Methodology of Corrosion Testing of Nuclear and Fusion Reactors Materials Using TGA/DSC and MS Complex Techniques

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Article info

Abstract

The behavior of structural materials of nuclear and fusion reactors during operation largely determines their safe and economical work. Structural materials of nuclear and fusion reactors are operating under conditions of interaction with various chemical active elements (gases, vapor-gas mixtures, fission products, etc.) in a wide temperature range; they are subject to high requirements in terms of their thermal and corrosion resistance. This paper presents the new methodology of complex studies on structural materials corrosion resistance of nuclear and fusion reactors with different gases and vapor-gas mixtures by thermal-gravimetric analysis (TGA), differential-scanning calorimetry (DSC) and mass spectrometry (MS) methods simultaneously.

1. Introduction

The National Nuclear Center of the Republic of Kazakhstan (NNC of RK) at various times tested the materials of nuclear and fusion reactors such as lithium ceramics, beryllium, vanadium and vanadium alloys, liquid metal systems for fusion reactor's blankets, graphite materials of the High Temperature Gas Reactors (HTGR), etc. [1–5].

Usually, the experiments were carried out by studying the change in the gas composition in the chamber with the sample being tested (for example, using the thermal desorption spectroscopy (TDS) method), which made it possible to evaluate the processes of the above mentioned materials interaction with gases (and hydrogen isotopes in particular). However, for a number of studies, in addition to information on the change in the gas composition in the chamber, it became necessary to have information on the change in the mass of the sample during the experiments. For example, in the study of beryllium, it was important to take into account its thermal sputtering. For graphite of the HTGR core reactor it is important to study the chemical sputtering of carbon from the surface of the sample.

The possibility of assessing the heat of the chemical reactions on the surface associated with the hydrogenation and dehydrogenation of samples is an important criterion for conducting studies that would essentially describe the mechanisms of the processes under study.

2. Experimental facility for corrosion resistance study of structural materials of nuclear and fusion reactors

There are many different experimental installations where different methods are used to study structural materials of nuclear and fusion reactors. Currently, the TGA, DSC and MS methods are the most popular and demanded research methods [6].

TGA is a method of thermal analysis which consists in observing and registration the mass of the investigated sample with its temperature changes. The results of TG analysis are thermal curves – thermograms that depend mainly on the chemical composition and structure of the sample.

The DSC method is based on the continuous recording of the heat flux difference from/to the investigated sample and reference sample (change in enthalpy) as a function of temperature or time when samples are heated in accordance with a

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specific program in a given gas atmosphere. This method provides information on the temperatures and heats of phase transitions, thermodynamics and kinetics of chemical reactions, chemical composition, and purity, thermal and oxidative stability of various materials.

The MS method is based on the measurement of the gas composition released from the tested sample. The obtained data are analyzed and conclusions are made about various chemical interaction processes. The mass of a tested sample in such experiments is determined by weighing it before and after the experiment.

Simultaneous use of methods will significantly expand the perception of the studied processes and will facilitate interpretation of the obtained data during testing. The list some of them:

1) First of all, a simultaneous analysis of thermo gravimetric and mass spectrometric dependencies will allow us to carry out a calibration over the absolute values of the evolved gases and directly obtain rate constants for surface reactions;

2) In addition, it will be possible to relate the interdependent processes of sputtering of the sample with chemical reactions on the surface; with the processes of gas evolution from the sample of dissolved gases; with phase transformations in the sample both of the basic structure and various alloys of incorporation (for example, hydrogen isotopes);

3) Separate analysis of the change dependence in the heat flux (in the DSC method) will allow us to directly determine the heat of chemical reactions both on the surface and in the bulk of the sample and to associate them with the observed changes in the gas composition (products of chemical reactions).

To implement the above methods at "Branch Institute of Atomic Energy of National Nuclear Center of the Republic of Kazakhstan" an experimental test bench that would combine all three methods of analysis in order to obtain more extensive experimental data in one experiment was developed and created. While developing the experimental complex the following steps were taken into account:

– the launch of separate units (measuring instruments and equipment) included in the complex must be synchronized;

