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INVESTIGATION OF CORROSION RESISTANCE OF METAL-CERAMIC COMPOSITE MATERIALS

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ABSTRACT
The article presents the results of a study of the corrosion resistance of metal-ceramic materials made on the basis of powders from chromium-nickel steels, according to the data developed by the method of measuring electrical resistance and by the amount of iron transferred to the solution with constant filtration of an aggressive medium.

Keywords: Corrosion resistance, metal-ceramic, powder, electrical resistance, steels, filtration.

INTRODUCTION

The structural features of metal-ceramic filters do not allow using methods that justify themselves on compact materials to assess the corrosion resistance of porous materials. The difficulty in determining the degree of corrosion of metal-ceramic porous permeable materials is that the filtered medium and the corrosion product remain in the pores of the porous body. An attempt to remove corrosion products by purging with air or other gases from the entire branched surface of the filter material can lead to distortion of the true corrosion destruction of the filter material.

There are data [1] on the study of corrosion resistance of metal-ceramic filters compressed from powders with spherical particle shapes by measuring the electrical resistance of the filter material. At the same time, it is assumed. that the electrical resistance of porous bodies depends on the state of interparticle contacts. In [2], the corrosion resistance of metal-ceramic materials is determined by measuring the mechanical properties of the filter material. In both methods, the sample was immersed in an aggressive medium and kept in it for a specified time. Then the sample was extracted from it and its electrical resistance and mechanical properties were measured without removing the aggressive medium and corrosion products contained in its pores from the sample. At the same time, the authors of the above-reviewed works themselves believed that such a setting of experiments to study the corrosion resistance of porous materials is not entirely correct, since the corrosion process, due to the difference in concentrations of aggressive media on the surface and in the volume of the sample, proceeds unevenly in the volume of the material. If we assume that the speed of corrosion processes of metal-ceramic filters is influenced by the shape of powder particles (source material), then it is impossible to get answers to these questions by immersing samples in an aggressive environment.

Therefore, in this work, the test was carried out in the mode of constant filtration of an aggressive medium through a filter, which, unlike the above method, is as close as possible to the real operating conditions of filters. And the electrical resistance of the sample was measured without stopping the test process, which ensures constant removal of corrosion products from the filter pores during measurement.

In order to study the effect of the shape of the powder particles (source material) on the corrosion process, samples were made from powders obtained by different methods with different particle shapes. The initial samples in the form of bushings with a size of 40x34x50 mm with a wall of 3 mm were prepared from powders (fraction 0.1-0.15 mm) of stainless steels of the mark: PRX18N10, PRX23N18 by pressing and sintering. The particle shape and methods for obtaining the initial powder materials are given in the table. The pressing pressure is 300 MPa. The samples were sintered at a temperature of 1200 -1250 °C for 2 hours in a hydrogen medium. The porosity of the sintered samples was 45-50%. Corrosion resistance was investigated in environments: 10% HNO_3, 10% H_2SO_4, tap water.

Properties of the initial powder materials

Method of obtaining	Mark	Particle shape	GOST
Sawn by air	PRX18N10 PRX23N18	Spherical Spherical	GOST 13084-67
Reduced by calcium hydride	PRX 18N10 PRX23N18	Spongy Spongy	GOST 14086-68
Mechanical mixing of components	PRX 18N10 PRX23N18	Fragmentation Fragmentation	GOST 14086-68

The experiment was carried out in stationary mode according to the method described in [1] and in the mode of filtration of an aggressive medium. To do this, the sample was weighed and placed in a glass case, where a filter was clamped to the base of the case in the end part. A metal washer was inserted between the end of the sample and the body. A wire was attached to this washer to measure the electrical resistance of the sample. The aggressive medium was supplied by the pump through the holes on the base of the housing, the drain passed through the holes of the housing. The working parts of the pump were made of acid-resistant plastic. Figure 1 shows the installation diagram.

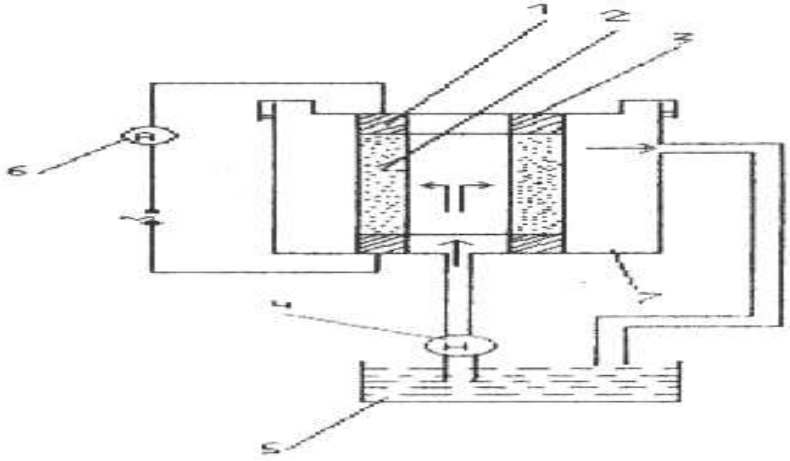

Fig. 1. The scheme of the experimental installation: 1 - washer, 2 - filter sample; 3 - housing cover; 4 - pump; 5 - drain tank; 6 – ammeter

The sample fixed in this way was tested for 2000 hours. After the selected time interval, the electrical resistance of the sample was measured without stopping the process. Such measurements were carried out through 5. 25. 70. 210. 520. 1000. 2000 hours.

