Development of Wear Resistant Coatings Formed by Plasma Spraying of Alloy Ni–Fe–Cr–Si–B–C System Reinforced with Ceramics Al₂O₃

A. S. Kalinichenko¹, O. G. Devoino¹, V. V. Meshkova¹

¹Belarusian National Technical University (Minsk, Republic of Belarus)

Abstract. Creating a functionally oriented, including nanostructured, anti-friction materials and coatings with qualitatively new complex of service properties is an important scientific and practical problem. In particular, for the cable industry it is urgent task of ensuring the high performance properties of fast deteriorating stretching and supporting rollers. Working surfaces of these parts operate under practically dry friction conditions with constantly updated material of stretching wire. Plasma spraying is one of the widely used methods of surface engineering to create wear resistant coatings and which is characterized with process flexibility and the ability to create coatings using various materials and alloys including composite ones. The installation UPU-3D with the PP-25 plasma torch was used for plasma spraying. The thickness of the sprayed layer was 0.8–1.1 mm. As a material for the deposition of composite coatings a powder mixture of self-fluxing nickel alloy PG-HN80SR4 (system Ni–Fe–Cr–Si–B–C) and a neutral oxide ceramics Al₂O₃ was used. The amount of ceramics varied from 15 to 33 %. This ceramic oxide was selected due to the desire to reduce coatings’ costs while providing high durability. Carried out phase and microstructural studies have shown when ceramics was added in an amount more than 20 % a formation of conglomerates formed by not melted alumina particles often was observed. These conglomerates serve as crack formation centers in the coating. The phase composition of the coatings practically does not depend on the content of ceramics compounds. Tribological tests have shown that the best results were obtained when the content of the oxide ceramic in the coating was in the range from 15 to 20 %.

Keywords: plasma wear-resistant coatings, oxide ceramics, microstructure, phase composition, tribological properties

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Разработка износостойких покрытий, сформированных плазменным напылением сплава системы Ni–Fe–Cr–Si–B–C, упрочненного керамикой Al₂O₃

Доктора техн. наук, профессора А. С. Калиниченко¹, О. Г. Девойно¹, асп. В. В. Мешкова¹

¹Белорусский национальный технический университет (Минск, Республика Беларусь)

Реферат. Создание функционально ориентированных, в том числе наноструктурированных, антифрикционных материалов и покрытий, обладающих качественно новым комплексом служебных свойств, является важной научной и практической задачей. В частности, для кабельного производства актуальна задача обеспечения высоких эксплуатационных свойств быстроизнашивающихся протягивающих и поддерживающих роликов кабельного производства. Рабочие поверхности этих деталей работают в условиях практически сухого трения при постоянно обновляющемся материале протягиваемой проволоки. Один из широко применяемых методов инженерии поверхности для создания износостойких покрытий – плазменное напыление, которое характеризуется гибкостью процесса и возможностью создавать покрытия из различных материалов и сплавов, включая композиционные покрытия. Для плазменного напыления использовали установку УПУ-3Д с плазмотроном ПП-25. Толщина напыленного слоя составила 0,8–1,1 мм. В качестве материала для создания композиционных покрытий применяли смесь порошков самофлюсирующегося нике-
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левого сплава ПГ-ХН80СР4 (системы Ni–Fe–Cr–Si–B–C) и нейтральной оксидной керамики Al2O3. Количество вводимой керамики изменялось от 15 до 33 %. Выбор данной оксидной керамики обусловлен стремлением снизить стоимость покрытия при обеспечении высокой износостойкости. Проведенные микроструктурные и фазовые исследования показали, что при вводе керамики в количестве более 20 % чаще наблюдается образование конгломератов из непроплавившихся частиц оксида алюминия, которые служат центрами образования трещин в покрытии. Фазовый состав покрытий практически не зависел от содержания керамики. Триботехнические испытания показали, что лучшие результаты получаются при содержании оксидной керамики в покрытии 15 и 20 %.

