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RESEARCH OF HIGH-TEMPERATURE OXIDATION OF ZIRCONIUM BY THE THERMO GRAVIMETRIC METHOD

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Abstract: It was investigated the oxidation of zirconium metal in air with an atmospheric pressure in the range of temperatures T=373÷973°C by the thermo gravimetric method. It is revealed that processes of oxidation in all studied ranges of temperatures with high precision are described by linear dependence on time. It was noted periodic change of rate of oxidation from time in experimental works. The oxide layer which was formed on a sample surface at long oxidation in comparison with an initial sample has become covered by network of deep cracks.

Keywords: radiation, nano-zirconium, surface oxidation, thermal treatment

1. Introduction

Zirconium and its alloys are the main constructional materials applied in the atomic industry to production of fuel elements of atomic reactors [1-3,7,9]. Conditions of their operation are very extremal: high temperature, existence of the oxidizing environment (superheated water vapor) and rather high pressure against the background of intensive radiation effects. But zirconium is quite active metal. It reacts with oxygen and nitrogen, and with water vapor, carbon dioxide, and also with hydrogen and hydrocarbons. Nevertheless, use of zirconium as material for reactors was promoted by its property to form the strong and chemically steady oxide films protecting him from corrosion on a surface.

A large number of works is devoted to studying of processes of oxidation of zirconium and its alloys. The received results are generalized in several collections and monographs [10-15,18]. The most part of researches defines corrosion resistance of zirconium and its alloys in the process of long operation. In water and its vapors, measurements were taken in the range of temperatures of T=100÷400°C, and in air - at T=200÷900°C.

When studying kinetics of oxidation of zirconium in oxygen-containing environments, different authors have received significantly various results. Oxidation process is influenced significantly by availability of impurity in metal, a condition of a surface, the nature of preliminary processing of the studied sample, and also availability of the oxygen dissolved in metal, etc. In a number of works it is noted that laws of oxidation of metal can change with cubic on parabolic forms and therefore with increase in time, oxide layers lose the protective properties [4-6].

Corrosion stability of zirconium weakens at high temperatures and in this regard, there is a question: whether loss of protective properties of zirconium oxide can lead to ignition of constructional elements? For the answer to this question, it is necessary to know kinetics of oxidation of zirconium metal at the different temperatures close to temperature of his spontaneous ignition which, according to experimental data, makes 900°C and more.

2. Methodology

For sensing of oxidation rate the gravimetric method with the continuous registration of mass of a sample and temperature is selected. Electronic gravimetric equipment with the mode of the synchronous automatic registration of an additional weight and temperature of the oxidizing environment with sensitivity to an additional weight at least 1 microgram was used. Absolute accuracy of measurement of samples makes 10^{-5} g.

Researches gheterogeneous radiolysis of water carried out in static conditions in special quartz ampoules. The quantity of nano-Zr in ampoules has made about 4×10^{-2}g. It was taken double distilled water for researches. Water into ampoules was entered by two methods. In the first case water from a steam state adsorbed (H_2O_s) on a surface of nano - Zr at T=77K. The amount of the entered water in ampoules corresponded to density of vapors of water in ampoules, at ρ=5mg/cm^3. In the studied intervals of temperatures, there is a balance between an amount of water in the steam and adsorbed state. In the second case, water from calibration volume was entered into ampoules to a full covering of the nano - Zr sample by liquid water with the mass of m_{wat} = 0,2g. Then ampoules with samples cooled to 77K and soldered.

Radiation and radiation thermal processes carried out on the isotopic source ^{60}Co. Absorbed dose rate of gamma radiation was determined by chemical dosimeters – iron sulfate, cyclohexane and methane. The analysis of products of radiation and heterogeneous processes was carried out on the Agilent-7890 gas-chromatograph. Experiments were made in the temperatures range of 373÷973K.

3. Results and discussion

In process of oxidation, the sample becomes covered by the dense oxide film, i.e. is covered with a solid line (fig. 1, a).

