d). The SHS process was performed in an argon Ar environment with a purity of 98 %.

The second stage involved crushing the resulting sinter to a powdered state, after which the crushed mixture in an amount of 10 to 30 % CM was added to the matrix material - a self-fluxing alloy of the NiCrBSi system of PG-10N-01 powder grade. The mechanical activation was carried out for 15 min. In order to determine the advantages of the SHS process for the synthesis of CM, some of mixtures were prepared from PG-10N-01 powder with the addition of a mechanical mixture (MM) of the source components of the charge (Ti-C-Al-SiO₂- Al_2O_3 -Fe₂O₃-PT-NA-01). The amount of MM, just as with the CM ratios, ranged from 10 to 30 %, respectively.

The resulting powder mixtures were applied to the surfaces of 65G steel samples with a thickness of 3 mm, after which arc spraying was carried out using a graphite electrode with a diameter of 9.5 mm, at a current of 100-120 A, in direct polarity. A DC welding inverter of the SV-290 NK model was used as a power source.

The methods of electron microscopy (Tescan Mira 3LMU scanning electron microscope with an Oxford X-max energy dispersive spectrometer) and X-ray diffraction analysis (Rigaku Ultima-IV X-ray diffractometer) were used to study the microstructure and phase composition of the deposited layers. The samples were etched in a 4 % nitric acid solution HNO_3 in ethanol. A PMT-3 microhardness tester with an indenter load of 0.1 kg was used to measure the microhardness of the deposited layers.

The Kh4-B test machine was used to study the wear resistance of the deposited layers using cylindrical samples with a diameter of 4 mm and a height of 15 mm, the ends of which



Fig. 4. The deposited layer of the composition 10% MS + 90% PG-10N-01 with a longitudinal crack

were located on the surface of the abrasive skin fixed to the end of a rotating disk. The diameter of the disk was 200 mm, and the friction path of the sample was 20 m. The deposited sample was pressed against the abrasive cloth with a load of 1 kg. To ensure wear of the sample along the fresh surface of the abrasive cloth, it was shifted in the radial direction. During the research, a fresh abrasive cloth with abrasive grains of aluminum oxide with a size of $150 \,\mu\text{m}$ was used for each sample. The relative wear resistance of the deposited layers containing CM and MM was evaluated in comparison with the amount of wear of the layer deposited with the self-fluxing alloy PG-10N-01. The amount of wear of the deposited layer was determined by the weight method using analytical scales VLR-200.

3. Results and discussion

The research using scanning electron microscopy and energy-dispersive analysis have shown that the morphology of the deposited layers formed during crystallization with directed heat removal [8]. The basis of the deposited layer of the PG-10N-01 alloy is a γ -Ni solid solution and the boride phase Ni₃B. Inclusions of chromium carbide Cr₃C₂ and boron carbide B₄C are also found in the layer (Fig. 2, a). In addition to the main phases of γ -Ni, nickel boride Ni₃B, Cr₃C₂ and B₄C inclusions, phases of titanium carbide TiC and silicon carbide SiC were also found in the deposited layer of 10 % CM + 90 % PG-10H-01 (Fig. 2, b).

The phase composition of the layer deposited using a mechanical mixture of 10 % (Ti-C-Al-SiO₂-Al₂O₃-Fe₂O₃-PT-NA-01) + 90 % PG-10N-01 is a y-Ni nickel solid solution, nickel boride Ni₃B, titanium nitride TiN, chromium silicate CrSi, and intermetallic FeAl (Fig. 2, c). The X-ray diffraction analysis using a Rigaku Ultima-IV diffractometer revealed phase inhomogeneity of the deposited layers at the macro- and micro-levels with phases of Y-Ni, Ni₃B, Cr₃C₂, B₄C, TiC, SiC, TiN, FeAl.



Fig. 5. Wear resistance of deposited layers in the process of abrasive wear: (a) - relative wear resistance; (b) - wear of deposited layers; 1) – PG-10N-01; 2) – 10 % CM + 90 % PG-10N-01; 3) – 10 % MM + 90 % PG-10N-01.