According to the method proposed by V. V. Skorokhod [3], according to the results of measuring the electrical resistance P, the value of interparticle contacts ξ was estimated - the ratio of the contact size to the particle size. It was shown in [5] that for porous bodies with imperfect contacts, the effect of porosity on electrical resistance P can be described by the following formula:

$$p_K = \xi p(1-1{,}5\Theta), \quad (1)$$

P_K – electrical resistivity of a material with zero porosity; Θ – porosity of the test sample. At ξ = 1, this expression passes into V. I. Odelevsky's formula for porous bodies with perfect contacts [4]:

$$p_K = p(1-1{,}5\Theta), \quad (2)$$

Having determined the value of P_K by the formula (2) based on the results of the measurement of P, it is possible to estimate the relative value of interparticle contacts from the expression:

$$\xi = \frac{P_K'}{P_K}, \qquad (3)$$

Where, P_K – electrical resistivity of a sample with imperfect contacts reduced to zero porosity.

From the results presented in Figure 2, the following conclusions can be drawn. In the stationary test mode, the most corrosion-resistant filter samples were made from powders of the brand X23N18, the methods of obtaining powders did not affect the corrosion process. Of all the media studied for the samples, a 10% solution of sulfuric acid turned out to be the most aggressive. In nitric acid, the samples are passivated and their solubility is low. The solubility of the samples in tap water is also low.

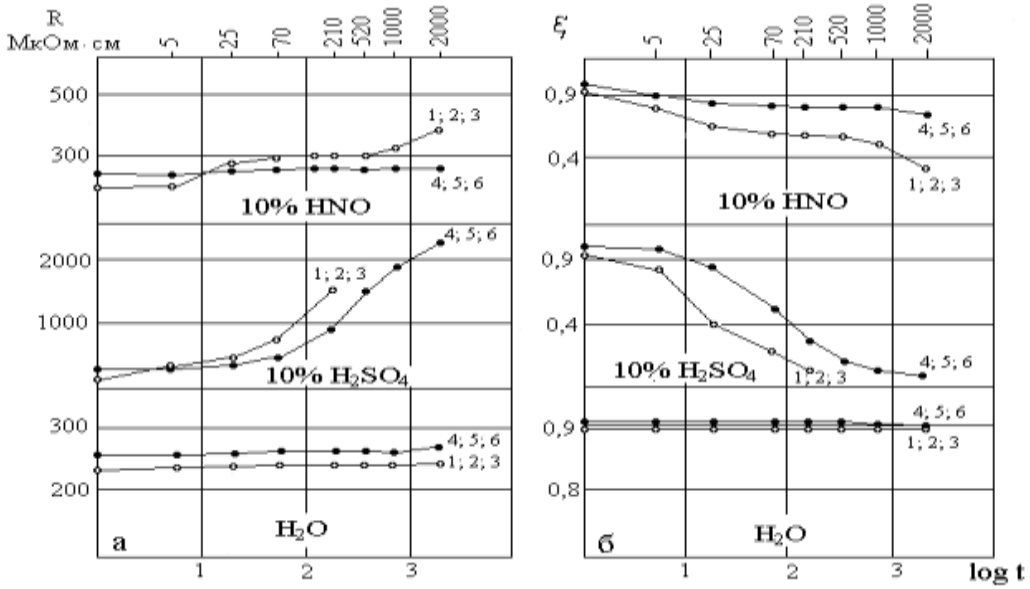

Fig.2. Kinetics of changes in electrical resistivity (a), and the magnitude of interparticle contacts (b), the mark of the initial powders and the firm of the particles: 1- PRX18N10 (spherical); 2- PVX18N10 (spongy); 3- PX18N10 (fragmentary); 4- PRX23N18 (spherical); 5- PVX23N18 (spongy); 6 - PX23N18 (fragmentary)

Figure 3 shows the kinetics of changes in the electrical resistivity (a), the magnitude of the interparticle contacts (6) and the amount of iron transferred to the solution (b) of the samples during the filtration test mode. The results of the test show that with the filtration test method, the corrosion process of samples occurs more intensively. The solubility curve of samples made with non-spherical (spongy, fragmentary) particle forms in all media, in contrast to the stationary test method, has significant differences.