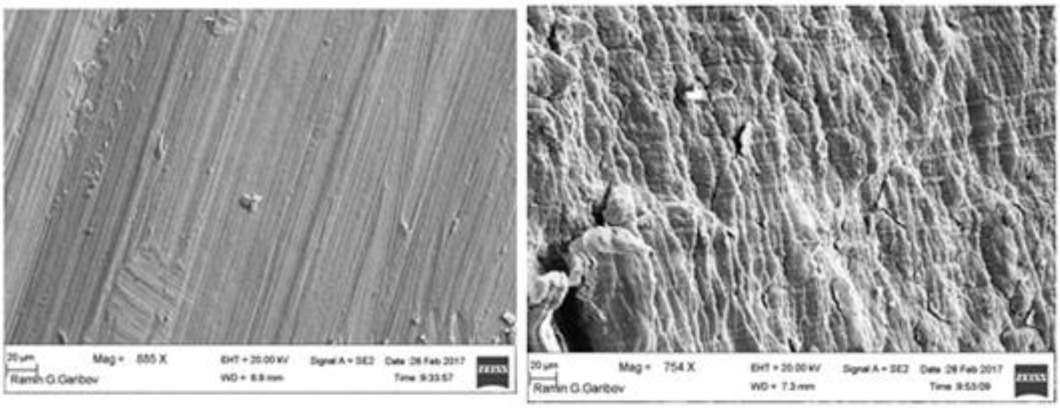

Fig. 1. The photo of a sample of initial zirconium before an oxidation in air: a- 373K, b- 973K, 45% of metal were oxidized

The sizes of plates visible by the naked eye depend on temperature of the oxidizing environment and average are 0.4 mm at T=773K and 1.1 mm at T=973K which thickness depends on oxidation time. Apparently from the drawing, cracks between plates are sharply expressed and, apparently, reach a surface of the oxidized sample. The network of cracks has fractal structure which dimension, as show further researches, remain during process of oxidation at the constant temperature and depend only on experiment temperature. At intensive oxidation at end faces of a sample there are a flaking of plates and their deformation with changing of a surface curvature (fig. 1, b) at which the hardness and durability of oxide are so big that it is possible to separate any plate from a sample surface only with use of great efforts, for example by means of nippers. Plates don't fall off, and their external surface has an appearance of dense glossy formation of cream color.

Since T=773K, an oxidation of zirconium in all studied ranges of temperatures, could be precisely interpret under the linear law. At the same time, it should be noted some feature of oxidation, the general for all values of temperatures, having quantitative distinction at different temperatures. Therefore, periodic fluctuation of oxidation rate is observed at a constant temperature.

As shown in fig. 2, the effect of increase in oxidation rate in certain time points is reproduced, and then there is a completion of an oxidation rate. In case of temperature drop of the oxidizing environment, the vibration amplitude decreases a little. Therefore, process of oxidation since T=773K with a fine precision, it is possible to describe by the linear law [16-17].

The form of curves in fig. 2, allows to assume that in case of small values of oxidation time (τ), it is possible to get on different sections of lines, and it can lead to a discrepancy in case of the description of the law of oxidation. In case of rather big times of oxidation, the linear interpretation of process contains errors in an explanation of thin structure curve (fig. 2).

Thermal and radiation thermal processes in contact of metal constructional materials with water are followed by accumulation of molecular hydrogen and oxidation of a metal surface. Therefore the kinetics of change of mass of metallic zirconium oxidation in case of thermal and radiation-thermal processes in contact with water in the range of temperatures T=473÷673K is investigated. Typical forms of observed kinetic curves of zirconium oxidation are provided in fig. 2a at above indicated interval of temperatures. Apparently from fig. 2 on kinetic curves it is possible to select two areas: I (120÷240min) – area of oxidation of metal with formation of a field-oxide layer on the surface of zirconium metal;

II – area of saturation of zirconium metal dependent on radiation time, i.e. completion of formation of protectively oxide layer on the surface of zirconium metal.

