Production of TiC – Co and TiC – NiCr Composite Powders and Study of Their Interaction with a Target under Cold Spray Conditions

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Abstract. In the first part of the paper, the effect of mechanical treatment of particles of reacting Ti + C + Me (Me = NiCr or Co) mixtures on the process of self-propagating high-temperature synthesis (SHS) is investigated. It is shown that as a result of SH-synthesis in the free burning mode, a metal-ceramic sinter of high porosity is formed, which is easily destroyed by mechanical action. An increase in the volume fraction of the metal binder (NiCr or Co) leads to a redistribution of the sizes of carbides towards smaller values.

In the second part of the paper, the results of cold spraying nickel-chromium alloy particles and cermet particles of the TiC – NiCr composition on an aluminum substrate are presented. Produced NiCr coatings have a high porosity (up to 10 %) and a layered structure with clearly defined contours of individual deformed particles (splat). Due to the high hardness and low plasticity of metal-ceramic particles of the TiC – NiCr composition, during their interaction with the surface of an aluminum substrate, continuous coating cannot be produced, only individual adhered particles are observed. With prolonged exposure to the flow of such particles, erosion of the substrate takes place.

Introduction

The main feature of cold gas-dynamic spraying [1, 2] is that the temperature of the sprayed particles before impact with the substrate is always lower than their melting temperature. Accordingly, there are no phase transformations during deposition, and the coatings retain the phase composition inherent in the initial powder, in contrast to coatings obtained by thermal spray methods, in which the particles have a temperature close to the melting point of the material or are in a molten state. In this regard, the deposition and study of the properties of cold sprayed coatings from multicomponent composite mixtures are of great interest, including for the production of new materials and coatings with unique functional properties [3 – 37]. As a rule, the preparation of composite powder mixture of a given composition for spraying is made using the original commercially available powders by simple blending. There are also a few papers, for example, [10 – 14], where a ball mill and the method of self-propagating high-temperature synthesis were used to prepare powder mixtures. This method is an effective, high-performance, cost-effective method for the production of composite (including nanostructured) cermet powders with different volume fractions of metal binder. As a result of SH-synthesis, a metal-ceramic compact is produced, in the volume of which hard ceramic inclusions are evenly distributed. Mechanical action on the compact allows it to be crushed into powder particles. It is known that the preliminary mechanical treatment (activation) of powder materials in planetary mills allows stimulating the reactions of interphase interaction of dissimilar elements; in particular, increasing the reaction rate of SHS of chemical compounds [38]. In papers [39, 40], it is shown that at the stage of preparation of composite powders, modification of the structure of metal-ceramic compositions is
achieved by preliminary mechanical treatment and activation of metal components of the initial powder composition for subsequent SH-synthesis of cermet compact.

The aim of this study is to obtain a metal-ceramic powder material, containing titanium carbide, by SH-synthesis in a free combustion mode, and to study the process of its deposition by cold spray method.

**Experimental methods**

It was shown in paper [41] that the size of treated metal particles of ductile material, depending upon the time of mechanical treatment, is influenced by the mass fraction of surfactant in the powder mixture under study. Here, the surfactant was lamp soot P803. An increase in the content of the mass fraction of soot in the powder mixture from 5 to 20 % leads to a significant decrease in the average volume size of metal particles, and at the same time to cladding them with soot.

Preparation of reactive mixtures, with a given volume fraction of metal binder of stoichiometric composition, includes the following steps: 1) mechanical treatment of titanium powder (PTOM2) for 90 seconds, of particle size less than 40 microns, with addition of soot 10 wt.% in planetary mill "Activator-251" with the next processing parameters: the mass of the loaded balls-160 g for each drum, the acceleration of the grinding media – 117 g, the loading mass of the treated powder – 30 g; steel balls of diameter 5 mm were used as grinding bodies; 2) mechanical treatment of cobalt powder (PK-1U) for 30 seconds, and nickel-chromium alloy (PKh80N20) for 45 seconds, both of particle size less than 40 microns, with addition of soot 10 wt.%, under the same treatment conditions; 3) subsequent mixing of reacting components (Ti + C) of stoichiometric composition with metal binder (NiCr, Co) in planetary mill for 60 seconds, under the same treatment conditions.

