Peculiarities of the Superhard Metallurgical Coatings Formation by Thermoreactive Electrospark Strengthening Method

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Abstract

The method of Thermoreactive Electrospark Surface Strengthening (TRESS) is presented in this paper. Thus the process of coating formation becomes a less energy consuming one as compared to the basic technology of the electrospark alloying. The additional heat of the chemical reaction of the synthesis final products formation on the substrate contribute to the increase of thickness and continuity of the coating, to the diminution of the inner tension due to smoother concentration gradients through the coating thickness. The opportunities of TRESS method are exposed on the example of wear-resistant coating formation in the systems of Ti+Al+diamond, Ti+B+diamond. Optimal conditions and technological parameters for diamond containing coatings deposition are found. The influence of a number of TRESS technological parameters (impulse discharge energy, grain size of the component of electrode materials) on the mass transfer kinetics, coatings composition, their structure and properties. The composition of coating was determinate by the X-ray analysis. The wear-resistance of coatings was evaluated by tests on the friction machine.

1. INTRODUCTION

TRESS is one of the prospective methods for the surface strengthening of the die, rolling and cutting tools.

Earlier in order to produce functional coatings the authors used electrodes, made by the method of Self-Propagating High-Temperature Synthesis (SHS). Every surface engineering task demanded a development of a particular electrode composition.

TRESS electrodes were produced by means of force SHS-pressing and SHS-extrusion technologies. The coatings produced with these electrodes can be divided into three groups by their composition and application: wear-resistant, heat-resistant and corrosion-resistant. The coating thickness and properties can be varied, for example, at the expense of the increase of the impulse discharges energy (growth of the consumed electric power), reduction of the structural durability, porosity growth, variation of the size of the electrode material structural
components, variation of the substrate composition. In spite of such a great variety of the factors, determining the ESA - coating structure and properties, the researchers worked out new technological decisions, allowing significant increase of the process efficiency.

The TRESS method idea is as follows: electric discharge of a given power initiates a chemical exothermic reaction between the electrode components. But the heat of the chemical reaction is to be comparable to the energy of impulse discharges. The physical essence of TRESS method is that the electrode presents a mixture of chemical reagents, which can interact with each other on the substrate with a high heat evolution after a local heat initiation of the synthesis reaction by the electric discharge energy. Thus the process of coating formation becomes a less energy consuming one as compared to the basic technology of the electrospark alloying. The additional heat of the chemical reaction of the synthesis final products formation on the substrate contribute to the increase of its thickness and continuity, to the diminution of the inner tension due to the smoother concentration gradients through the coating thickness.

The present work purpose was to study the peculiarities and regularities of the mass transfer during the TRESS process and structure formation of diamond-containing coatings, based on titanium aluminide and titanium borides.

2. EXPERIMENTAL PROCEDURE

A TRESS process was fulfilled in the nitrogen with such equipment as «Elitron-22A». The charge electrodes were composed of exothermic mixtures of titanium with aluminum and titanium with boron. /1/ Diamond powder (60 vol. %) of different size fraction was added into the mixture. The mixture electrodes or electrodes consisted of exothermic powder mixtures, 3÷4 mm in diameter and 30÷60 mm in length were made by extrusion method or by drawing in Cu and Fe tubes the exothermic mixtures of aluminum (ASD–4, 99,5% purity, particle average size is 5÷10µm) and of titanium (PTM, 98,9% purity, particle average size is 45-63µm) and of titanium with boron.

The X-ray studying was carried out by diffractometers DRON-3 and DRON-4 in Co-Κα-emission with a step equal to 0.05° and with the exposition of 3 seconds in every point. /2/

The wear-resistance of coatings was evaluated by the tests on the friction machine. The scheme of wearing contact - an area with a coating (S) on the rotating cylindrical surface of diamond-containing disc. The coating was deposited on the preliminary reseated surface (S) of the substrate. Test’s parameters: S=0,33cm²; w=690min⁻¹, where w-frequency of rotating; the rate of sliding friction was 1.45 m/sec, loading on the fiction pair was 3,3N. Diamond wheel data: d=40mm; diamond grain size: 50/70µm; concentration- 50 vol.%; binder-M1.