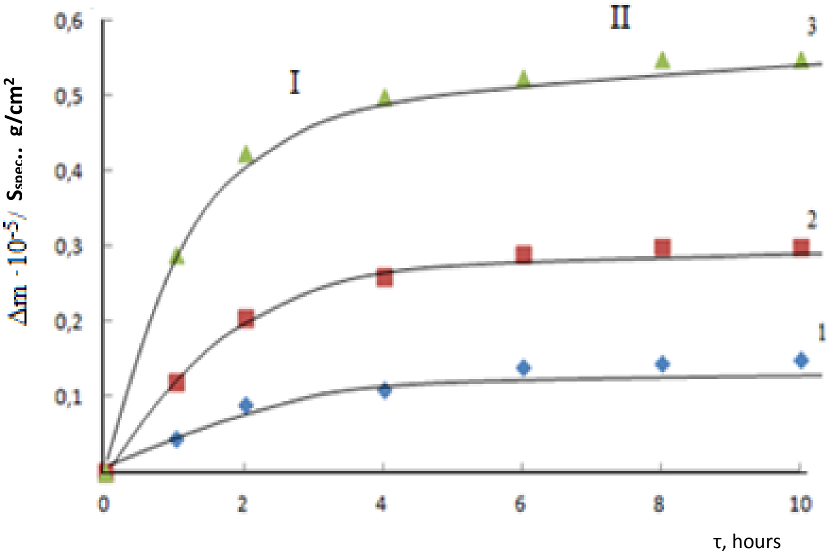

Fig. 2. Kinetic curve of metallic zirconium oxidation at thermal and radiation-thermal processes in contact with water:

1. T=573K - radiation;
2. T=773K - thermal;
3. T = 973K-radiation and thermal

In Arrhenius system of coordinates, results of measurements well keep within on one straight line (fig. 3):

$$\frac{dm}{dt}=16.5\times10^{-3}\exp(-\frac{E}{RT}),$$

where E =92 kJ/mol ± 4%, dimension of oxidation rate (additional weight) – g/(cm^2 s)

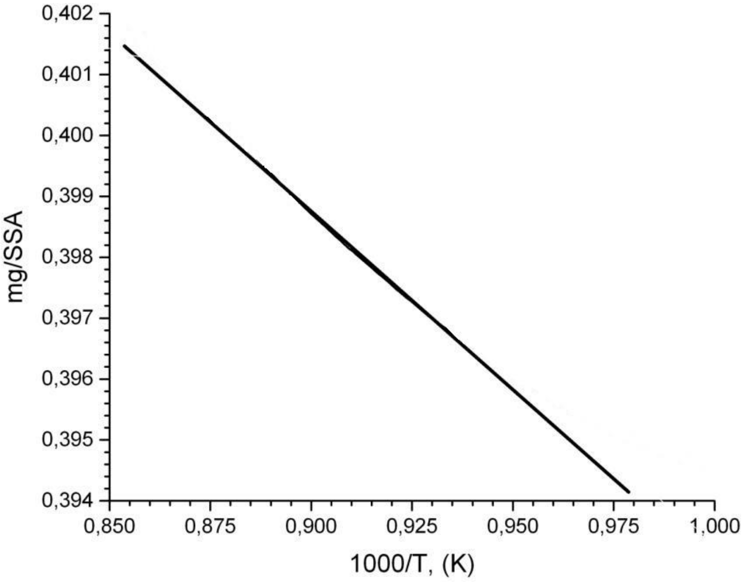

Fig.3. Temperature dependence of oxidation of zirconium rate in Arrhenius coordinates

The oxide films on a surface of samples keep the protective properties and oxidation of metal happens slowly, under "protective" laws at a temperature of the oxidizing environment T ≤ 500°C. Process of oxidation is limited by the rate of diffusion of an oxidizer through films, and also by the rate of dissolution of reagents in metal and kinetics of phase transformations. This range of temperatures is described in work [5] and confirmed by other researchers.

