

DEVELOPING ANTICORROSIVE COATING COMPOSITION WITH HALLOYSITE NANOTUBES WITH EFFECT OF SELF-REGENERATION

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Corrosion of metals is one of the main processes of destruction leading to huge economic losses. Use natural nanotubes of halloysite as nanocontainer promotes much more long life cycle of an anticorrosion coating and, therefore, hardware. In article the way of activation the nanotubes of halloysite of the field White is offered Glinishche (The Karaganda region, Kazakhstan). Use of a mechanical way of crushing the halloysite clays at the specified modes and achievement of the set fractional structure allows to reduce the price considerably of receiving and activation of nanotubes, to avoid losses of the nanotubes which are carried away in a dekantat flow and also to increase products volumes which size is connected with only productivity of mills. The structure of an anticorrosion coating with use nanotubes of halloysite is also considered. Use of composition of the offered structure as an anticorrosion coating allows to increase efficiency of anticorrosive protection of a hardware at the general reduction in cost of a covering.

Key words: coating, corrosion, halloysite, steel, microstructure

INTRODUCTION

It is known that corrosion leads to significant economic losses due to the processes of metal destruction. According to some data, metal losses due to corrosion account for about 25% of the entire production volume. When selecting a method of anticorrosive protection, a number of basic factors should be taken into account: the conditions and the expected life of the product, the nature and quality of the metal surface.

The most common form of corrosion is electrochemical corrosion, i.e. destruction of the metal under the action of electrolytes (alkalis, acids, salts). Depending on the operating conditions, electrochemical corrosion can be atmospheric, underwater, soil, etc. It should be emphasized that practically all the equipment of the mining and metallurgical sector operates under atmospheric or soil corrosion, so the development of low-cost, long-lasting, easy to apply anticorrosive coatings is an extremely urgent task for the region.

One of the main ways to fight against corrosion is application of non-metallic coatings onto the surface of the metal products that provide a protective barrier and thereby prevent the development and spread of corrosion.

However, in case of damage to the protective barrier, the coating system itself in most cases is not capable of self-regenerating and inhibiting the development of the corrosion process. In some cases the integrity of the coating violation on the contrary provokes the corrosion

process, because it forms an increased potential difference.

In this paper there has been defined the task to develop an anticorrosive coating with an extended service life due to self-regeneration.

The world trend in the development of new generation materials is introducing nanocontainers into their composition, natural or artificially developed hollow microvolumes that allow releasing active substances at a slowed speed. The controlled releasing of the active substance opens up truly limitless possibilities of using nanocontainers, in particular, it allows the system self-regenerating. The use of nanocontainers in the development of anticorrosive coatings will allow controlling the release of the active anticorrosive substance and thus, the coating becomes capable of self-repairing.

The proposed technology of producing anticorrosive coatings consists of two stages: the 1st stage is obtaining nanocontainers; the 2nd stage is developing a suspension consisting of nanocontainers, an anticorrosive substance and a binder (solvent); the 3rd stage is filling nanocontainers with the resulting suspension.

At present there known a lot methods of manufacturing artificial nanocontainers (for example, the production of carbon nanotubes [1-3]) that provide relatively high productivity. In addition, in these cases it is possible to obtain a product with a relatively high number of layers and uniformity of the fraction along the diameter of the tubes. Due to this there are achieved strength characteristics of the structural materials.

A disadvantage of the abovementioned methods is a rather complicated technology of manufacturing nanotubes, and, consequently, high costs of the product. In

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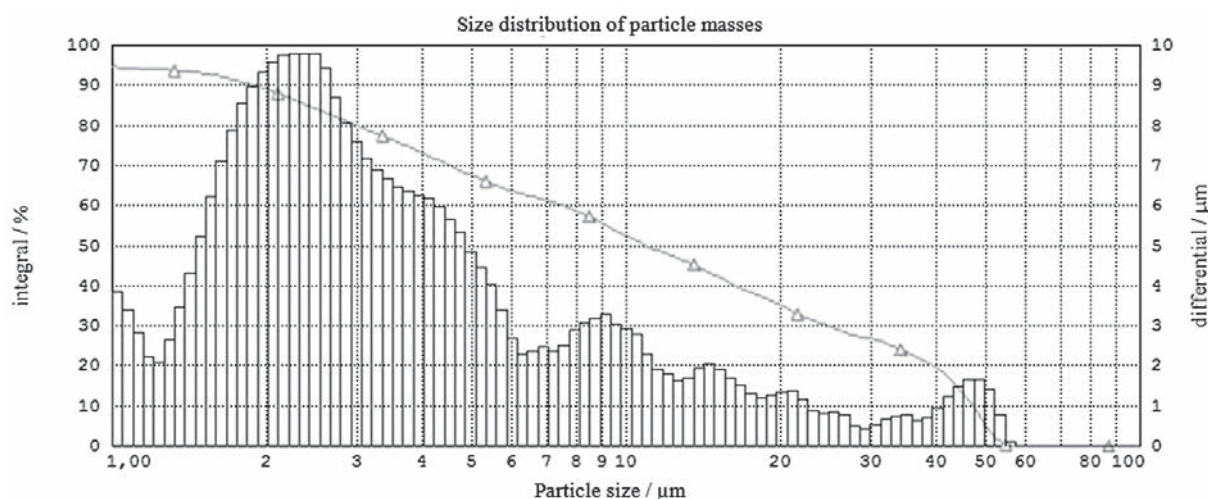