Wearied thickness of the coating was measured by electromagnetic chip in-situ and by optical microscope after some range of diamond disc on the coated surface of substrate.

3. RESULTS AND DISCUSSION

To study the peculiarities and regularities of diamond coatings formation a titanium alloy VT3-1 was taken as a substrate and the electrode was mixed of titanium, aluminum powders and diamond of a dispersion equal to 8/16, 30/40, 70/90 µm, IRM brand made by «Tomei Diamond» (Japan). This is connected with the fact that metals of Fe group and their intermetallides doesn’t allow to identify a diamond phase by means of X-ray study because
main diamond lines (A4) match the lines of these metals and of their alloys. We shall further prove the influence of a number of TRESS technological parameters (impulse discharge energy, nitrogen consumption, a content of gas evolving titanium hydride addition) on the coating composition, their structure and properties.

The main purpose of the process carrying out in the nitrogen medium is diamond protection against high-temperature oxidation. Thus becomes obvious the necessity to determine the dependence of the main phases content, diamond A4 phase in particular, in a coating upon nitrogen consumption under a constant impulse discharge energy, and also the dependence of the coatings composition on the impulse discharge energy under a constant and a optimal nitrogen consumption.

The increase of nitrogen consumption from 0.1 to 10 l/min results in the noticeable growth of a diamond share being transferred from the mixture electrode (an anode) to the coating. /3/ At the same time a consumption about 10 l/min results in a significant retardation of the chemical reactions of titanium carbide and carbonitride and of intermetallide formation as a result of the intensive heat elimination when blowing the electrode off the reaction zone. On the other hand, such great nitrogen consumption makes the technological process significantly more expensive. So, the next stage of the investigation was aimed at the search for an alternative effective method for raising the rate of diamond preservation in the TRESS process./3,4/ In particular, was determined a positive role of small gas-evolving additions, up to 5 mass% of the titanium hydride, to the initial exothermic mixture. This turned to be enough for the creation of the protective hydrogen medium preserving diamond against graphitization in the most high-temperature zones of the combustion wave (owing to titanium hydride dissociation). Similarly a complex of investigations was fulfilled for studying TiH2 effect being a component of mixture electrodes on diamond preservation in a coating (Fig.1).

Discharge energy, equal to 0.04 J, and nitrogen consumption, equal to 1.0 l/min, were fixed and TiH2 concentration varied from 2.5 to 15 mass%. The qualitative X-ray-phase analysis of the coatings allowed making the dependencies of the main phases concentration on TiH2 content in the electrode (Ti+Al). This allows decreasing nitrogen consumption from 10 to 1l/min.

The working regime of «Elitron-22A» with discharge energy equal to 0.04J is considered to be an optimal one from the point of view of producing a coating with a high diamond concentration of the different fractions equal to 8/16, 30/40, 70/90µm (Fig.2, 3). In the optimal case diamond content in a coating is practically equal to that in an electrode. (Fig.2) Fig.4 demonstrates the microstructure of diamond-containing coating produced under discharge energy equal to 0.04 J. This energy is optimal for deposition of coating with a high diamond concentration with grain size of 8/16 µm up to 70% vol.
Fig. 1 Dependencies of diamond’s concentration on concentration titanium hydride (TiH₂)
Parameters: Q=0.043J-impulse discharge energy; N₂=1l/min-nitrogen consumption, t=2min-duration of TRESS-process
Electrode composition: Ti+Al+TiH₂+diamond(30/40µm)

Fig. 2 Dependencies of the main phases concentration (C) on impulse discharge energy (Q)
1-C (diamond); 2-intermetallides (summary); 3-carbonitrides (summary); 4-copper.
Composition electrode: Ti+Al+60vol% diamond(8/16µm)+5mass%TiH₂ .
Nitrogen consumption-1.0 l/min
Fig. 3 Dependencies of diamond’s concentration on impulse discharge energy under various grain size diamond

1-diamond 8/16µm; 2-diamond 30/40µm; 3-diamond 70/90µm;
nitrogen consumption-1.0 l/min
Electrode composition: Ti+Al+TiH₂+60vol%diamond

The Ti-B-diamond system is interesting from the viewpoint of the TRESS-process above all by production of diamond and borides and diborides in the coating. We studied two types of charge electrodes in copper and steel tubes.

