

СТРУКТУРОУТВОРЕННЯ. ОПІР РУЙНУВАННЮ ТА ФІЗИКО-МЕХАНІЧНІ ВЛАСТИВОСТІ

STRUCTURE FORMATION. RESISTANCE TO DESTRUCTION AND PHYSICAL-MECHANICAL PROPERTIES

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COMPARATIVE STUDIES OF THE CORROSION RESISTANCE OF STAINLESS STEEL SHEETS FOR THE COATING LAYER OF BIMETALS

Purpose. Evaluation of the influence of the chemical composition and structure on the corrosion resistance of steels of different structural classes used as a cladding layer of bimetallic reactors and other devices of titanium-magnesium production.

Research methods. In order to choose a rational cladding layer of the developed bimetal, a comparative analysis of the corrosion resistance of steels 12X18H9, 10X14AГ15 and 08X18T1 and steels 04X18ч, 03X18ТБч and 03X17H3Г9МБДЮч, taken as standards for comparison, was carried out [1]. Titanium tetrachloride and a one-molar solution of sulfuric acid were used as chemically active media.

Results. The results of the investigation of the corrosion resistance of steels of different structural classes by gravimetric and potentiometric methods in chemically active environments showed that the most suitable option for the cladding layer is steel 03X17H3Г9МБДЮч, which has similar coefficients of linear thermal expansion and high corrosion resistance to the base of bimetal - 14X17H13МБч [2].

Scientific novelty. It was established that the use of bimetal with a cladding layer made of 03X17H3Г9МБДЮч, 03X18H or 04X18ч steel reduces the nickel impurity content by 10 times or more in the titanium sponge during the reduction process.

Practical value. The use of a bimetal with a base steel of 14X17H13MB Ψ in combination with a cladding layer of steel 03X17H3Г9МБДЮ Ψ makes it possible to obtain a titanium sponge that is particularly clean of nickel impurities and will significantly expand the scope of use in the aviation and rocket industry.

Key words: corrosion-resistant steel, base steel, titanium sponge, reactor, bimetal, cladding layer, impurities.

Introduction

The modern industrial magnetothermic method of obtaining titanium in batch reactors allows the production of titanium in the form of a sponge. Smelted titanium ingots must meet strict quality standards. However, this method has a significant disadvantage – contamination of the titanium sponge with nickel entering the sponge titanium from the reactor material during the recovery process.

In this regard, the application of bimetals, which can be used in the manufacture of reactor bodies for recovery and separation in magnesiumthermic titanium production, is becoming increasingly relevant. Existing steels used for the manufacture of reactors are subject to deformation, corrosion, contamination of titanium sponge and are limited in service life.

Analysis of research and publications

The modern development of the metallurgical industry in Ukraine and abroad guides researchers to create new corrosion-resistant steels. The reactor body in titanium-magnesium production is usually made of steels capable of withstanding high temperatures and aggressive conditions of the technological process. However, during long-term operation, the reactor undergoes warping and deformation as a result of cyclic heating and cooling, corrosion damage when interacting with chlorides and reaction products, contamination of the titanium sponge. These shortcomings stimulate the search of new materials that have high heat resistance, mechanical strength, and corrosion resistance at the same time [3–8].

The use of bimetals in reactor designs for titanium-magnesium production can be a promising direction for increasing the efficiency, reliability, and economy of the technological process [9-10]. Bimetallic materials can eliminate most of the shortcomings of traditional reactor

housings, provide a longer service life of the equipment, reduce costs and improve the quality of the titanium sponge. Further research in the field of selection of optimal combined metals, their joining technologies and operational tests will accelerate the introduction of bimetals into the industrial practice.

Purpose of work

The purpose of this work is to study the corrosion resistance of sheet stainless steels for the cladding layer of bimetals in aggressive environments.

