ATLANTIS PRESS
Atlantis Highlights in Material Sciences and Technology (AHMST), volume 1
International Symposium "Engineering and Earth Sciences: Applied and Fundamental Research" (ISEES 2019)

Intermetallides in the Structure of Gas-Thermal Coating With Additives of Complex Concentrate of Rare-Earth Elements

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***Abstract* – The article presents the results of researches of electrometallic coatings made of flux-cored wires with modifying additives of complex concentrate of rare-earth elements, obtained by extraction and leaching from ores of Tomtorskiy rare-metal deposit of the Republic of Sakha (Yakutia). Metallographic studies of the structure and properties of coatings revealed the presence of heterogeneous structures with increased values of microhardness. The conducted phase analysis showed the presence of intermetallic compounds Al-Ni in the structure of coatings caused by the influence of rare-earth modifying additives on the morphology of the structure. As a result of the conducted works it is shown that microalloying by rare-earth elements leads to essential improvement of structural and phase composition and increase of physical and mechanical properties at creation of new materials.**

Keywords – cored wire; complex concentrate; rare-earth elements; electric arc metallization; structure; intermetallic; diffractometer.

I. Introduction

Nowadays, rare-earth chemical elements are of special interest and strategic importance for modern global industrial production. Rare earth elements and their chemical compounds are widely used in innovative researches and practical technologies in metallurgy, atomic energetics, optics, medical, chemical and glass industries, manufacture of telecommunication equipment, electronics, laser equipment and other fields.

Over the past decades, the generally accepted group of so-called "rare" elements has changed, with more than 50 currently known chemical elements. For example, relatively recently they included titanium, vanadium, tungsten, molybdenum, tin and even inert gases. Currently, the number of "rare" elements includes 35 elements, including groups of rare metals (lithium, beryllium, zirconium, tantalum, niobium, etc.) and rare earth elements (lanthanides, yttrium and scandium).

Despite their name, rare-earth elements are not always rare in their total mass, sometimes they are widespread in the Earth's crust. However, their concentration in ores is generally so low that it limits the cost-effective recovery and enrichment of these substances for processing and use. Some rare earth elements are accumulated as a by-product of more common ore containing, for example, copper, gold, uranium, phosphates and iron. But even small amounts of these substances in industrial production allow to obtain technical products and products unique in their properties and quality.

The unique physical and chemical characteristics of rare earth elements make them attractive for use in a number of traditional and innovative production areas. For example, alloys of some rare-earth elements are the main component of strong permanent magnets that are in high demand in a wide range of high-tech products. These end uses range from automotive combustion catalysts to cellular phones, monitor displays, microelectronics and medical devices. Rare earth elements are also essential for the manufacture of defence products, jet engines and satellite systems.

Complex use of alluvial slurry concentrates with their inclusion in the technological process directly - without preliminary separation of pure components is a promising direction of obtaining a wide range of multi-component metal and ceramic powder materials. Presence in concentrates of numerous various mineral associations allows, using various ways of physical-chemical and mechanical processing of concentrates and bypassing a number of intermediate operations, at the minimum expenses to receive composite powders for creation on their basis (or with their participation) new constructional, electrode, cladding and other materials [1, 2].

The literature widely covers the influence of rare-earth metals (REM) modification on mechanical and corrosion properties of alloys and steels. [3, 4]. As research shows, complex alloying of steel with rare-earth elements has a positive effect on increasing the characteristics of strength, viscosity and plasticity. Rare-earth elements introduced into steel in a certain combination have a much greater impact on the properties of steel than other known alloying elements. However, studies also show that with some combination of alloying elements, some of them strengthen, while others, on the contrary, weaken the effect of the influence of rare earth element [4]. According to available literature, rare earth elements are used in foundries and iron and steel industry for modification, deoxidation, desulfurization and alloying processes. It is known that rare-earth metals show great chemical affinity to the metalloids present in ferrous metals. Interacting with these elements, REMs contribute to the removal or redistribution of harmful impurities and have an active positive impact on the structure and properties of metals [5].