Ключевые слова: плазменные износостойкие покрытия, оксидная керамика, микроструктура, фазовый состав, триботехнические свойства

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Introduction

In modern mechanical engineering scientific and applied studies in the field of developing functionally oriented, including nanostructured, anti-friction materials and coatings with qualitatively new service complex of properties are intensively carried out. This is especially true for new technical applications.

In this regard, the achievements of surface engineering can provide the creation of new high-quality materials in a much shorter development time. Depending on the technological methods and processing modes, different kinds of surface properties, such as optical properties and mechanical properties can be locally improved while maintaining the properties such as the strength of the base material. The application of these developments in friction pairs can significantly expand the range of operation modes, load capacity and service life of friction units [1].

Currently, plasma spraying process is rather widespread both for surface hardening and restoration of worn-out surfaces. Advantages of this process are flexibility and possibility to deposit different materials including ceramics onto surface of substrate [2].

From the standpoint of practical realization plasma spraying could be divided into three groups depending on the feedstock and its state within the plasma: plasma spraying CVD, plasma spraying PVD and plasma spraying of powder [3, 4]. New methods of plasma spraying process occur on a regular basis and, as a result, there are new scientific questions should be solved. For example, there is a spraying the liquid raw material in the form of particles of submicron size or chemicals in a solvent when coating is formed by condensa-

of these materials on the substrate. This relatively new technology makes possible the production of thinner coatings compared to air plasma spraying with the formation of ultrafine or nano-size microstructures [5]. The new process of tunnel gas plasma spraying can provide high quality ceramic coatings based on Al2O3 and ZrO2 on steel SUS304 substrate as compared with other plasma method. In particular, coating based on the ZrO2 has high surface hardness and a gradient distribution of hardness within the deposited layer [6].

Coatings made of self-fluxing alloys are recommended for the protection of surfaces from wear under the simultaneous action of corrosive environment and high temperatures with moderate shock loads. These alloys have high performance properties, but their use is limited by high cost. Self-fluxing powder materials based on Ni–Cr–B–Si–C system are rather attractive as they can also be the basis for deposition of coatings with composite structure [7]. Classical technology for production of composite wear-resistant coatings based on self-fluxing alloy is the addition of tungsten carbide powder resulting in an additional increase in the cost of technology. So, it is more attractive to use materials that can reduce cost of coating while maintaining a high level of physical, mechanical and service properties. In particular, alumina powder could be considered as an addition to self-fluxing alloy to form a composite structure. Thus, the problems can be solved concerning the technology cost and improvement of the tribological properties of coatings. Moreover, the adhesion component of friction force can be reduced as alumina is chemically neutral to the material of stretching wire.

This approach to the development of wear-resistant composite coatings has been applied to
solve the problem of increasing service life of stretching rollers used in the cable production. Working surfaces of these rollers are operated under practically dry friction conditions with constantly updated material of stretching wire. Under these conditions there is exposure of juvenile surfaces which leads to the growth of the adhesive component of friction force and increased wear of working surfaces of the rollers resulting in deterioration of rolling wire.

The purpose of this work was to develop a composition of wear-resistant coatings for spraying on a working surface of stretching rollers for cable production, as well as the analysis of their structure and tribological properties.

**Experimental Procedures**

Plasma spraying technology for the formation of wear-resistant coatings was used. A powder mixture of self-fluxing nickel-basis alloy PG-HN80SR4 (system Ni–Fe–Cr–Si–B–C) and a neutral oxide ceramics $\alpha$-Al$_2$O$_3$ was applied as a coating material. Selection of ceramics based on $\alpha$-Al$_2$O$_3$ was due to its considerable practical interest [8], as well as aiming lowering the processing costs and reduce the interaction between copper wire and self-fluxing nickel matrix coating. Powder of neutral oxide ceramics Al$_2$O$_3$ was added in an amount from 15 to 33 %.