To achieve this goal, the following tasks were formulated and solved:

- a comparative analysis of the corrosion resistance of steels of different structural classes in a one-mole (1M) solution of sulfuric acid H₂SO₄ was carried out;
- an evaluation of the behavior of selected steels in the melt of titanium tetrachloride TiCl₄ was carried out.

Research material and methodology

Gravimetric and potentiometric methods were used to study the corrosion resistance of steels. The chemical composition of the studied steels is given in Table 1.

The essence of the gravimetric method is to determine the change in the mass of a sample of a certain size immersed in an aggressive environment for a certain time.

The essence of the potentiometric method is to obtain passivation characteristics by obtaining polarization diagrams using the fast scanning technique. To do this, the test sample is immersed in the test solution and cathodically polarized with a high scanning speed to a current density of 10⁻² A/cm² then anodically polarized at a rate of 50 V/h. Research was carried out using a PP-5848 potentiostat with a preset value current speed. The scheme of the setup for conducting polarization measurements is shown in Figure 1.

Table 1 – Chemical composition of the studied steels

Steel grade	C	Cr	Si	Mn	Ni	W	Mo	V	S	P	Al	Ti	Fe
12X18H9	0,12	18,2	0,65	0,4	9,4	-	-	-	0,02	0,02	-	-	bees
10X15AГ14	0,1	15,2	0,21	14,35	-	-	-	-	0,03	0,03	-	-	-
08X18T1	0,08	18,0	0,46	0,2	-	-	-	-	0,017	0,03	-	0,8	-
03X17H3Г9 МБДЮ Ψ	0,029	16,6	-	9,09	2,3	0,018	0,262	0,256	0,0097	0,0219	0,14	0,042	-
04X18 Ψ	0,04	18,4	0,26	0,31	-	-	-	-	0,01	0,023	0,001 рзм	-	-
03X18ТБ Ψ	0,03	18,1	0,5	0,2	-	-	-	-	0,01	0,02	0,001 рзм	0,15	Nb 0,15

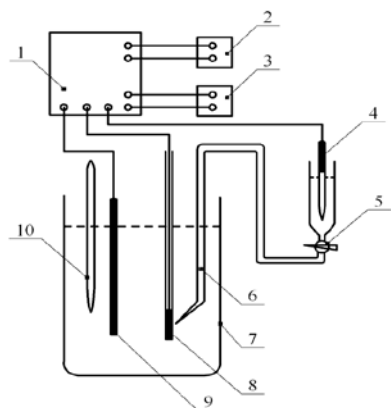


Figure 1. Scheme of the installation for conducting polarization measurements. 1 – potentiostat, 2 – electronic millivoltmeter, 3 – electronic ammeter, 4 – reference electrode, 5 – ground tap, 6 – Luggin capillary, 7 – beaker, 8 – sample, 9 – auxiliary electrode, 10 – thermometer

Research results

On the basis of the conducted research, a bimetal consisting of a cladding layer of steel 03X17H3Г9МБДЮч and a base steel 14X17H13МБч was developed, which allows to reduce nickel impurities in spongy titanium by 12 times and increase the service life of reactors by 30%.

Experimental electrode potentials are determined in relation to the hydrogen potential, which is assumed to be zero. The tests were carried out in a chemically active one-molar (1M) solution of H₂SO₄, and the dependence of the potential on the current was constructed for the analysis (Fig. 2–7).

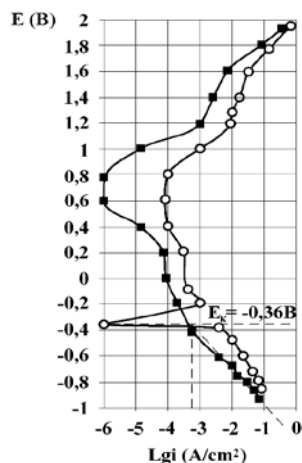


Figure 2. Polarization diagram of steel 03X17H3Г9МБДЮч in 1M sulfuric acid solution

It follows from the polarization diagram that the studied steel 03X17H3Г9МБДЮч can be transferred to a passive state with a small shift of the potential in the positive direction, which indicates its ability to passivation. The negative potential of steel 03X17H3Г9МБДЮч

indicates that at first the steel corrodes, but soon the corrosion slows down and this is explained by passivation. The passivation current (I_n) of steel 03X17H3Г9МБДЮч indicates the steel's ability to self-passivation.