At the same time, the search for new ways of complex use of mineral raw materials and the development of welding materials on the basis of concentrates and mining waste is carried out [6, 7].

The mineral resource base of rare-earth metals in Russia (primarily in Siberia and the Far East) is unique in terms of volume and quality of raw materials, economic, geological and mining parameters. As the analysis shows, Russian reserves of rare-earth metals account for 30% of the world level. Currently, the most promising undeveloped facility is the superlarge Tomtor field (West Yakutia).

At present, various powder metallurgy technologies are widely used to harden the surface of machine parts and mechanisms. The most promising of them are high-energy methods of application of wear-resistant coatings (plasma and gas-flame spraying, electric arc metallization by wires, etc.). As the analysis of works shows, for restoration of the worn out details of technics in industrial scales of repair manufacture on technical and economic indicators technology of electroarc metallization by powder wires is most effective.

High-energy technologies of wear-resistant coatings mainly use self-fluting nickel or cobalt-based alloys and their mixtures with modifiers of refractory metals, carbides, nitrides, oxides, etc., which provide the formation of hardening phases and improve the coating structure. Cored wire coatings are characterized by a high degree of heterogeneity of the structure - excess disperse and coagulated phase emissions, layered structure and porosity. This is due to the specificity of high-energy technological processes, which consists in fast (10-3 - 10-5s) high-temperature (up to melting point) heating of particles of powder material and their subsequent high-speed cooling and solidification.

In this paper, electrometallic coatings from the developed experimental flux-cored wires modified with the complex concentrate of Tomtor Rare Metal Deposit of the Republic of Sakha (Yakutia) were chosen as the objects of comparative research.

II. Methods and materials

The research was carried out on the basis of the methodology, which consists in the sequential passage and study of all technological stages: from the selection of components of the powder material to obtaining samples of finished coatings. The research uses the method of gas-thermal coatings used in the works of researchers of the V.P. Larionov Institute of Physical and Technical Problems of the North of the Siberian Branch of the Russian Academy of Sciences [8,9].

As for technical purposes it is expedient to exclude expensive separation of rare-earth metals, concentrates obtained from samples of Tomtor deposit by alkaline decomposition with phosphorus removal and extraction of rare-earth metals (Nb2O5 - from 5.03% to 13.56%; admixtures of TR2O5, including Y2O3 - from 15.45% to 31.03%) were used as modifying additives.

Aluminum oxide, ferrochrochrombor and silicon carbide powders were introduced into the powder charge to obtain hardening phases and to provide heterogeneous structure of plastic metal coating matrix. The main matrix is the industrial wear-resistant Ni-Cr-B-Si powder (PGCP-4).

Experimental flux-cored wires are shells made of low-carbon steel St08kp, filled with a powder charge with particle sizes of 40-100 microns; filling coefficients are 0.28-0.3. Table 1 shows the compositions of prepared powder charges for experimental wires, from which coatings for research are obtained.

TABLE I. COMPOSITIONS OF CORED WIRE CHARGE, %.

No. content	*Powder PGCP-4*	*Concentrate of the Tomtor deposit*	*SiC*	*FHB-1*	*Al_2O_3*
1	41.24	8.25	0	41.24	9.28
2	45.05	1.8	3.6	40.54	9.01
3	34.6	--	18.69	38.06	8.65

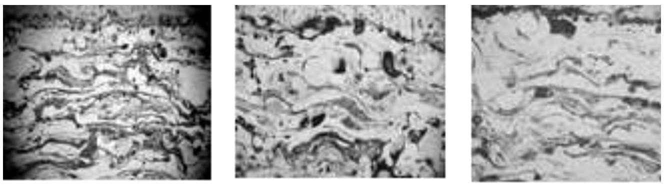
The coatings were obtained on the electric arc metallization unit EDU-500 at the following technological modes of spraying: arc current I=200-300 A, arc voltage U=40-70 V, air pressure P=7-7.5 atm, spraying distance L=130 mm. Technological modes of coating are selected based on the conditions of arc stability and reliability of the work on the life of the used metallizer. The coatings were applied to steel substrates pre-treated on a sandblasting chamber to clean the spraying surface and give the necessary roughness for sufficient adhesion of the coating to the substrate.

