Materials Science

Red Mud Composite Electric Arc Coatings with Improved Mechanical Properties

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(Presented by Academy Member Tamaz Shilakadze)

The utilization of red mud (aluminum production waste) is an urgent environmental problem around the world. This work is devoted to the study of the possibility of using red mud powder as filler for composite electric arc coatings spraying. An analysis of modern methods of red med utilization, including thermal spraying technology, was carried out. Specimens of composite electric arc coatings on the basis of Al-Si aluminum alloy wire with red mud additions were deposited by using of a modernized gun EM-14M. Metallographic analysis of cross sections showed that they are characterized by a porosity of about 6% vol. The phases were identified by determining their microhardness on cross sections at a load of 20 g on the indenter. It is established that the microhardness of the metal matrix is 526 MPa; red mud – 658 MPa. The planimetric method determined the amount of red mud in the coatings, which amounted to 12.2% vol. To improve the mechanical properties of composite coatings, the optimal mode of their pre-recrystallization heat treatment (temperature 150°C, holding time 4 min) was established, while the microhardness of the metal matrix increased by 18.8% and the bond strength with steel substrate by 30%. The increase in bond strength is explained by a decrease in the level of internal stresses in the coating. © 2024 Bull. Georg. Natl. Acad. Sci.

red mud, composite coating, hardness, bond strength

With the increase in world consumption of aluminum, the amount of waste red mud generated during the production of alumina using the Bayer process is increasing. Depending on the composition of the initial bauxites and technology, from 0.9 to 1.5 tons of these wastes are formed per 1 ton of alumina [1, 2]. Until now, red mud has not been processed, but accumulated in special sludge storage facilities. Due to the high content of alkalis and high dispersion of the red mud, its storage poses a danger to humans and the environment [3]. Research into the recycling of red mud is being conducted around the world and hundreds of methods have now been developed for its disposal. In recent years, the number of publications on the topic of red mud recycling has increased significantly. However, despite numerous studies, so far only a small part of red mud has been recycled, which is due to the low profitability of most technologies, high initial costs for the development of new one and the complexity of selling manufactured products.

In scientific works [4-6], the process of separating iron from red mud by direct magnetic separation was studied, however, the resulting concentrates contained no more than 47% iron at a low degree of its extraction. Therefore, direct magnetic separation cannot be considered as a way to separate iron into a separate product, but only as a way to enrich red mud. The authors of [7] report that additions of Na₂CO₃ and CaF₂ also improve the efficiency of magnetic separation of carbothermally reduced iron from red mud. A sample of red mud was annealed without additives for 180 min at a temperature of 1150°C. The experiments showed that the degree of iron metallization was below 90%. When the mixture was annealed at 1150°C for 180 min with the addition of 3% Na₂CO₃ and 3% CaF₂ under the same conditions, the efficiency of magnetic separation increased, and the iron content in the magnetic concentrate increased to 92.79%.

Red mud has been accumulated in huge quantities, therefore, in order to achieve the greatest environmental effect, it is proposed to use the slag obtained after the reduction smelting of red mud for the production of various building materials. On a pilot-industrial scale, the technology of production from red mud of cast iron [8] and mineral wool was tested. The paper [9] describes the use of red mud reduction smelting slag as an additive in cement. In 2009, Shanxi Aluminum Plant (China) successfully developed refractory thermal insulation brick for industrial furnaces using red mud and ash as raw materials, and the addition ratio of sludge and ash was over 50%. The production line with a capacity of 100 thousand tons was launched in 2010 [10]. Quite promising is the use of red mud as a filler material in the manufacture of plastic products. Such products consist of polyvinyl chloride resin (or PVC plastic waste), red mud, used motor lubricant, and glass fiber [11].

The decision of the authors of the work [12] to use red slime as a sprayed material during plasma coating is innovative. Coatings with a thickness of up to 210 µm were deposited at different powers of the gun (6, 9, 12, 16 kW) on substrates made of carbon and stainless steel, aluminum, and copper. Analysis of the microstructure of the deposited coatings showed the presence of cracks along the separation boundary, which is associated with a large difference in the coefficient of thermal linear expansion of the substrate material and the coating. Further studies [13] consisted in the formation of composite plasma coatings with the addition of red mud. Mixtures of red mud with ash (30%, 50%), carbon (20%) and aluminum (5%) were deposited. The highest hardness and wear resistance values were observed for the composition with aluminum. However, plasma spraying is characterized by a rather high cost and complexity of equipment and a low energy utilization factor. At the same time, electric arc spraying is characterized by simplicity and manufacturability, high energy efficiency of spraying and material utilization, high productivity and low cost.