The analysis of polarization diagrams shows that in a 1M solution of H₂SO₄, all studied steels, with the exception of 12X18H9 and 03X17H3Г9МБДЮч, are in a stable active state (Fig. 2–7) and corrode with the release of hydrogen.

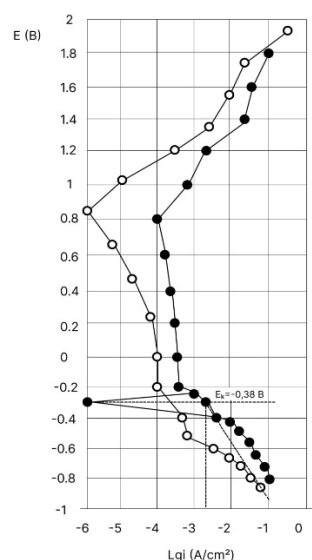


Figure 3. Polarization diagram of 12X18H9 steel in 1M sulfuric acid solution

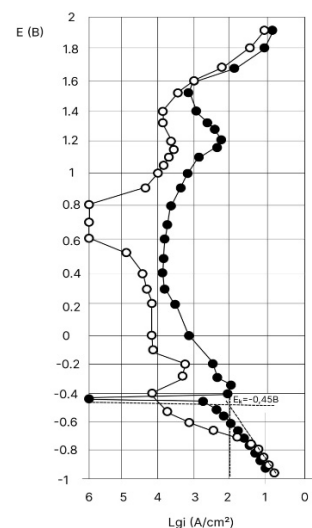


Figure 4. Polarization diagram of 10X14AГ15 steel in 1M sulfuric acid solution

The passivation current (I_n) is an order of magnitude higher than $10^{-3} \text{ A} \cdot \text{cm}^2$ – the maximum cathode current that can be provided by dissolved oxygen in the air. Therefore, all studied steels, with the exception of 12X18H9 and 03X17H3Г9МБДЮч, are not capable to self-passivation

in strong acidic solutions even with intensive aeration.