– the presence in the complex of a system for preparing a gas medium of a given composition for purging of a sample in a reaction chamber, in order to study certain reactions/processes; a gas medium preparation system must be connected to complex
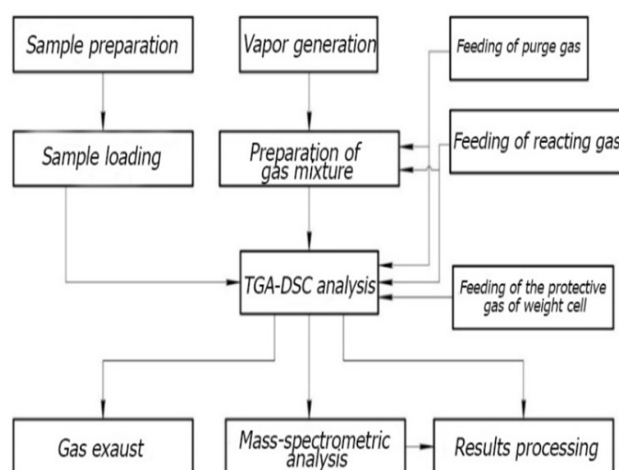

Fig. 1. Block diagram of the experimental complex for the study of the interaction processes of chemically active gases with structural materials of NR and FR.

for preparing the gas medium of a specified composition;

– the exhaust system of the experimental complex should be designed to lower the pressure of the residual gases in the working chamber, to ensure purification of the purge gas and to prevent the exhaust gases from getting back into the working chamber.

Figure 1 presents the block diagram of the experimental complex.

In accordance with the block diagram, a schematic diagram was composed (Fig. 2). This scheme allows giving the most complete description of the technological aspects for carrying out the complex studies of the structural materials' corrosion resistance.

Before carrying out the complex studies, this sample (1) was weighted on analytical scales (2), its geometrical parameters were measured and visual inspection for visible defects was performed. Then the sample was placed in a high-strength aluminum oxide-based melting pot. This melting pot with the sample inside was placed on the platinum substrate of the ceramic TGA/SDTA sensor installed in the TGA-DSC 3+ analytical instrument (3). The experiment parameters were set using special software (licensed STARe software from METTLER TOLEDO company) installed on the PC (4). While creating the experimental method, the temperature regime of the experiment was set, the selects and rates of the reaction (5), purge (helium) (6) and protective (7) gases were set. Protective gas (helium) was used to purge microbalances, in order to protect them from penetration of unwanted gases released during the experiments.
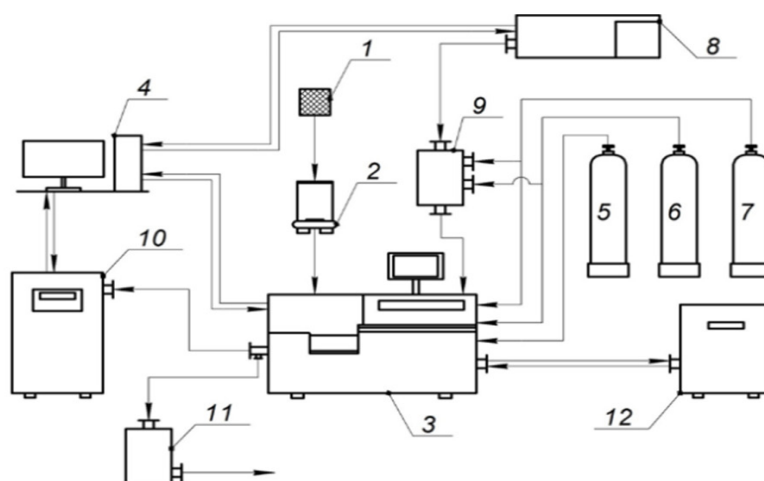
Fig. 2. Schematic diagram of the experimental complex: 1 – sample; 2 – analytical scales; 3 – thermal gravimetrical analyzer; 4 – computer; 5 – reaction gas; 6 – purge gas; 7 – shielding gas; 8 – humidity generator; 9 – mixing chamber; 10 – mass spectrometer; 11 – gas filter; 12 – cryostat.

Since the built-in ultra-microbalances were calibrated for a certain constant temperature, the temperature control of the weight cell was carried out by the cryostat (12). The gases were fed and controlled by the TGA-DSC 3+ type integrated gas analyzer. In order to monitor and set the humidity parameters of the working gas mixture, this research complex was equipped with a humidity generator (8). The gas-vapor mixture for the experiment was prepared in a special mixing tank (9). Continuous measurements of the gaseous medium composition over the sample during the experiment were carried out using a mass-spectrometer (10). To filter out the flow of gas mixtures discharged into the atmosphere, a special sorption filter (11) was used.