At the initial moment of time, the solubility curve of samples, especially those made with a fragmentary particle shape (Figure 3, c), increases sharply. After 5 hours of testing, the solubility curve stabilizes. Such a rise in the solubility curve is not observed in samples made with spherical particle shapes. In this case, the electrical resistance curve of all images rises uniformly (figure 3, a) and, accordingly, the values of the interparticle contacts are uniformly narrowed (figure 3, b). The reason for this may be the micro-dimensions located on the surface of the pore channels of the sample made of powders with non-spherical particle

shapes. These micro-roughnesses have a significant resistance to the flow of an aggressive medium, therefore, the micro-roughnesses are smoothed out within 5 hours of testing, intensively dissolving in solution.

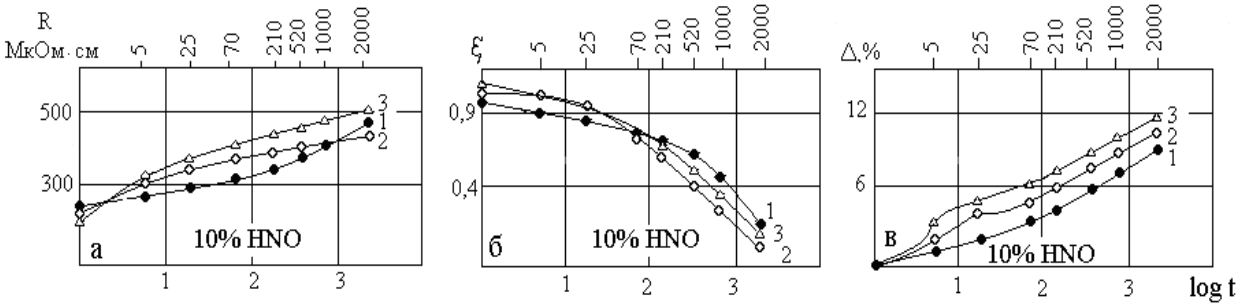

Fig.3. Kinetics of changes in electrical resistivity (a), the magnitude of interparticle contacts (b) and the amount of iron transferred to the solution (c), the initial powder PRX18N10: 1 - spherical; 2- spongy; 3- fragmentation

It should be noted that the results of the evaluation of the size of the contact points and the amount of dissolved iron show compliance with the kinetics of their change. Thus, the measurement of electrical resistance in the mode of filtration of an aggressive medium through a filter is an effective method for studying the corrosion resistance of porous (more than 30% porosity) cermet materials. In this regard, it is advisable to point out the possibility of evaluating the service life of metal-ceramic filters in aggressive environments.

To compare the two methods, the service life of a metal-ceramic filter in a 10% solution of sulfuric acid was calculated according to the method proposed in the literature [5]. So, having determined the value of contacts by formulas (2) and (3) and knowing the corrosion rate of compact materials from the literature data, it is possible, given the permissible final value of contacts, to estimate the maximum duration of the stay of a porous material in an aggressive environment.

According to the data of [6], the corrosion rate of X23N18 and X18N10 grade steels in 10% sulfuric acid is 0.1-1 and 2-5 mm/year, respectively. If we accept an acceptable minimum contact size equal to half the value of the initial one (for samples X23N18 ξ_{init} = 0.8, for X18N10 ξ_{init} = 0.76, or the initial contact radii are approximately 0.05 and 0.047 mm, respectively), then the service life according to the stationary method for a sample of steel X23N18 will be 200-2000 hours, and for a sample of steel X18N10 - 40-100 hours, regardless of the shape of the particles of the initial powder. According to our experimental data, in stationary mode (Figure 2, b), a halving of ξ occurred for a sample of steel X23N18 - in 100 hours, and for a sample of steel X18N10 - in 20 hours.

According to the filtration method, taking into account the shape of the initial powder particles and the filtration rate of the aggressive medium, the service life is 186-1840 hours for a sample of steel X23N18 made with spherical powder particles, and 36-93 hours for a sample of steel X18N10. For samples made of powders with non-spherical particle shapes, respectively - 174-1740 and - 34-87 hours. Thus, with the filtration method of testing samples, a decrease in ξ occurred depending on the shape of the particles of the initial powder (Figure 3, b).

Based on the test results, the following conclusions can be drawn: by measuring the electrical resistance and the amount of dissolved iron in stationary and filtration modes, the behavior of porous stainless steels in various aggressive environments has been studied; the stationary test method proved to be acceptable for preliminary determination of the service life of porous materials made with spherical particle shapes; the filtration test method fully reveals the behavior of ceramic-metal porous permeable materials in aggressive

environments, regardless of the particle shape of the source material: among the tested samples, the most resistant in aggressive environments were samples made of powders of steel X23N18 with spherical particle shapes. A method for estimating the service life of porous permeable metal-ceramic materials made with non-spherical particle shapes is proposed.

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