For the comparative study of microstructure, elemental composition and properties the cross metallographic slices of coatings were made. Metallographic studies of the structure were carried out on the Neophot-32 microscope (Germany); the elemental composition of coatings was studied on the HitachiTM 3030 scanning electron microscope equipped with EDS analyzer XFlash 6 and scanning (scanning) electron microscope JEOL JSM-7800F LV. Microhardness of coatings is measured on the microhardness meter "PMT-3M" at the load on the indenter of 100 g. Processing of experimental statistical data and construction of diagrams was carried out in the MSOffice Excel software environment. Phase analysis was performed on a D8 DISCOVER diffractometer with Bruker's GADDS (General Area Detector Diffraction System) system.

III. Results

It is known that rare-earth metals have different activity, but they are considered to be quite active elements. At high temperatures their activity increases, and at electric arc metallization the arc temperature reaches 4000-5000K. It should be expected that the complex concentrate of rare-earth elements and their high activity introduced into the composition of cored wire should contribute to the formation of intermetallic phases of various systems of the metals present.

Fig. 1 shows images of the structure of the obtained coating samples. As can be seen from the images, the formation of the coating structure occurs by superimposing molten particles consisting of the shell phases and the cored wire packing.



a) b) c)

Fig. 1. Electrometallic coating structure with modifying additives: a) composition No.1; b) composition No.2; c) composition No.3.

Coatings have a characteristic structure of gas-thermal coating, consisting of heterogeneous alternating broad layers, thin layers and individual particles of different shapes. It can be seen that in contrast to the spraying of disperse cored materials, electric arc metallization with cored wires leads to more complex forms of coating particles, which deviate strongly from the spherical and ellipsoidal ones. The thickness of layers of coatings reaches up to ~ 40 microns, and the sizes of individual particles up to ~ 25-30 microns. The boundaries between the coatings and the substrate material are wave-shaped, and a strip of intermediate layer melted by the sprayed material has been revealed in the transition zone to the base metal. Dark thin layers (films) between the light metal layers are formed by the successive passage of the burner metallizer. The presence of a large number of alloying elements (Table 1) determines the occurrence of a large number of phases, clearly differing on metallographic grinding on the degree of etching.

The elemental analysis of the obtained electrometallic coatings was carried out on scanning microscopes. Figure 2 shows the results of the study of the elemental composition of the electrometallic coating of wire composition No. 1. As the analysis of the obtained results shows, the distribution of basic and alloying elements is relatively uniform, there is a local arrangement of some elements in the structure of coatings.

It is shown that the main elements of cored wire (Fe - from steel shell, Ni, Cr, Si - from PGSSR-4 powder) are distributed evenly (Fig. 2,b-d). Low concentration or lack of basic elements is observed in areas where there is a high content of aluminium in the individual particles. Aluminum powder in the coating structure introduced into the wire charge is allocated in the form of undistributed separate areas of different shapes (Fig. 2, e). Distribution of rare-earth elements in the coating is uniform, strongly pronounced concentration in some areas is not observed (Fig. 2, e). The same distribution of elements is observed at the coating of cored wire composition No.2. In the case of wire coatings without complex concentrate with rare-earth elements, the distribution of the main elements is relatively uniform, and there is also a local arrangement of undistributed aluminum oxide phases.

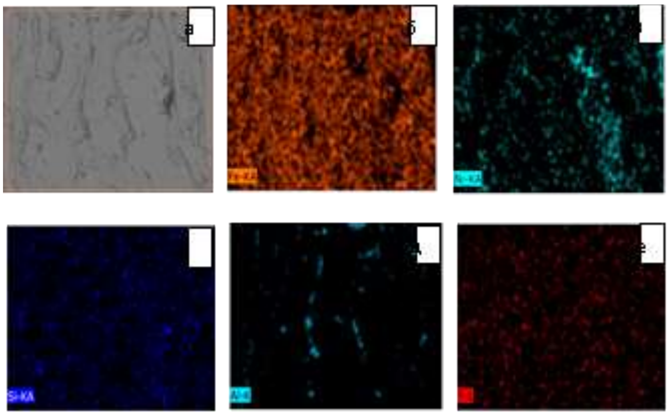


Fig. 2. Distribution of elements in the coating structure (composition #1): a) metallographic image, b) Fe, c) Ni, d) Si, e) Al, f) Y.