Before conducting SH-synthesis in the free-burning mode, the reactor was purged with argon for 5 minutes at gas flow rate of 30 l/min, after which the synthesis reaction was initiated. All synthesized cermet sinters had a porous structure similar to that shown in figure 1, and were quite easily destroyed into coarse powder. Further mechanical treatment of this coarse powder in planetary mill for 15 – 90 seconds allows obtaining cermet particles of the main fraction of sizes from 20 to 90 microns.

![Fig. 1. Samples of cermet sinters of composition TiC – 30 vol.% NiCr (a) and TiC – 30 vol.% Co (b), produced via SH-synthesis.](image)

The results of x-ray phase analysis (Fig. 2) of synthesized particles of metal – ceramic powder TiC – Me (NiCr, Co), performed with aid of D8 ADVANCE diffractometer (Bruker Corporation, USA) using monochromatized CuKα radiation, have shown the presence of peaks corresponding to the phases of titanium carbide (TiC) and metals (Ni, Cr and Co).
Fig. 2. Typical x-ray pattern of produced cermet particles: a) TiC – n vol.% Co (n = 19, 30, 40, 50 vol.%), b) TiC – n vol.% NiCr (n = 19, 30, 40, 50 vol.%).

Sieving of powder particles by size was performed using vibrating stand with a set of analytical sieves. Histograms of the volume and counting distributions of particles were determined using particle size analyzer (0.04 – 2000 microns) LS 13 320 (Beckman Coulter). Figure 3 shows the particle size distribution after sieving the synthesized cermet powder into four fractions.

Particle morphology was determined using Evo MA15 electron microscope (Carl Zeiss). Figure 4 shows typical shape and structure of cermet particles of synthesized compositions. One can observe the evolution of sizes of titanium carbide inclusions in the composite material: increase in volume fraction of metal binder leads to change of the size of the carbides to the region of smaller values.
Figure 4. Overall views (a – d) and cross-sections (e – h) of initial (a, e) and mechanically treated powder particles of fraction 71 – 90 μm TiC – NiCr: a, e – 19 vol.% NiCr; b, f – 30 vol.% NiCr; c, g – 40 vol.% NiCr; d, h – 50 vol.% NiCr.

Figure 5 shows histograms, plotted using the results of more than 4,000 measurements for each composition, which characterize the count size distribution of carbide inclusions during visual processing of images (figure 4) captured by scanning electron microscopy. An explanation for increase in sizes of hard ceramic phase in produced cermet materials is given in paper [40].

Cold spray setup (ITAM SB RAS) with an axisymmetric de Laval nozzle of length 140 mm and of critical and exit cross-section diameters 2.8 mm and 6.5 mm, respectively, was used for coating deposition. As a working gas, air was used at pre-chamber pressure of 3.0 MPa and pre-chamber temperature of 600°C. Distance from nozzle exit to substrate surface was constant and equal to 30 mm. When NiCr powder was sprayed, the nozzle moved relative to the substrate at a speed of 25 mm/s with a step of 3 mm to obtain a continuous coating over the entire surface of the substrate. During deposition powders of TiC – NiCr composition, the nozzle did not move (i.e., it stood still), but interaction time of two-phase flow with the substrate surface changed (within 2–8 s).

Prior to the deposition of coatings, the 30×30×3 mm aluminum alloy AMG2M substrates were sandblasted with a 300÷320 μm P63 grade alumina abrasive. The air–abrasive jet at a constant pressure of 0.9 MPa treated evenly over the entire surface of substrate plate from a distance of 20 mm for
10 – 15 seconds. Sandblasting activates and creates a micro-roughness of the substrate surface, which helps to increase the adhesive strength of coatings.