The installation UPU-3D with the PP-25 plasma torch was used for plasma spraying deposition. As plasma and carrier gas nitrogen was used. Arc voltage – 80 V, current was 410 A; volumetric flow rate of plasma gas (N$_2$) $G$ = 40–50 l/min. The thickness of the sprayed layer was in the range from 0.8 to 1.1 mm. To improve the adhesion between the coating and base material samples were preliminary coated with a thin layer of self-fluxing alloy. The coating was formed in cladding mode with melting (specimens were preheated to 800 °C).

To analyze the coating microstructure investigations were performed using optical and electron microscopy. X-ray studies were carried out with an automated X-ray complex on the basis of diffractometer DRON-3M in scan mode with step 0.1° and using Cu-K$_\alpha$-radiation according to conventional methods [9]. Micro-hardness of the sprayed layers was determined using PMT-3 unit.

**Results and Discussion**

Studies have shown that it is inappropriate to increase the content of aluminum oxide powder above 25 % due to danger of conglomerates formation, porosity and deterioration of the coating quality [10].

For not optimal conditions of plasma spraying one can observe in a coating along with dispersed aluminum oxide particles conglomerates of aluminum oxide serving as a source of crack development during solidification due to different values of thermal expansion coefficients (Fig. 1 and Tabl. 1). Furthermore, in the coating tungsten compounds are observed due to erosion of the plasma torch.

There was a danger of “floating” Al$_2$O$_3$ particles towards the outer surface of the coating due to significant difference in the specific density of the oxide ceramics and self-fluxing nickel matrix. However, studies of the material structure under optimized spraying conditions showed that Al$_2$O$_3$ particles were evenly distributed over the volume of the coating for various ceramics content (Fig. 2, 3).

| Spectrum | For stat. | Al  | Si  | Cr  | Fe  | Ni  | W   | Sum  |
|----------|-----------|-----|-----|-----|-----|-----|-----|------|
| Spectr. 1| Yes       | 40.84 | 3.95 | 11.16 | 2.67 | 41.38 |      | 100.00 |
| Spectr. 2| Yes       | 73.26 | 8.81 | 8.74 | 2.60 | 6.59 |      | 100.00 |
| Spectr. 3| Yes       | 4.71  | 7.29 | 3.76 | 84.23 |      |      | 100.00 |
| Spectr. 4| Yes       |       | 4.43 | 1.54 | 20.97 |      |      | 73.07 |
| Max.     |           | 73.26 | 8.81 | 11.16 | 3.76 | 84.23 |      | 73.07 |
| Min.     |           | 40.84 | 3.95 | 4.43 | 1.54 | 6.59 |      | 73.07 |
Analysis of the microstructures showed that all coatings, regardless of the Al₂O₃ concentration, had a similar structure: base – Nickel eutectic with distributed fine particles of chromium compounds and rather big particles of aluminium oxide, often having a lamellar form (a consequence of particles melting in the plasma jet). Sometimes there were non-melted Al₂O₃ particles having a spherical shape as well as conglomerates of the oxide particles. Chemical interaction of aluminum oxide with components of self-fluxing alloy was not observed.

Analysis of phase composition showed that all coatings observed had following phases: a Nickel matrix, intermetallic compounds Cr₇Ni₃ and (Fe, Ni), nickel borides NiB, Ni₃B, Ni₅B; nickel silicide Ni₃Si, chromium borides CrB, Cr₂B; chromium carbides Cr₅C₂, Cr₇C₃, Cr₂₃C₆. All these phases are classical in plasma coatings made of self-fluxing alloys on nickel-chromium basis.

The next research step was devoted to tribological tests. Counter body was made of tool steel U₈ (Hₐ = 810–820 kg/mm²). The tests were performed at a load P = 1.5 MPa for dry friction mode during 15,360 cycles, which corresponds to the testing distance 921.6 m.