At T>500°C, thermo elastic tension between zirconium and an oxide film, owing to an essential difference in coefficients of linear expansion reaches big sizes, than durability of a film and durability of coupling of a film with metal. There is an essential deformation of zirconium and an oxide film, and in result, the last one bursts and partially exfoliates from metal. The share of an unprotected surface increases and oxidation rate increases that in turn, leads to emergence of new thermo elastic tension and peelings of oxide scales. As shown in [6], through cracks on zirconium and even on the thinnest films are observed. At the same time it is revealed that coefficient of linear expansion of zirconium oxide ($\alpha_L=\frac{1}{L}(\frac{\partial L}{\partial T})_P$) is equal to 10×10^{-6}, and for metallic zirconium 5.7×10^{-6} 1/K. Thus, the total amount of the formed oxide of zirconium is twice more than the volume of oxidized metal. It is obvious that such big lengthening for metal and compression for oxide isn't left without consequences which lead to destruction of metal and oxide. As shown in [2], so-called "deformation of samples of metal, due to growth of an oxide layer, is followed by a rupture of metal". This continuous process of cracking and peeling of an oxide layer at T>500°C leads to the linear law of oxidation.

It must be kept in mind that by the nature, destruction has discretely continuous character and owing to this process all local micro destructions are integrated and in result, the general process of oxidation adopts the linear law.

Nevertheless, probably, except micro cracks at rather big layer of oxide, tensions collect in him occupying rather big areas. The total contribution of this effect is commensurable with small destructions therefore on some sites there is an essential increase in a free surface of metal. Gradually these surfaces "are healed" and the general level of oxidation rate falls up to the initial size. After a while due to increase of a layer of oxide, the condition of a film comes to an unstable state again and process of destruction repeats.

Follows from the above it can be concluded that except directly chemical kinetics of oxidation in experiences, the concrete condition of a sample is shown. Therefore the difference in laws of oxidation is observed not only at change of temperature, but also at change of the geometrical sizes of a sample, and also a condition of his surface especially as durability of coupling of an oxide layer with metal depends on the last one in strong degree.

On the other hand from the above-stated experiences, it is possible to draw a conclusion that for objectivity of results about dependence of kinetics of oxidation on temperature, it is necessary to analyze not only the kinetic curves received at different constant temperatures but also to watch how oxidation rate changes without cooling of a sample (change of temperature of the environment by small jumps) [8]. At the same time, the condition of a surface of a sample doesn't undergo essential changes and therefore, difference in the speed of process will depend on temperature level. Results of measurements in this case yield the best result of the measured sizes.

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ИССЛЕДОВАНИЕ ВЫСОКОТЕМПЕРАТУРНОГО ОКИСЛЕНИЯ ЦИРКОНИЯ ТЕРМОГРАВИМЕТРИЧЕСКИМ МЕТОДОМ

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Резюме: Термогравиметрическим методом исследовано окисление металлического циркония в воздухе при атмосферном давлении в интервале температуры T= 373÷973^0 C. Обнаружено, что процессы окисления во всех исследованных диапазонах температуры с высокой точностью, описаны линейной зависимостью от времени. В экспериментальных работах отметили периодическое изменение скорости окисления от времени. Слой оксида, который образовался на поверхности образца при длительном окислении по сравнению с исходным образцом, покрылся сетью глубоких трещин.

Ключевые слова: радиация, нано-цирконий, поверхностное окисление, термообработка

SİRKONİUMUN YÜKSƏK TEMPERATURLU OKSİDLƏŞMƏSİNİN TERMOQRAVİMETRİK ÜSULLA TƏDQİQİ

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Xülasə: Sirkonium metalının hava şəraitində atmosfer təzyiqində və T= 373÷973^{0}C intervalında oksidləşməsi termoqravimetrik üsulla tədqiq olunmuşdur. Müəyyən olunmuşdur ki, qeyd olunan temperatur intervalında oksidləşmə prosesləri zamandan xətti asılılıqla dəyişir. Təcrübi işlərdə qeyd olunur ki, zaman keçdikcə oksidləşmənin sürəti dövri olaraq dəyişir. İlkin nümunədən fərqli olaraq, uzunmüddətli oksidləşmə zamanı səthdə yaranan oksid təbəqəsində dərin çatlar yaranmışdır.

Açar sözlər: radiasiya, nano-sirkonium, səth oksidləşməsi, termiki işlənmə