

Techniques of Helium Content Measurement in Irradiated Structural Materials

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Introduction

Helium effect on radiation damage of structural materials governs the necessity of the detailed study in the field of helium accumulation in these materials under different operating conditions. Helium interaction with different defects of the structure is one of the factors, which influence on the change of the structure, porosity evolution and material embrittlement during irradiation and finally can be a reason of service life shortening or even damage of structural components in nuclear reactors.

Calculation methods are used to determine quantitative characteristics of helium accumulation in the irradiated materials. These methods require both a sufficient volume of source information related to parameters of nuclear reactions (n, α) on the basis of which helium accumulates and precise determination of irradiation conditions for material. The acquisition of reliable data on helium accumulation in these experiments requires the application of experimental procedures to measure the content of radiogenic gases in irradiated materials in addition to calculation methods. As a rule, the methods of gas phase analysis are used as the experimental methods. The gas phase is produced as a result of extraction process in the irradiated material specimen during its heating in vacuum. Methods demonstrating a high degree of measurement sensitivity are of advantage because of low concentrations of the measured element and specific nature of handling with irradiated materials.

SSC RF RIAR developed a set of certified techniques that allows the helium content to be measured in irradiated reactor materials using mass-spectrometry with the help of two independent methods of the gas phase analysis to solve this task.

1. Materials under examination and helium content measurement facility

Structural materials with melting temperature of no more than 2000°C limit the field of application for the developed techniques. Stainless steels, beryllium and zirconium alloys should be referred to this category of materials mainly.

Solid-phase specimens in the form of disk (may be of irregular shape) are used for measurement of helium content in the irradiated structural material under examination. They are cut out from the source material given for examination purposes. The minimal sizes of specimens are limited with the minimal allowable mass of specimen to be 10mg. The maximum sizes of specimens are limited with the maximum ionizing dose rate allowable outside the hot cells. It makes up $500 \mu\text{R}\cdot\text{s}^{-1}$ from the specimen at a distance of 3cm. They are also limited with the inner diameter (4mm) and height (5mm) of the crucible used for heating purposes. The specimen should be decontaminated from possible impurities of external environment just before weighing. Ethyl alcohol is used for its washing. The specimen is also subjected to ultrasonic cleaning in case of necessity.

An experimental facility on the basis of production-run mass-spectrometer MI-1201 with gaseous source of ions was designed and installed for mass-spectrometer measurements of helium content in irradiated structural materials. A static analyzer with uniform cross sector-type magnetic field form a part of mass-spectrometer. Analytical capabilities of the mass-spectrometer allow the mass spectra to be recorded within the mass number range (ion mass-charge relationship) from 1 to 600s with a resolution capability of $500\div 600$ r.u. (at a level of 10%). Amplification of the ion currents by a value of no more than 10^{-4} A (in the case of low isotope content in the analyzed gas mixture) was achieved with the help of the secondary electronic multiplier VEU-2A. A computer-based measuring system of MI-1201 mass-spectrometer was designed to increase the expressiveness of mass spectra recording. It allows for automatic recording of 20 mass-spectra ranges for the analyzed gas phase and displaying of digital and image information on PC display. A vacuum extraction technique is used

for helium extraction from the specimen. A gas extraction facility was designed and made for this purpose.

A specimen is subjected to the induction heating using the induction coil of high-frequency oscillator (Fig.1). For this purpose the specimen is placed into the crucible made of refractory and current-conducting material (Mo, Ta). A crucible (without specimen) is subjected to vacuum annealing just ahead of measurements. The crucible is annealed at a temperature that is equal to the maximum heating temperature of the specimen. An optical pyrometer is used for measurement of the crucible heating temperature. The crucible is inserted into the quartz holder that is placed into the specimen cell (degassing cell). The cell consists in a quartz or glass capsule with a ~1.5mm thick wall. The capsule is brazed tightly to the stainless steel pipe union with the help of adapter made of alloy with high thermal expansion coefficient. It is connected with the vacuum lock meant for specimen loading using the vacuum threaded coupling that is made leak-tight with metal gasket. A vacuum bellows rectifier forms the basis of the vacuum lock. Its body is made of stainless steel. The design of the vacuum lock provides for preliminary pumping of the vessel where the specimen is placed before its loading into the crucible. The possibility of the specimen reloading into the degassing cell at a high vacuum allows for lowering of the air effect on the degassing cell walls, specifically it decreases the condensation of water on them that can introduce an essential error in measurement of hydrogen isotope signals. The lock and capsule are connected with the high-vacuum chamber of the gas extraction facility that is made of stainless steel. The exterior heater allows the high-vacuum chamber to be heated up to 400°C to degas the inner surface of the chamber walls. Capsules with marker element and standard mixture, calibrated capsules and differential pressure transducer are connected to the vacuum chamber using vacuum bellows rectifiers.