Therefore, the aim of this work is to study the possibility of forming composite electric arc coatings with the addition of red mud with a complex of improved mechanical properties.

Materials and Methods

Red mud powder from the Nikolaev alumina plant was used as filler for electric arc composite coatings. Drying of red mud powder was carried out in an oven SHSV 3.5.3.5.6/3.5 at a temperature of 250°C for 3 hours. Sieve classification was carried out on a vibrating sieve SO-130U2, using grid numbers 004 and 008. As a result of sieving, a powder with a fraction of 40...80 µm was isolated, which was used for deposition a composite electric arc coating. As a metal matrix, a wire with a diameter of 1.2 mm from an aluminum alloy Al-Si of the brand ER4043 was used. Electric arc spraying was carried out by KDM-2 unit with modernized spray gun which had powder feed unit to the high-temperature arc discharge zone [14]. As the atomizing and carrier gas, the compressed air was used. The surface preparation of the samples was carried out immediately before spraying using a 026-7 "Remdetal" device for grit blasting operation. The roughness of the treated surface was 50...90 μm. The spraying was carried out on steel plates made of high-quality carbon steel C45 (0.45% of C) with dimensions 50×20×5 mm. The spraying mode parameters were chosen based on previous studies of the formation of composite cermet coatings [14]: current 120A, arc voltage 30V, compressed air pressure 0.6 MPa, carrier gas pressure 0.02 MPa, spraying distance 100 mm. The phase's identification and the microhardness determination in composite electric arc coatings were carried out using a PMT-3 microhardness tester on cross sections with a load 20 g. The microstructure was analyzed using a Delta Optical HDCE-20C digital camera equipped with Scope Image 9.0 image processing software on an MMU-3 optical metallographic microscope. Determination of the porosity of the coatings and the amount of red mud was carried out by the planimetric method according to the obtained microstructures. The choice of this method is explained by the fact that in metallographic practice it is quite effective at a low content of the analyzed phase (on the order of several percent), and in such cases it is more reliable than the

point and linear methods. Pre-recrystallization heat treatment (PHT) of composite coatings was performed in SNOL-1.6.2.0.08/M1 laboratory electric furnace. The pin method was used to determine the bond strength of coatings, since it allows one to quickly conduct tests immediately after spraying. The specimens were made of high-quality carbon steel C45. The thickness of the deposited coatings did not exceed 0.5-0.6 mm. To obtain the results of the bond strength of the coatings to the substrate, spraying in the same mode was performed in one pass on 5 samples simultaneously. The bond strength of the coatings to the substrate was determined using a UMM-5 tensile testing machine.

Results and Discussion

The microstructure of electric arc sprayed composite coatings is shown in Fig. 1*a*.

The metallographic analysis of the given microstructures showed that the electric arc composite coatings of the wire system ER4043(Al-Si) – red mud are characterized by a fairly low porosity, which is about 6% vol., dark particles (presumably red mud particles) and light particles (alloy Al-Si) phases. Phases in the composite coating were identified by measuring their microhardness (Fig. 1*b*).

The average microhardness of the light phase (Al-Si alloy) was 526 MPa; dark 658 MPa, which corresponds to the microhardness of red mud [15]. The volume content of red mud in the obtained coat-



Fig.1. Cross section optical micrographs (*a*) and microhardness measurement results (*b*) of different phases of red mud composite electric arc coatings.

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ings was 12.2% vol. Compared to the composite metal-carbide coatings of the 65G-TiC system obtained in a similar deposition mode in [19], the filler content is lower, which is explained by the low density of red mud. Lighter sprayed particles are carried to the periphery of the high-temperature jet during spraying and are less often fixed in the formed coating.

It is known, that improved physical and mechanical properties of deformed metals and sprayed coatings can be achieved by prerecrystallization heat treatment [16]. The optimal mode of PHT was chosen according to the maximum values of microhardness (Fig. 2). The heating temperature was 150 °C.

It is clear from Fig. 2 that after PHT the hardness of red composite electric arc coating increases with extreme nature and maximum hardness (+18.8%) was obtained at holding time of 4 minutes.