Figure 1 The result of the photosedimentometer analysis

addition, the resulting nanotubes are an artificial product, i.e. their volume depends on the performance of equipment and technology. As a rule, these technologies are realized in the laboratory conditions, therefore the production volumes are measured in grams.

Recently halloysite clay as a natural nanocontainer has been widely used [4-6]. Halloysite clay is a clayey rock that belongs to the group of finely dispersed water silicates that were formed in the process of weathering aluminum silicates and silicates. In their structure they belong to layered silicates with different “multi-storey” structure. Halloysite clays have a “two-story” structure. Unlike the kaolin clays in the same group, halloysite clay contains more hydrated water, that weakens the bond between adjacent layers due to the difference in atomic radii of aluminum and silicon. As a result, the crystal begins to spin forming a tubular structure (a natural nanotube).

Unlike a lot of other nanotubes, halloysite tubes are almost a natural product that is available in tons. Deposits of halloysite clay are also found in the territory of the Republic of Kazakhstan. Halloysite nanotubes are used as a nanocontainer for loading, storing, and controlled releasing of various substances such as drugs, anticorrosive substances, paints, and the like [7-9].

In work [10] there is proposed a method of obtaining nanotubes of halloysite clays by separating and subsequent purifying the liquid slurry of suspended clay particles entering the filter with simultaneous separation into transverse flows of the decantate and the filtrate, the filtrate flow having a higher concentration of nanotubes than the inlet flow.

However, this method has the following drawbacks:

- the need of developing a suspension based on dry halloysite clay and the associated processes of mixing and selecting a liquid inert base;
- the degree of nanotubes extraction directly depends on the size of the filter cells, while a significant uncontrolled part of nanotubes passes into the decantate.

Therefore, the task aimed at reducing the cost, increasing the volume of nanotubes produced and simplifying the method of obtaining and activating nanotubes through a single-phase process without participation of a suspension and the use of existing standard equipment (planetary ball mills) is relevant.

EXPERIMENTAL PART

In the experiments there have been used clays of the Beloe Glinishche deposit (the Karaganda region) [11]. Halloysite clay has been preliminarily dried at the temperature of 30 °C until moisture reached no more than 1 %, then grinded in a ball mill using corundum balls with the diameter 20 mm (70 %), with the diameter 35 mm (30 %) to the fraction - 20 μm with the content no less than 80 % and the rotational speed of the mill 24 - 32 revolutions per minute.

The use of the mechanical method of grinding halloysite clays under specified conditions and achieving a specified fractional composition has made it possible to reduce significantly the cost of obtaining and activating nanotubes, avoiding the loss of nanotubes carried away in the decantate stream, and increasing the volumes of products whose value in this case is only related to productivity of the mills.

The grinding has been carried out on the Emax mill of the RETSCH company, the fractional composition has been monitored on the photosedimentometer FSH-6K (Figure 1).

Then the obtained clay fraction has been mixed with benzotriazole as an anticorrosive substance and with an organic solvent as a binder. The ratio of the components has been as follows: 15:65:20. Mixing There has been performed mixing within 15 minutes under vacuum of 0,4 kPa. the action of vacuum intensifies the process of filling nanotubes.

The test results are shown in Table 1.

The resulting suspension has been applied to the pre-cleaned metal surface, alloyed steel 30HGS has

Table 1 The results of the laboratory tests

Sample	Mass loss within 24 hours / g	Mass loss within 48 hours / g	Mass loss within 72 hours / g
Reference	0,0498	0,0775	0,0867
Experimental – 30HGS steel	0,0496	0,0564	0,0576

been used as the samples. Then the samples with the mass 50 g with the coating have been placed in the aggressive medium: the 10 % solution of hydrochloric acid. Tests for corrosion resistance have been carried out by controlling the mass change and comparing with the reference. A similar sample with the coating consisting of pure benzotriazole has been used as the reference.

RESULTS AND DISCUSSION

As it can be seen from the data in Table 1, the corrosion process and the associated mass loss are less experienced on the test sample than on the reference. If at the first stage of the test the sample mass loss due to corrosion on the reference and test samples is practically the same (discrepancy is 1,5 %), then this difference increases in the process of testing. After 48 hours of testing the mass loss difference is already 27,2 %, and after 72 hours it is 66,4 %. This difference in the mass change due to the development of corrosion indicates more effective protection of the coating with halloysite nanotubes.