Figure 3 presents the general view of the experimental complex for investigation the corrosion resistance of structural materials as a result of their interaction with various gases and gas-vapor mixtures.

Table 1 provides a brief description of the main modules of the experimental complex.

Fig. 3. The experimental complex for investigating the corrosion resistance of structural materials of NR and FR as a result of their interaction with various gases and gas-vapor mixtures.

Table 1
Features and characteristics of the modules of the research complex

Module	Appointment	Defined parameters	Specifications
TG-analyzer (TGA-DSC 3+)	synchronous analysis of materials by temperature change	TGA: weight change; DSC: temperature and thermal effects of phase transitions	temperature range from 22 to 1600 °C; heating rate from 0.02 to 150 °C/min
Mass-spectrometer	to identify different substances in atmosphere over a test sample	continuous registration of the partial pressure of residual gases in the working chamber of the unit	simultaneous determination of 128 different atomic masses in the range from 1 amu up to 300 amu
Humidity generator	synchronous analysis under heating in an environment with controlled humidity	generation and maintenance of a medium with a specified humidity	range of relative humidity: from 2 to 98 %
Analytical balances	high-precision weighing	samples mass at the stage of sample preparation	weighting limit: 120 g. Discreteness up to 42 g – 0.01 µg, over 42 – 0.1 µg

3. Methodical experiment

After the completion of installation and operational-verification testing of the experimental complex, a methodical experiment was carried out. The graphite of HTGR type reactor was studied, the reaction gas was a vapour-air mixture. The mechanisms of hydrogen transport in graphite and carbon materials using the TDS method, before and after neutron irradiation are discussed in [7–9]. In [10] 29 brands of graphite charged with deuterium gas are tested up to the temperature of 1735 K with a heating rate of 0.1 K/s. The graphite was chosen for study due to the fact that its corrosion in a vapor with an air mixture proceeds immediately through the several reaction pathways. The sample had a cube shape with dimensions of $5 \times 5 \times 5$ mm and weight of 212.3 mg. Figure 4a shows the graphite sample with a melting pot and (b) the type of the TG analyzer working chamber after installing the melting pot with a sample on a TGA SDTA sensor.

A methodical experiment with a graphite sample was carried out in the following order. After the melting pot was placed on the substrate on the TGA sensor, the chamber was blown with helium at a flow rate of 150 ml/min for 1 h. Further, the experiment was carried out which consisted in linear heating of the sample at a rate of 100 °C/min. When the sample temperature reached 1100 °C, the sample was cooled linearly to the room temperature.
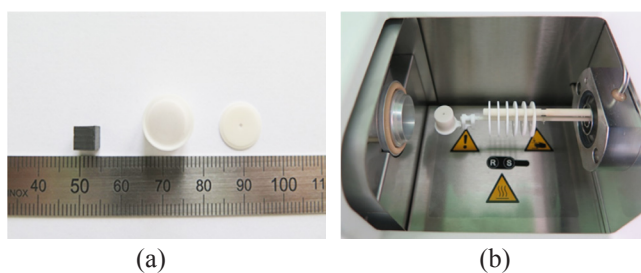

Fig. 4. View of melting pot with the sample and the type of the TG analyzer-working chamber: (a) – general view of the melting pot and test sample; (b) – view of the melting pot with a sample on TGA/SDTA sensor.

4. Results and discussion

Figure 5 shows the dependence of the change in the partial pressures of gases and their masses during the experiment. For a more detailed analysis of the masses of interest, let us consider the Fig. 6.
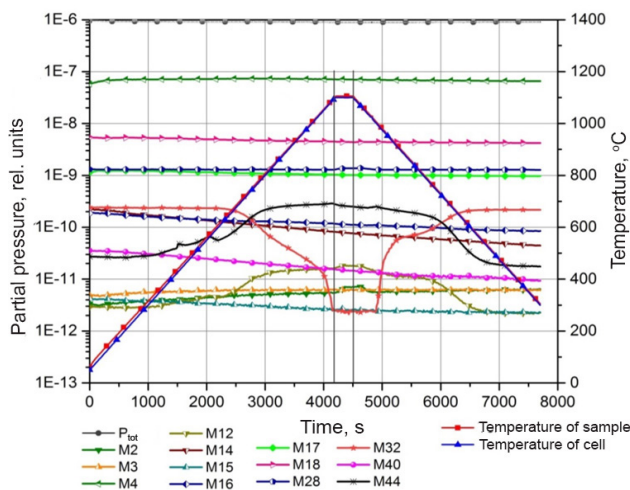