Weight loss of samples at the end of the tests was in the range from 3.80 mg to 14.75 mg. Moreover, it was found that the amount of weight loss depended on the surface roughness, especially for the running-in stage. Analysis of weight loss dependence on the number of cycles shows that after the running-in process (2048 cycles for coatings containing 15; 25 and 33 % of ceramics and 5120 – for one with 25 % of ceramics) this relation can be described as linearly dependence with different inclination (Fig. 4). One can see when ceramic content is 20 % the tangent of the line is significantly higher than for other samples. In our opinion this was due to greater surface roughness of the coating containing 20 % ceramic.

Since the tribological tests require long time then to estimate expected future behavior of coatings it is important to analyze the rate of specific weight loss (Fig. 5).

Analysis of the specific mass loss defined as \( \Delta m_i/(l_i - l_{i-1}) \) shows that when the content of ceramics is 15 % after running-in stage the rate significantly reduces for all remaining friction distance. For coatings with 20 % of oxide powder stabilization of weight loss rate is also observed.
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For coatings containing 25 % ceramics, there is a high mass loss rate during running-in stage and then it sharply decreases. High mass loss rate during running-in stage can be explained by low ceramics concentration in upper layer of coating (Fig. 3). Further reduction of mass loss rate is due to influence of oxide particles. Due to high volumetric content oxide particles are not covered with matrix material and can be mechanically removed out from layer during service. As a result the tendency shows again the rise of mass loss rate.

![Graph](image)

*Fig. 5. Dependence of specific weight loss on friction distance for different content of ceramic powder: — 25 %; — 15; — 20; — 33 %*

Coatings with 33 % of alumina are characterized with similar mass loss behavior but at smaller rate value during running-in stage. Rate values become practically equal after 2/3 of friction distance both for coating with 25 % of ceramics and one with 33 % of oxide powders with tendency for growth.

Changes in the coefficient of friction during the tests for different content of ceramics were determined aiming obtaining additional information on the tribological properties of composite coatings (Fig. 6). For comparison, the changes of the friction coefficient for coatings without ceramic additions were determined during tests at load of 1.0 MPa.

The nature of the changes of friction coefficients shows that all coatings containing ceramics are characterized with running-in period. Duration of this period varies from 15 % (coating with 20 % of ceramics) to 65 % (coating with 33 % of ceramics) of total test cycles. At the end of the test coatings containing above 20 % of ceramics are characterized with higher coefficient of friction than the non-modified coatings (without oxide ceramics). Coatings containing up to 20 % of alumina are characterized with lower coefficient of friction as compared to coatings of pure self-fluxing alloy and coatings containing 25 and 33 % of ceramics after 10300 cycles. The best combination of the tribological properties was obtained for coating with 15 % of oxide ceramics (Fig. 5, 6).

![Graph](image)

*Fig. 6. Dependence of friction coefficient on number of cycles for coatings with different content of ceramic powder: — clean SR4; — 15 %; — 20; — 25; — 33 %*

**CONCLUSIONS**

1. Investigations have established the positive influence of adding oxide ceramics Al₂O₃ into spraying mixture on the tribological properties of the coatings made of self-fluxing alloys due to formation of composite structure.

2. The study of the phase composition showed that all coatings observed were characterized with classical phase composition of the plasma coatings made of self-fluxing nickel-chromium alloys: Nickel matrix, intermetallic compounds Cr₂Ni₃ and (Fe, Ni), nickel borides NiB, Ni₃B, Ni₅B; nickel silicide Ni₃Si, chromium borides CrB, Cr₂B; chromium carbides Cr₇C₃, Cr₇C₅, Cr₃C₆.

3. Coatings containing up to 20 % of oxide ceramics were characterized with lower friction coefficients compared to coatings formed by pure self-fluxing alloy or when the ceramic content was 25 % or higher. The best combination of the tribological properties was obtained for coating with 15 % of oxide ceramics.
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