Fig. 2. The dependence of hardness on holding time and temperature of the PHT of red mud composite electric arc coatings.

Figure 3 shows bond strength of convention and red mud composite electric arc coatings without and after PHT.

According to the presented data, composite coatings with red mud are characterized by a lower bond strength to the substrate (-18%) compared to coatings without filler. During electric arc spraying, most of the red mud particles do not melt and enter the base metal in a solid state, since they have a high melting point, and their time in the arc discharge zone is not enough to achieve it. Therefore, the decrease in this characteristic is explained by a decrease in the actual area of contact between the coating and the substrate. The PHT of coatings provides an increase in bond strength by 30% compared to coatings after spraying, probably due to a decrease in internal stresses.



Fig. 3. The bond strength of different electric arc coatings.

Conclusions

The main directions of processing and utilization of aluminum production waste - red mud are analyzed. The prospect of using this material for deposition of thermal sprayed coatings, in particular composite ones, is indicated. Composite electric arc coatings from the composition ER4043 (Al-Si) red mud were obtained due to the use of the modernized EM-14M gun. The microstructure of the sprayed coatings is analyzed. Phases were identified by determining their microhardness. It is shown that the porosity of the composite coating is about 6%, and the amount of red mud is 12.2% by volume. It is proposed to use pre-recrystallization heat treatment for further improvement of the mechanical properties of the coating. The pin method determined the bond strength of different sprayed coatings: wire ER4043 (12.1 MPa); composite ER4043 (Al-Si) + red mud (10 MPa), and after PHT - 13 MPa. The decrease in bond strength is explained by a decrease in the actual contact area of the coating with the substrate due to incomplete melting of the filler particles during spraying. Further research prospects consist in the establishment of new dependences and optimization of the application process of the specified electric arc coatings, as well as in determining their wear resistance.

მასალათმცოდნეობა

წითელი შლამის კომპოზიტური ელექტრორკალური საფარები გაუმჯობესებული მექანიკური თვისებებით

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(წარმოდგენილია აკადემიის წევრის თ. შილაკაძის მიერ)

წითელი შლამის (ალუმინის წარმოების ნარჩენი) უტილიზაცია მთელი მსოფლიოსთვის წარმოადგენს აქტუალურ ეკოლოგიურ პრობლემას. ნაშრომი ეძღვნება წითელი შლამის ფხვნილის გამოყენების შესაძლებლობას კომპოზიტური ელექტრორკალური საფარების დაფრქვევის შემავსებლად, გაანალიზებულია წითელი შლამების უტილიზაციის მეთოდები, მათ შორის, აირთერმული დაფრქვევის ტექნოლოგია. კომპოზიტური ელექტრორკალური საფარების ნიმუშები, რომლებიც მიღებულ იქნა Al-Si ალუმინის შენადნობის მავთულისაგან წითელი შლამის ფხვნილის დამატებით, დატანილ იქნა მოდერნიზებული დამფრქვევის ЭM-14M-ის გამოყენებით. საფართა მეტალო-გრაფიკულმა ანალიზმა აჩვენა, რომ მათ ახასიათებთ მოცულობის 6%-მდე_ფორიანობა. კომპოზიტურ საფართა ფაზების იდენტიფიკაცია ჩატარდა მათი მიკრო-სიმყარის განსაზღვრით განივ ნახვეწზე, ინდენტორზე 20 ჰც დატვირთვის პირობებში. დადგინდა, რომ ლითონის მატრიცის მიკრო-სიმყარე შეადგენს 526 მპა-ს, ხოლო წითელი შლამის - 658 მპა-ს. პლანიმეტრული მეთოდით განისაზღვრა მიღებულ საფარებში წითელი შლამის შემცველობა, რამაც შეადგინა მოცულობის 12,2%. კომპოზიტურ საფართა მექანიკური თვისებების გაუმჯობესების მიზნით დადგინდა მათი რეკრისტალიზაციისწინა თერმული დამუშავების ოპტიმალური რეჟიმი (ტემპერატურა – 150°C, დაყოვნების დრო – 4 წთ.); ამ დროს ლითონის მატრიცის მიკრო-სიმყარე იზრდება 18,8%-ით, ხოლო ფოლადის საფენზე შეჭიდულობის სიმტკიცე – 30%-ით. შეჭიდების სიმტკიცის ზრდა დაკავშირებულია დაფარვის მასალაში შიდა დამაბულობის დონის კლებასთან.

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