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THERMAL STUDIES OF THE PROPERTIES OF SAMPLES Zr AND ALLOY Zr1% Nb AFTER CORROSION IN WATER VAPORS AT DIFFERENT TEMPERATURES

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Abstract: The process of corrosion of samples of zirconium and zirconium alloy in water vapor has been investigated in the temperature range of T = 300 ÷ 800^{0}C. The corrosion kinetics was studied, the activation energy of the processes and the thickness of oxide films formed on their surfaces were determined. It has been established the reduction regions of corrosion resistance in the studied temperature ranges.

Key words: thermal processes, temperature, corrosion

1. Introduction

In early works [1÷5], the results of thermal studies of the properties of zirconium and zirconium alloy samples were carried out in the temperature range of T=600÷1200^{o}C. Zirconium and its alloys have a number of features in corrosion processes that are not observed in other metals and alloys. Despite the numerous publications on the issue of the investigation of corrosion resistance of zirconium and zirconium alloys, the study of this unique material continues. The latter is due, in particular, to the fact that they are looking for ways to improve the material in order to increase the service life of fuel in nuclear power engineering. Zirconium and its alloys are the main structural materials used in the nuclear industry for the production of fuel (fuel rods), elements of nuclear reactors. Zirconium - is a fairly active metal that reacts with oxygen, nitrogen, water vapor, carbon dioxide, hydrogen and hydrocarbons [6-8]. However, while using zirconium and zirconium alloy as structural materials for reactors, it promotes the formation of durable and chemically resistant oxide films on the metal surface protecting them from corrosion promotes. In [9-10], the data have been obtained on their corrosion rate and thickness, which are formed on the surface of oxide films under similar conditions, on changes in the structure of zirconium and zirconium alloy, after heating up to certain temperature.

The purpose of this work is to study the kinetics of corrosion of zirconium and zirconium alloy, as well as a change in the properties of the studied materials after heating and in the studied temperature ranges of T=300÷800^{o}C.

2. Experimental methods

The reactor metal zirconium and the alloy of Zr1% Nb have been taken as an object of the study. The studies have been conducted under static conditions in special molybdenum ampoules with a volume of 15 cm^3. The plates of reactor zirconium with a purity of 99.99%, the thickness of d=0.12÷0.20 mm, the width of b=2.0÷4.0 mm and length of l=20÷25 mm have been

investigated. The contacting surface of the samples was determined on the basis of their geometric dimensions, which was 34.6 cm^2/g.

In order to exclude the contribution of organic pollutants on the surface of zirconium and Zr1%Nb alloy, the samples were preliminarily cleaned with organic solvents — ethanol, acetone, and then washed with distilled water. This operation was repeated 3 times, after which, the samples were dried at a temperature of T=100÷150ºC in an inert gas environment. Drying was continued with simultaneous pumping of the medium, after which, the samples in molybdenum ampoules were subjected to thermal vacuum treatment, first at T=100°C, then at T=150°C, P≈ 10^{-3} Pa. The filling of ampoules with water and sealing was carried out on a vacuum-adsorption unit. The density of water vapor in ampoules was $\rho_{н2о}$=5mg/cm^3. The temperature during the experiments was maintained with an accuracy of ± 1ºC.

As a result of thermal processes, the transformation of water in contact with metallic materials - they are corroded. Corrosion of zirconium and alloy of Zr1%Nb studied by the gravimetric method. For this, the metal samples after cleaning were weighed before the process. After the process, the samples were dried by vacuuming at T ~ 100ºC, then cooled in a vacuum, weighed with an accuracy of ±0,005 mg. The processes of metal corrosion as a result of thermal processes were characterized by the difference in the weight of the samples before and after the process $\Delta m=m_i-m_o$.

In order to identify the reliability of the gravimetric method of thermal oxidation of materials, they were simultaneously studied in a flow system using a derivatographic method. The study was conducted on a derivatograph D-102 of the MOM Company. Comparison of the results obtained on the corrosion of Zr materials and at T=300÷800ºC by gravimetric and derivatographic methods, it is revealed that satisfactory coincidences are observed between them within the accuracy. Therefore, further studies of the thermal processes of corrosion of metallic materials are carried out by the gravimetric method.