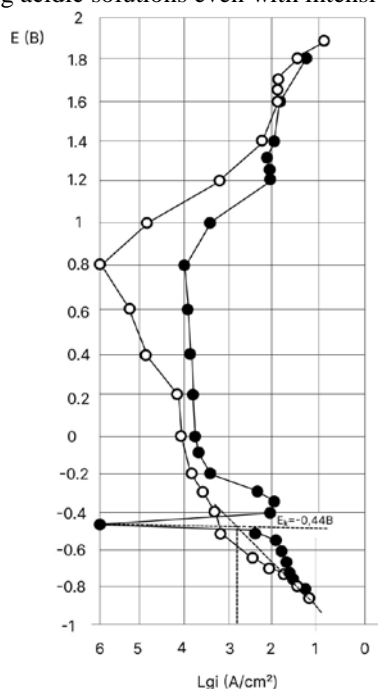


Figure 5. Polarization diagram of 08X18T1 steel in 1M sulfuric acid solution

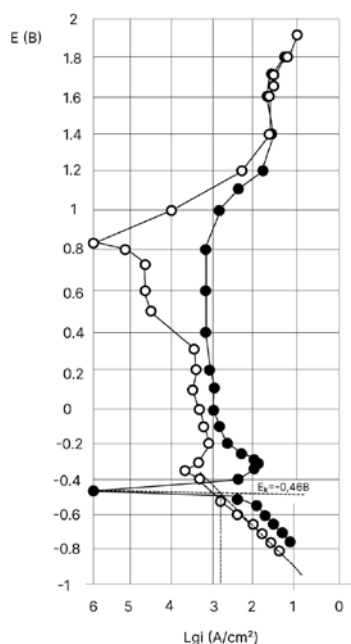


Figure 6. Polarization diagram of steel 04X18h in 1M sulfuric acid solution

This conclusion was confirmed during gravimetric tests: samples of 12X18H9 steel, actively corroded in a 1M solution of H_2SO_4 , easily went into a passive state after being exposed to air for a few seconds and then immersed in the solution again. A similar effect was observed in steel 03X17H3Г9МБДЮч.

Samples of other steels began actively corrode again

after abovementioned operation. The results of determining the corrosion of steel in a 1M solution of H_2SO_4 by the gravimetric method correlate well with the results obtained by the extrapolation method of the Tefel part of the polarization curves (Table 2).

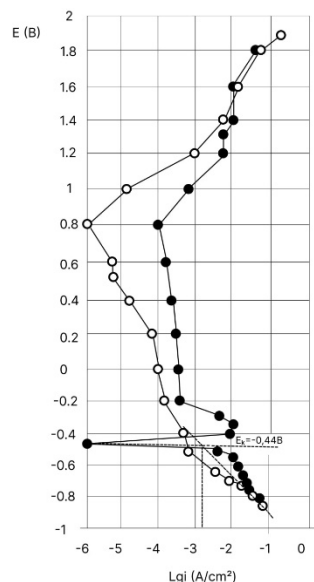


Figure 7. Polarization diagram of 03X18ТБч steel in 1M sulfuric acid solution

Table 2 – Results of measurement of corrosion rate in steels in 1M H_2SO_4 solution

Steel brand	Δm , g/sm ² ·h	П Mm/year	Lg I corr, gravim- etry	Lg I corr Po- tent. meas- ure
03X17H3Г9МБДЮч	$4,3 \cdot 10^{-4}$	4,6	-3,55	-3,6
12X18H9	$3,51 \cdot 10^{-4}$	4,1	-3,45	-3,4
10X14АГ15	$4,3 \cdot 10^{-2}$	495,5	-1,36	-1,9
08X18T1	$1,9 \cdot 10^{-3}$	22,6	-2,7	-2,8
04X18ч	$2,1 \cdot 10^{-3}$	24,1	-2,69	-2,7
03X18ТБч	$1,3 \cdot 10^{-3}$	15,4	-2,87	-2,9

The corrosion rate of steel 10X14АГ15 in these conditions exceeds the corrosion rate of 08X18T1, 06X18ч and 03X18ТБч by an order of magnitude. At the same time, their corrosion resistance is lower than that of 12X18H9 steel in the active, and even more so in the passive state. Some discrepancy between the measured and calculated values of Lg I corr. for steel 10X14АГ15 is explained, apparently, by the presence of a significant self-dissolution current, which is not registered by the device, and occurs at high dissolution rates.

It also follows from the polarization diagrams that all investigated steels can be transferred to a passive state with a relatively small displacement of the system potential in the positive direction. The magnitude of the corrosion current in the passive state obtained from the polarization

data is 0.0001–0.001 A·cm² and is obviously overestimated, since the corrosion rate of 12X18H9 steel in the passive state actually measured by the gravimetric method is almost two orders of magnitude lower than the calculated value (Table 2).