Fig. 2 shows that aluminum phases are present in the coating mainly in the form of elongated regions. In electric arc metallization, molten or not fully melted cored wire components form a flaky coating structure, which consists of individual, layer-by-layer stacked gossips, streaked and hardened phases on the substrate. Therefore, the transverse grinding is mainly characterized by elongated forms of the different phases of the applied components of the blend.

Table 2 shows the results of coating microhardness measurements. Taking into account the complex structure of the coatings obtained, we measured the microhardness of different phases, differing in the shades of etching degree. For each coating, statistical processing of the results of 30-50 measurements was carried out and the following statistical characteristics of microhardness of coatings were determined: average microhardness, maximum and minimum values.

TABLE II. COATING MICROHARDNESS DATA VALUES

	Average value, MPa	Minimal value, MPa	Maximal value, MPa
1	6500	4100	14000
2	5500	4100	16500
3	5800	4400	8100

As can be seen from the table, the average value of microhardness of all coatings lies on the interval from ~5500 MPa to ~6500 MPa. The highest average value of microhardness (~ 6500 MPa) of the wire coating of composition

No.1. The high value of average microhardness of coatings is due to the presence of phases and inclusions with high hardness, associated with the formation of intermetallic compounds. Comparatively smallest spread of maximum and minimum values of microhardness was found at the coating of composition No.3 (without complex concentrate additives).

In the coatings obtained from the wires of compositions No. 1 and No. 2, with the addition of complex concentrate, high values of microhardness ≈ 14000-16500 MPa are observed. High (more than 10000 MPa) values of microhardness were not recorded in the wire coating of composition №3.

Later on, the diffractometer was analyzed for the presence of intermetallic compounds in the structure of the obtained coatings.

From the conducted analyses it is clear that in the structure of wire coating with modifying REM concentrate (Fig.3, a) compounds (Fe,Ni), $Al_{0.7}Fe_3Si_{0.3}$, $C_{0.08}Fe_{1.92}$ are found. Also in the coating of the composition № 2 (Fig.3, b) is observed the presence of (Fe, Ni), $Al_{0.7}Fe_3Si_{0.3}$ and $Al_{0.42}Ni_{0.58}$.

As a result of the conducted researches on phase analysis of the received coatings, it is established that the complex concentrate with content of rare-earth elements introduced into the powder charge leads to formation of intermetallic compounds of nickel and aluminum. The presence of these compounds has affected the high values of microhardness, which ultimately affect the operational properties of the resulting coatings, to increase its wear resistance.

In general, the use of complex concentrates with rare-earth elements as modifiers in powder metallurgy, without preliminary allocation of pure components, opens up wide opportunities for obtaining materials for various purposes.

IV. CONCLUSION

1. Coatings with modifying additives were obtained from complex concentrate with rare-earth elements of the Tomtor deposit of the Republic of Sakha (Yakutia). In order to obtain hardening carbide and boride phases with high wear resistance and to provide heterogeneous structure of plastic metal coating matrix, aluminium oxide, ferrochrochrombor and silicon carbide powders were introduced into the powder charge.

2. It is established that the distribution of the main elements of the powder charge in the coating structure is relatively uniform. At the content of complex concentrate of rare-earth elements of 8% the average value of microhardness reaches 6500 MPa. There are phases with high values of microhardness, up to 14000-16500 MPa.

3. Investigation of phase compositions of the obtained coatings with additives of complex concentrate with rare-earth elements showed the formation of intermetallic phases of Al-Ni system, which have a positive effect on the increase of microhardness of the obtained coatings. There is a promising application of complex concentrate with rare-earth elements as modifying additives for coatings with increased hardness and wear resistance properties.

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