Figure 5 shows the results of quantitative X-ray phase analysis as the major phase composition being dependent of pulsed discharge energy.

The diamond content is greater in the coating produced by a steel-enveloped electrode at pulsed discharge energy of 0.04 J. The diamond content diminishes when the pulsed
discharge energy increases. This is bound up with the diamond graphitization, and, in addition, iron acts as a catalyst on artificial diamond. Therefore, an appreciable increase in titanium carbide and carbonitride content is found at higher pulsed discharge energies in both cases. Titanium boride was found in the version of the steel envelope (Fig. 6). Microstructure of coating is presented on Fig.7. In this case diamond grain size is 8/16 µm.

4. Wear test

It is generally known that diamond in a coating improves its wear-resistance. To demonstrate it we have carried out a series of wear tests. Coating was applied onto a titanium to correlate with the X-ray phase analysis. The testing diagram is shown in Fig. 8. Figure 9(a) depicts a coating produced with the help of steel-enveloped Ti+B+diamond electrode. Wear-resistance decreases with increasing the pulsed discharge energy, and at the same time the thickness of the worn layer increases. As already noted, this is bound up with the fact that at up-the-ladder energy the graphitization takes place and a fraction of diamond in the coating decreases, adversely affecting the wear-resistance.

Fig. 5 Dependencies of the main phases concentration (C) on impulse discharge energy (Q) (Copper tube)

1-C (diamond); 2-intermetallides (summary); 3-carbonitrides (summary); 4-copper; 5-Ti
Composition electrode: Ti+B+diamond(8/16µm)+TiH₂(5%)
Nitrogen consumption-1.0 l/min
Fig. 6 Dependencies of the main phases concentration (C) on impulse discharge energy (Q) (Steel tube)

1-C (diamond); 2-intermetallides (summary); 3-carbonitrides (summary); 4-TiB; 5-Ti
Composition electrode: Ti+B+diamond(8/16µm)+TiH₂(5%)
Nitrogen consumption-1.0 l/min

Fig. 7 Diamond containing coating
Electrode: Ti+B+diamond+TiH₂ (Steel tube)
Nitrogen consumption-1l/min; t=2 min
Scheme test(a) and Wear test(b) of different composition coatings been produced TRESS

![Diagram](image)

Test’ parameters:
- S=0,33 cm²
- P=3,3 N
- \(\omega\)=690 min\(^{-1}\)

diamond wheel data:
- \(d=40\) mm
- diamond grain size: 50/70
- concentration: 50 vol%
- binder: M1

**Fig. 8** Scheme test(a) and Wear test(b) of different composition coatings been produced TRESS

The coating thickness increases at the cost of more intensive mass transfer bound up with higher temperatures. Figure 9(b) shows wear-resistance by the same electrode but copper enveloped. High wear-resistance indices were also found with the coating produced with the help of a copper-enveloped Ti+Al+diamond+TiH\(_2\) electrode (Fig. 9(c)). In all the cases the diamond-bearing coatings have higher wear-resistance in comparison with that of uncoated base. With regard to each to other, these coatings differ negligibly in wear-resistance if compared by the regimes. This is bound up with both diamond content and existence of intermetallic compounds, carbides and carbonitrides, borides, also possessing high wear-resistance, in the coating.
Fig. 9(a) Wear tests of different diamond-containing coatings
Electrode: Ti+B+diamond(8/16µm)+TiH₂(5%) (Steel tube)

Fig. 9(b) Wear tests of different diamond-containing coatings
Electrode: Ti+B+diamond (8/16µm)+TiH₂(5%) (Copper tube)
CONCLUSIONS

The production of diamond-containing coatings is shown to be possible using charge electrodes of different composition and in different envelopes. These coatings have high wear-resistance. The results of quantitative and qualitative X-ray phase analysis are comparable with the results of wear tests. Optimal compositions of an electrode (nitrogen demand, TiH₂ gasifying additive, dispersion of diamond) and electrical performance of the installation have been found. The energy of impulse discharges determines the efficiency of TRESS process when producing diamond-containing coatings and also their composition and properties /5/.

5. REFERENCES