The kinetics of the mass loss changes (Figure 2) indicate that the greatest efficiency of protection is achieved after a certain period of operation. It is logical to assume that over time the coating begins to collapse partially, at this the coating of the reference is incapable of self-repair, which leads to the further intensive development of the corrosion process. The coating with halloysite nanotubes works more efficiently, because the presence of halloysite nanotubes in the composition of the coating makes it possible to carry out a delayed release of the anticorrosive substance, which leads to “overgrowing” local destructions.

Comparison of the the surface layer microstructure of the reference and the experimental sample (Figure 3) shows more relief changes at the coating-metal inter-

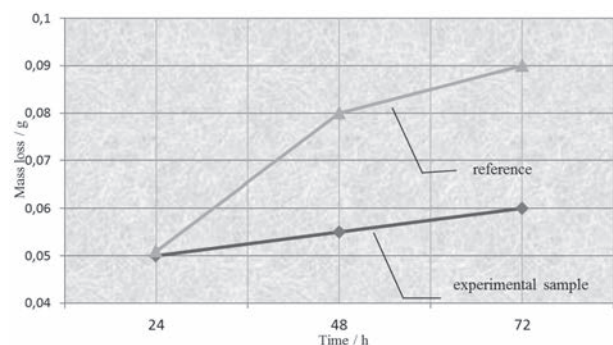
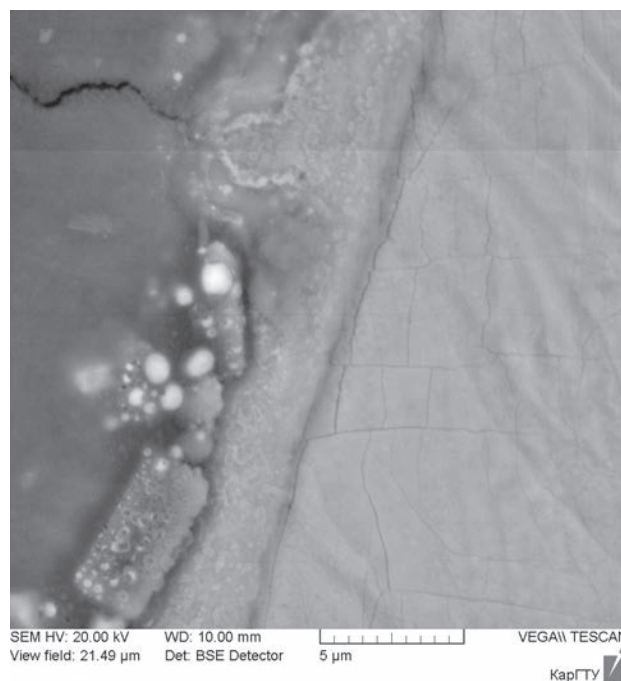
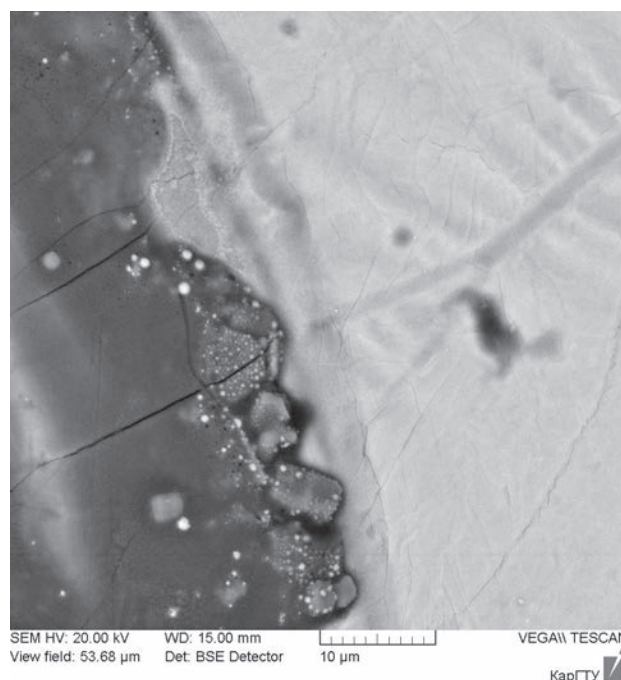


Figure 2 The sample mass changing due to corrosion over time



a)



b)

Figure 3 The microstructure of the layer at the coating-matrix interface: a – experimental sample; b – reference

face, which indicates the ability of the coating with halloysite nanotubes to self-repair and, therefore, greater efficiency during operation.

CONCLUSION

The studies carried out have shown the possibility of obtaining an anticorrosive coating using natural halloysite nanotubes that has a more effective protective effect due to the ability to self-regenerating. The composition of the proposed anticorrosive coating with halloysite nanotubes includes an anticorrosive agent, a sol-

vent, as well as halloysite clay of a certain fractional composition in the amount of 15...25 %; the anticorrosive agent: 60...70 %; the organic solvent: 25 ... 35 %; mixing the components should be carried out under 10 ... 50 kPa vacuum.

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