3. Results and discussion

Figure 1 shows the curves of weight gain at temperatures of T = 300; 400; 500ºC within 10 hours. As it is seen from Figure 1, the corrosion curves are described by the equation:

$$(\Delta m/S)^n = K \cdot t,$$

where, K is a corrosion constant; Δm/S - gain in weight; t-time, hours; n- is the exponent of the equation, equal to 2 in the case of parabolic corrosion.

Figure 2 presents a logarithmic plot depending on the corrosion constant versus the inverse absolute temperature of the process in the same temperature range. Equations of logarithms of the corrosion constant versus the inverse absolute temperature were obtained from the graphs and calculated data:

$$\text{Ln } K_{Zr} = -121667x+24{,}735 \text{ - for Zr,}$$
$$\text{Ln } K_{Zr1Nb} = -92632x + 19.789 \text{- for alloy Zr1\%Nb}$$

where x=1/rt. From the equation, it follows that the value of the activation energy at temperatures of T=300÷500ºC is 21.9 kcal/mol for the Zr alloy and 29,5 kcal/mol for Zr1% Nb.

The calculated thickness of the oxide film is determined by the formula:

$$h= (\Delta m/S)\cdot 1/\rho\cdot M/m=\Delta m\cdot M/S\cdot\rho\cdot m,$$

where, h - is the thickness of the oxide film, microns; ρ- is the density of monoclinic oxide of ZrO_2, g/cm^3; M and m are the molecular mass of ZrO_2 and the atomic mass of Zr, respectively.

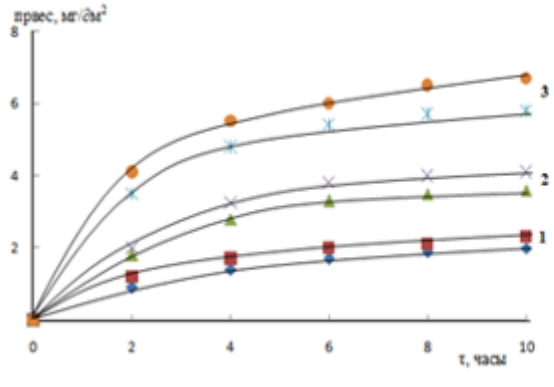

Fig.1. The dependence of weight gain on samples of zirconium and Zr1%Nb alloy during the corrosion in water vapor at different temperatures: 1. T=300^{0}C, 2. T=400^{0}C, 3. T=500^{0}C

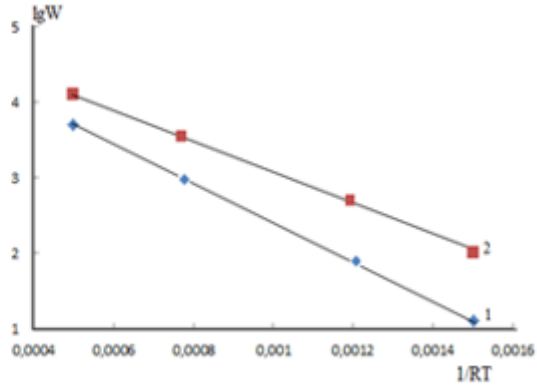

Fig.2. The dependence of the corrosion constant on the inverse absolute temperature in the temperature range: T=300÷500^{0}C

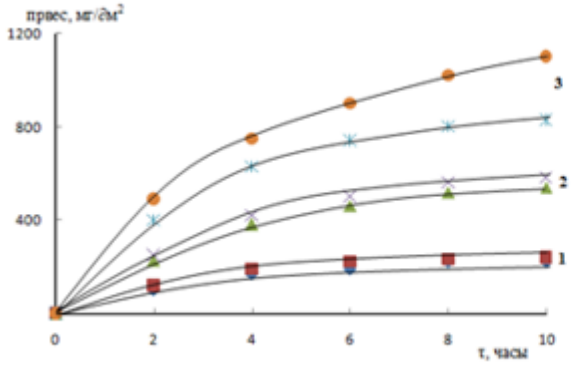

Fig.3. Dependence of weight gain on samples from zirconium and Zr1%Nb alloy during corrosion in water vapor at various temperatures: 1. T = 600^{0}C, 2. T = 700^{0}C, 3. T = 800^{0}C