This effect, apparently, is due to the fact that at such a high scanning speed, a stable passive state is not completely achieved due to the short exposure time at the potentials corresponding to the passive region. However, a relative comparison of the curves shows that the corrosion current in the passive state for steel 04X18ч is noticeably

Table 3 – Comparative indicators of the corrosion resistance of studied steels of molten titanium tetrachloride TiCl₄ for the cladding layer of the bimetal

Steel grade	Duration of test, hour	Media	Corrosion speed
			g/(cm ² ·h)
03X17H3Г9МБДЮч	1440	TiCl ₄	0,0000762
04X18ч	1440	TiCl ₄	0,000029
12X18H9	1440	TiCl ₄	0,0000744

As a result of the tests carried out in the titanium tetrachloride melt, it was established that the corrosion resistance of the steels chosen as the cladding layer 03X17H3Г9МБДЮч and 04X18ч are not inferior to steel 12X18H9. In addition, due to the low content of nickel in steel 03X17H3Г9МБДЮч up to 3.8% and the complete absence of nickel in steel 04X18ч, nickel impurities in the titanium sponge decreased 12 times in the process of magnesium thermal reduction of titanium.

Conclusions

Studies of steel 03X17H3Г9МБДЮч fully confirm the expediency of using it as a material for the cladding layer of a bimetal for reactors of magnesithermic production of titanium, which in terms of corrosion resistance exceeds steel 12X18H9, and the coefficients linear thermal expansion are very close in a wide range of temperatures, in contrast to martensitic-ferritic steel 04X18ч, nevertheless, this steel can also be used as a cladding layer of bimetals for other devices of titanium-magnesium production, the working temperature of which

higher than for other steels. This is a serious sign of the presence of active, poorly passivating areas on its surface and a possible tendency this steel to pitting or intergranular corrosion. Such chemically active non-passivating areas in steel 04X18ч may be the release of excess rare earth metals, not related to oxygen and sulfur.

A comparative analysis of the corrosion resistance of steels 12X18H9, 10X14AГ15 and 08X18T1, taken as standards of comparison with steel 03X17H3Г9МБДЮч and 04X18ч, 03X18ТБч, was carried out.

Table 3 shows comparative indicators of corrosion resistance of studied steels as a cladding layer of bimetal. does not exceed 200 °C.

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ПОРІВНЯЛЬНІ ДОСЛІДЖЕННЯ КОРОЗІЙНОЇ СТІЙКОСТІ ЛИСТОВИХ НЕРЖАВЮЧИХ СТАЛЕЙ ДЛЯ ПЛАКУЮЧОГО ШАРУ БІМЕТАЛІВ

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Мета роботи. Оцінка впливу хімічного складу та структури на корозійну стійкість сталей різних структурних класів, що використовуються як плакувальний шар біметалів реакторів та інших пристроїв титаноманієвого виробництва.

Методи дослідження. З метою вибору раціонального плакуючого шару біметалу, що розробляється, проведено порівняльний аналіз корозійної стійкості сталей 12X18H9, 10X14AГ15 і 08X18Т1 і взятих як еталони порівняння сталей 04X18г, 03X18ТБч також 03X17H3Г9МБДЮч. Як хімічно активне середовище використовували тетрахлорид титану і одномольний розчин сірчаної кислоти.

Отримані результати. Результати дослідження корозійної стійкості сталей різних структурних класів гравіметричним і потенціометричним методами в хімічно активних середовищах показали, що найбільш прийнятним варіантом для шару, що плакує, є сталь 03X17H3Г9МБДЮч, що має близькі коефіцієнти лінійного термічного розширення та високою корозійну стійкість з основою біметалу - 14X17H13МБч [2].

Наукова новизна. Встановлено, що використання біметалу з плакувальним шаром з 03X17H3Г9МБДЮч, 03X18H або сталі 04X18гч, знижує вміст домішки нікелю в 10 разів і більше в титановій губці при відновлювальному процесі.

Практична цінність. Застосування біметалу з основою сталь 14X17H13МБч у поєднанні з плакувальним шаром із сталі 03X17H3Г9МБДЮч дає можливість отримувати особливо чисту за домішками нікелю титанову губку та суттєво розширить сферу використання в авіаційній та ракетній промисловості.

Ключові слова: корозійностійка сталь, сталь основи, титанова губка, реактор, біметал, плакуючий шар, домішки.

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