Fig. 5. Dependence of partial pressure changes of gases in experiment.
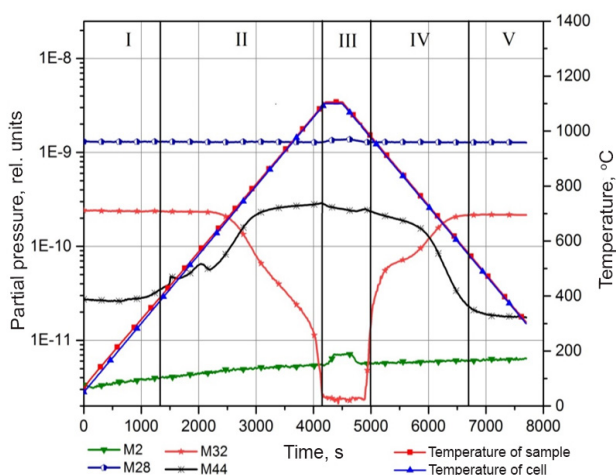

Fig. 6. Dependence of partial pressure changes of gases as a result of chemical interaction with the sample.

The results of mass spectrometric analysis can be broken down into 5 intervals. When analyzing the obtained spectrum of the mass variation curves, it can be seen that graphite practically does not enter into a chemical interaction in the interval I with an increase in temperature to 400 °C. However, with a further increase in temperature with the transition to interval II, it can be seen how the reaction between graphite and oxygen begins, as shown by a decrease in the mass of 32. As can be seen from Fig. 6, with a decrease in the oxygen content, there is a rapid increase in mass up to 44, which is carbon dioxide. Therefore, it can be assumed that when the temperature is raised to 600 °C, the process of chemical interaction of graphite with oxygen begins, according to the following reaction:

$$O_2 + C = CO_2, \Delta H = -393 \text{ kJ/mol}$$

In interval III at 1100 °C, you can see a small dip of mass 44 and an increase of mass 28. These variations indicate a change in the mechanism of the graphite-oxygen reaction, and the formation of carbon monoxide according to the following reaction:

$$\frac{1}{2}O_2 + C = CO, \qquad \Delta H = -110.5 \text{ kJ/mol}$$

Also in this interval at ~ 1100 °C, there is a probability of a partial formation of CO as a result of carbon dioxide interaction with graphite, according to the following reaction:

$$C + CO_2 = 2CO, \qquad \Delta H = 172.5 \text{ kJ/mol}$$

At 1100 °C during the thermal shelf, one can notice another chemical process associated with an increase in mass 2. Hydrogen, in this case, is a product of the chemical reaction of graphite with residual water vapors presented in the atmosphere. The graphite-water reaction has the following form in this case:

$$C + H_2O_{vapour} = CO + H_2, \qquad \Delta H = 131.3 \text{ kJ/mol}$$
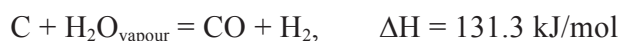
With a decrease in the temperature of the sample to ~1000 °C and a transition to the interval IV, it can be seen how the dip of mass 44 and the increase in mass 28 disappear. Also, there is a gradual increase in oxygen and a decrease in the partial pressure of carbon dioxide and hydrogen. This is due to the fact that, as the temperature is lowered, the equilibrium of the proceeding chemical reactions shifts towards the formation of initial substances.

With a further decrease in temperature, the chemical reactions are attenuated, and at ~500 °C after the transition to the interval V, it can be seen how the partial pressures of all gases equalize and become constant.

Owing to the mass spectrometry data, made certain conclusions about the process by high-temperature corrosion of reactor graphite occurs for HTGR. Based on the TG analysis data shown in Fig. 7, we can determine at what temperatures the sample mass is lost and quantify.