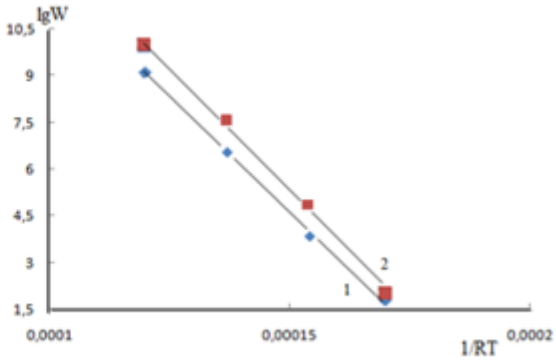

Fig.4. Dependence of the corrosion constant on the inverse absolute temperature in the temperature range: T=600÷800^{0}C

Figures 3 and 4 show the dependence of the weight gain of samples on the corrosion period in water vapor, for 10 hours at T=600÷800ºC. From the graphs, it follows that the corrosion curves are semi-parabolic in nature. It can be seen that the magnitude of the weight gain at temperatures up to 700ºC in the Zr1% Nb alloy is slightly larger than that of metallic zirconium, but the differences are insignificant. The film on the alloy and metallic zirconium has a strong bond with the surface of the samples. By the end of thermal testing at T=800ºC, films were formed on the surface of the alloy and metal, minor cracks appeared, which in turn broke up. The activation energies of the process of corrosion of samples of zirconium and zirconium alloy in a pair were determined at temperatures of T=600÷800ºC when tested for 10 hours. The dependencies that are described by the following formulas were obtained from the graphs:

$$LnK_{Zr}=-161406x + 28{,}510, \text{ where } x = 1/RT$$
$$LnK_{ZrNb}=-161741x + 28{,}611$$

It has been calculated the activation energies at temperatures of T=600÷800ºC for zirconium and zirconium alloy, which are approximately the same – 41.2 kcal/mol.

Data on the film thickness determined from the above calculations was approximately 7; 11 and 30 μm at the temperatures of 500, 600 and 700ºC - respectively. At 800ºC the oxide film thickness reached 45 μm for Zr and 70 μm for Zr1% Nb alloy.

4. Conclusion

The corrosion kinetics of zirconium and zirconium alloy samples was studied in the atmosphere of water vapor in the temperature range of T=300÷800ºC. It is shown that the kinetics of corrosion is determined by the parabolic oxidation law. Oxide films with corrosion for several hours (10 hours), at temperatures up to 600ºC, retain high and protective properties. At temperatures up to 700ºC, there is a decrease in these characteristics, at which cracking of films on the surface of the alloy and metal occurs. Thermal studies of samples of zirconium and zirconium alloy at temperatures from 400 to 700ºC, depending on the period (10 hours), showed high characteristic resistance to corrosion resistance. During corrosion in water vapor above T>800ºC, corrosion resistance and mechanical properties of zirconium and zirconium alloy are reduced.

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ТЕРМИЧЕСКИЕ ИССЛЕДОВАНИЯ СВОЙСТВ ОБРАЗЦОВ Zr И СПЛАВА Zr1%Nb ПОСЛЕ КОРРОЗИИ В ПАРАХ ВОДЫ ПРИ РАЗЛИЧНЫХ ТЕМПЕРАТУРАХ

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Резюме: Исследован процесс коррозии образцов циркония и сплава циркония в парах воды в интервале температур T=300÷800ºC. Изучена кинетика коррозии, определены энергии активации процессов и толщины образующихся на поверхностях оксидных пленок. Установлены области снижения коррозионной стойкости в исследованных интервалах температур.

Ключевые слова: термические процессы, температура, коррозия

MÜXTƏLİF TEMPERATURLARDA Zr VƏ Zr1%Nb ƏRİNTİSİNİN KORROZİYADAN SONRA SU MÜHİTİNDƏ TERMİKİ XASSƏLƏRİNİN TƏDQİQİ

T.N. Ağayev, A.Q. Əliyev

Xülasə: T=300÷800ºC temperatur intervalında su mühitində zirkonium və zirkonium ərintisinin korroziya prosesi tədqiq olunub. Korroziya proseslərinin kinetikasi öyrənilmiş, aktivləşmə enerjisi təyin edilmiş və metalların səthində əmələgələn oksid təbəqəsinin qalınlığı təyin edilmişdir.Tədqiq olunan temperatur intervalında korroziyaya davamlılığının ilkin olaraq azalması prosesi müşahidə olunmuşdur.

Açar sözlər: termiki proseslər, temperatur, korroziya