To study the microstructure and porosity of the coatings on the substrates, cross-sections of samples were prepared. Coating porosity was determined using Image Analysis Software supplied with OLYMPUS GX-51 metallographic microscope.

**Results and discussion**

Internal structure of deposited nickel-chromium alloy coatings is characterized by sufficiently high porosity up to 10% (fig. 6). Layer-by-layer formation of the coating with clearly defined contours of individual deformed particles (splats) is observed. Formation of this type of coating structure is typical for deposition of particles that are "cold" before impacting on the substrate surface, i.e. have a temperature much lower than the melting point of the material, or have not a high enough speed. The performed estimates have shown that the temperature of the nickel-chromium alloy particles before impact on the substrate surface did not exceed 0.4 of the melting point of the material, and their average velocity was about 600 m/s.

![Fig. 6. Microphotos of cross-section of nickel-chromium coating.](image1)

![Fig. 7. Substrate cross-sections in the places where TiC – NiCr cermet particles were deposited, fraction +71 – 90 μm (a - c) – 19 vol.% NiCr; (d-f) – 40 vol.% NiCr. Spraying time a, d – 2 s; b, e – 4 s; c, f – 8 s.](image2)

Reinforcement of nickel-chromium alloy with ultrafine hard inclusions of titanium carbide significantly increases the hardness of the material and reduces its ductility. Figure 7 shows individual metal-ceramic particles embedded in the surface of the aluminum substrate with clearly visible
boundaries in shape, which is identical to the shape of the original (sprayed) particle. An increase in the interaction time between the flow of metal-ceramic particles and the substrate surface leads to the removal of some volume of material from the substrate (i.e., erosion of the substrate), while the number of adhered particles does not increase (i.e., no coating build-up is observed).

Figure 8 shows substrate cross-sections in the places where TiC – 40 vol.% NiCr cermet particles of fraction +71 – 90 microns was deposited for 8 seconds. It can be seen that second and third coating layers begin to form on individual particles adhered to the surface layer of the substrate material, but they are separate islands in the sprayed zone. Thus, for the production of coating, it is necessary to increase the volume fraction of metal binder in the metal-ceramic alloy.

However, producing a cermet material of volume content of metal binder more than 50% by SH-synthesis is difficult at present, as the metal binder in the reactive powder mixture is an inert material which actively absorbs the heat of reactants, which leads to lower rate and temperature of the reaction, down to its complete stop.

Further research will focus on the production of cermet composite powders with a volume fraction of metal binder more than 50% by the method of mechanical treatment of blended metal-ceramic and metal particles in a planetary mill.

Conclusion

Composite powders of TiC – NiCr and TiC – Co compositions with titanium carbide content of 50 to 81 vol.% were produced by mechanical treatment in a planetary mill followed by SH-synthesis in a free combustion mode. Cermet particles, after sieving into fractions, have similar surface shape and structure. An increase in volume fraction of metal binder (NiCr or Co) leads to redistribution of carbide sizes towards smaller values.

Cold spraying of nickel-chromium alloy particles on aluminum substrate produces coating characterized by high porosity (up to 10 %) and layered structure with clearly defined contours of individual deformed particles (splats).

Due to the high hardness and low ductility of TiC – NiCr cermet particles, during their interaction with the surface of aluminum substrate continuous coating cannot be produced, only individual embedded particles are observed.

Increase in the interaction time between flow of metal-ceramic particles and substrate surface leads to the removal of volume of material from the substrate (i.e., erosion of the substrate), while the number of adhered particles does not increase (i.e., no coating build-up is observed). Thus, in order to provide more favorable conditions for production of cold sprayed coatings from such materials, it is necessary to increase the content of metal binder in sprayed powder.

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