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Fig. 6. Relative wear resistance of deposited layers depending on the amount of additive, %: a) – CM; b) – MM.

The microhardness of the deposited layers, measured in the direction from the surface of the deposited layer to the surface of the base, is shown in Fig. 3.

The average microhardness was 660 HV for the 10 % CM + 90 % PG-10N-01 deposited layer, 720 HV for the 20 % CM + 80 % PG-10N-01 layer and 760 HV for the 30 % CM + 70 % PG-10N-01 layer; these values exceed the average microhardness of the PG-10N-01 coating, which is 510 HV. The stable nature of the microhardness distribution indicates a uniform distribution of hard inclusions in the deposited layers, while with an increase in the amount of CM in the PG-10N-01 alloy, the microhardness increases.

The microhardness of the 10 % MM + 90 % PG-10N-01 deposited layer is 415 HV. It is important to note that during the crystallization of the deposited layer and its subsequent cooling, cracks occur in the layer (Fig. 4). The formation of the cracks can be explained by the presence of bound oxygen O_2 in the residues of original silicon oxide SiO_2 , aluminum oxide Al_2O_3 , and iron oxide Fe_2O_3 . Oxygen passes into the molten metal during heating, causing its embrittlement [9]. Aluminum Al and thermosetting powder PT-NA-01, due to the exothermic reaction, intensify this process and increase the temperature in the surfacing zone on the base. This leads to penetration of the base material to a greater depth compared to applying a powder mixture with CM.

The results of research on the wear resistance of deposited layers during abrasive wear are shown in Fig. 5.

The deposited layers containing CM have higher abrasive wear resistance compared to the self-fluxing alloy PG-10N-01, which is explained by the presence of chromium carbide Cr_3C_2 , boron carbide B_4C , titanium carbide TiC, silicon carbide SiC, and nickel borides Ni₃B in the deposited layer. With an increase in the amount of CM in PG-10N-01, the wear resistance of the deposited layers in the process of abrasive wear increases (Fig. 6, a). The abrasive wear resistance of the deposited layers containing MM is lower compared to the wear resistance of PG-10H-01, which is explained by the presence of intermetallic FeAl and silicides CrSi in the layer. With an increase in the amount of MM in PG-10H-01, the wear resistance of the deposited layers decreases during abrasive wear (Fig. 6, b).

Thus, the self-propagating high-temperature synthesis using the Ti-C-Al-SiO₂-Al₂O₃-Fe₂O₃-PT-NA-01 composition makes it possible to obtain a composite material containing titanium carbide TiC and silicon carbide SiC, which increase the hardness of the deposited layer based on the PG-10N-01 alloy. The addition of the Ti-C-Al-SiO₂-Al₂O₃-Fe₂O₃-PT-NA-01 mechanical mixture to the PG-10N-01 alloy reduces the hardness of the deposited layer and causes cracks in it. That is explained by the action of oxygen O₂, which is present in the source components of the mixture and leads to embrittlement of the deposited layer.

4. Conclusion

The developed composite material consisting of powders of titanium, technical carbon, iron oxide, aluminum, thermosetting powder PT-NA-01 and refractory clay PGOSA-0 was obtained by self-propagating high-temperature synthesis and can be used to modify the selffluxing alloy PG-10N-01, which increases its abrasive wear resistance.

The deposited layer based on the self-fluxing alloy PG-10N-01 with the addition of 10 % of the developed composite material with the phase composition of γ -Ni solid solution, titanium carbide TiC, silicon carbide SiC, chromium carbide Cr₃C₂, boron carbide B₄C, and nickel boride Ni₃B ensures an increase in its microhardness compared to the PG-10N-01 alloy.

According to abrasive wear measurements, the wear resistance of the deposited layer of PG-10N-01 powder doped with 10 % composite material is 1.8 times higher compared to the wear resistance of the layer deposited with the self-fluxing PG-10N-01 alloy.

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