Thus, at the beginning of the process of linear heating up to 620 °C there is a small increase in mass, this is characterized by the fact that the adsorption of the oxidant proceeds to the surface of the sample. With a further increase in temperature, it can be seen how the process of sample corrosion starts which is accompanied by a loss of mass, due to the formation of gaseous reaction products. As the temperature rises, the rate of corrosion also increases, with a decrease in temperature, the reverse
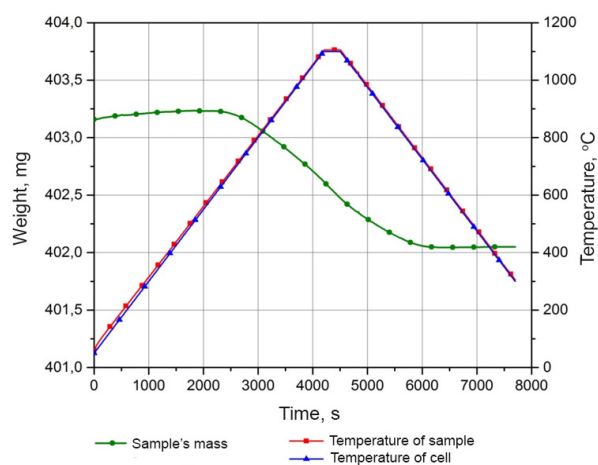

Fig. 7. Changes of sample's mass during heating.

process occurs. When the sample was cooled to ~ 620 °C, its mass goes to the stationary level and the chemical corrosion reactions cease. The mass loss during this experiment was 1.11 mg.

Using the DSC analysis, the dependence of the change in the heat flux of the sample during the heating process was obtained (Fig. 8). It can be seen that at first the heat flux drops. This fall is characterized by the fact that the heat from the furnace is directed at heating the sample. During the heating of the sample at a temperature of ~ 400 °C a small peak is seen. This peak indicates that a chemical reaction of oxygen and graphite occurs, which is exothermic. Since the oxidation reactions are exothermic, in this connection, a slight increase in the heat flux curve from 600 to 1100 °C is visible. When an 1100 °C temperature shelf is reached, the change in the heat flux curve can be traced, this may be because reactions of chemical interaction of graphite with water vapor and carbon dioxide begin to occur at this temperature, which in turn is endothermic. In the process of cooling, the heat flux begins to grow rapidly, this is justified by the fact that the heat from the sample is released into the system.

Based on the results of the obtained data and analysis, the energies of the chemical reactions that occur during the high-temperature corrosion of the graphite material were also calculated. The calculation was carried out according to a standard procedure, using the

TGA-DSC 3+ analytical instrument software. The inaccuracy in determining the energies of chemical reactions relative to the literature data was about 20%. The obtained data are shown in Table 2. The data obtained in the experiment agree well with the data obtained in [11].
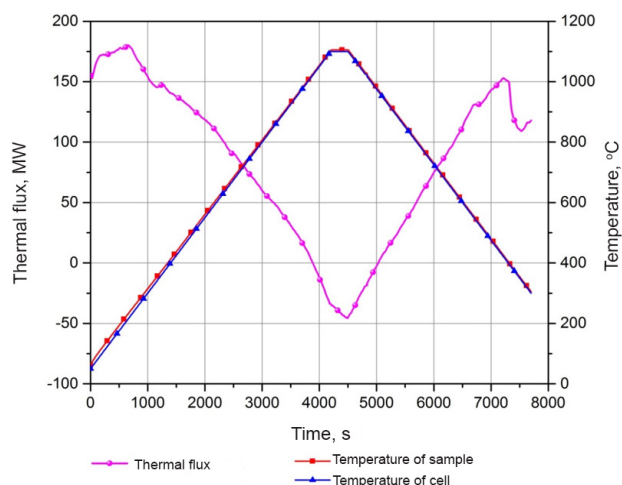
Fig. 8. Changes of heat flux of sample during heating.

Table 2
Energy of chemical reactions

Reaction	Experimental data, ΔH, kJ/mol	Literature data, ΔH, kJ/mol [12]
$O_2 + C = CO_2$	- 358	- 393
$\frac{1}{2}O_2 + C = CO$	- 99	- 110.5
$C + CO_2 = 2CO$,	193	172.5
$C + H_2O_{vapour} = CO + H_2$	- 79	- 82.4

5. Conclusions

Thus, as a result of the work carried out in the Institute of Atomic Energy of NNC of RK, an experimental complex has been created for corrosion resistance investigations of nuclear and fusion reactors structural materials as a result of their interaction with various gases and vapor-gas mixtures, operational and verification testing has been carried out.

The results of the methodical experiment confirm the applicability of the developed method of complex studies and allow to fully describe the processes occurring during the high-temperature corrosion of NR and FR structural materials.

This methodology and experimental complex will be used in future to carry out the complex studies of high-enriched uranium and low-enriched uranium fuel of the Impulse Graphite Reactor (Kurchatov, Kazakhstan), as part of the program to reduce the enrichment of uranium-graphite fuel.

Acknowledgments

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