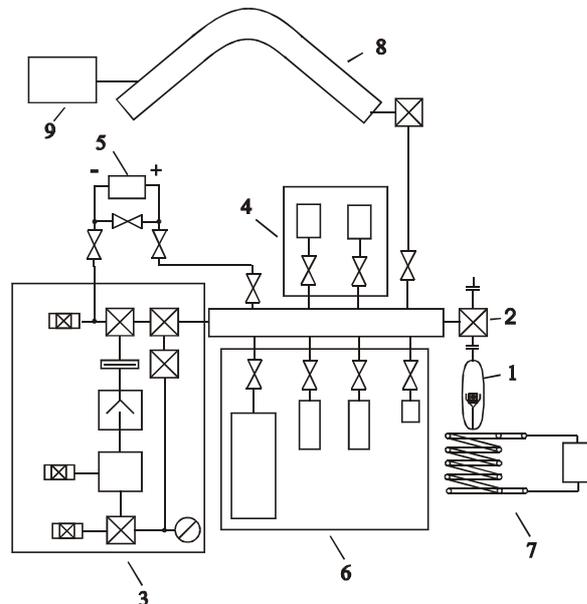


Fig.1 Scheme of experimental facility to measure helium content using isotope dilution:

1- specimen chamber; 2- vacuum lock for specimen loading; 3- vacuum pumps and vacuum gauge; 4- ampula with marker and standard mixture; 5- marker pressure gauge; 6- calibrated volumes; 7- induction heating; 8- mass-spectrometer; 9- computer-based measuring system of mass-spectrometer

The capsule with the specimen inside is pumped down with mercury diffusion pump to high vacuum after specimen loading into the crucible. A degree of inleakage (vacuum deterioration) is determined inside the high-vacuum chamber and capsule with the specimen using thermocouples and ionization pressure gauge. Mass spectrograms of the residual gases are recorded just ahead of the specimen heating inside the whole measuring system including volumes of the specimen cell, vacuum chamber, commutation between the high-vacuum chamber and mass-spectrometer and volume of the mass-spectrometer analyzer chamber.

The differential pressure transducer is used for measurement of pressure that allows for the marker element to be injected. It measures the gas pressure in the closed volume with reference to the outlet pressure of the diffusion pump. The piezoresistive transducer SAPFIR-22DD is used for the marker pressure measurement in the range of 13÷620Pa with a measurement error of 0.75%. The marker element is subjected to volumetric dilution using calibrated capsules (of a given volume) made

of stainless steel. They are connected with the high-vacuum chamber of the gas extraction facility. Lead blankets, which surround the capsule with the specimen inside, are used to protect the staff from ionizing radiation emitted by the irradiated specimen under examination.

2. Mass-spectrometry method of helium content measurements using isotopic dilution

A method of relative comparison between the unknown quantity of helium-4 isotope and known quantity of helium-3 isotope forms a basis for the mass-spectrometry method of absolute amount measurement of helium-4 isotope that is present in the solid specimen of the structural material under examination with the use of isotopic dilution.

The standard procedure of analysis for helium-4 isotope content measurement using mass-spectrometry and isotopic dilution is as follows:

- A certain amount of gas marker enriched in isotope-indicator (helium-3) is supplied into the closed and vacuum-sealed volume (capsule) that contains a specimen of material under examination and vacuum;
- Gas phase (sample) that contains helium-4 is extracted from the specimen into the closed volume of the capsule with marker inside;
- The resultant gas mixture of the sample and introduced marker are kept in the capsule during a certain period of time for isotopic equilibration;
- Helium-3/helium-4 ratio in the gas mixture sample and marker is measured after isotopic equilibration using mass-spectrometry;
- The isotopic helium-3/helium-4 ratio is measured in the standard gas mixture having a given isotopic helium-3/helium-4 ratio to determine the relative sensitivity coefficient of the mass-spectrometer for helium isotopes. Mass-spectrometry is used for measurements;
- Mass-spectrometry is used for measurement of isotopic helium-3/helium-4 ratio in the marker that contains helium-4 in relatively small amount (isotopic helium-3/helium-4 ratio should be much more than 1 in the marker).

3. Mass-spectrometry method of helium content measurements using volume calibration

The same method of vacuum extraction of the gas sample incorporating helium but without marker introduction forms the basis of this method. The helium content is measured in the specimen under examination based on the results of mass-spectrometer measurements of ^4He ion current that is in proportion to the partial pressure of ^4He extracted from the specimen in the closed volume. The mass-spectrometer is used as the high-sensitivity transducer of ^4He partial pressure. High sensitivity of this method and limitation on the operating vacuum of the mass-spectrometer requires the quasistatic (by helium) conditions of the analyzer chamber pumping during the analysis of the gas phase (sample) extracted from the specimen. More than that there is a need for instrument calibration that is the determination of mass-spectrometer sensitivity coefficient according to the target component (^4He). The available mass-spectrometer was subjected to upgrading to comply with the above-given conditions of the volumetric quasistatic method application. To provide the quasistatic conditions of residual gas pumping-out in the chamber of the mass-spectrometer analyzer the standard diffusion pump located in the area of ion collector was replaced by getter pump based on the non-evaporable titanium alloy that allows for selective pumping of residual gases. ^4He sensitivity coefficient was determined during the individual procedure of the mass-spectrometer calibration using the developed calibration device that forms a part of the gas extraction facility. All volumes of the vacuum system, which are required in measurements, were subjected to precision measurements including volumes of the analyzer chamber and all intermediate volumes between the specimen cell and mass-spectrometer. Volumes of the vacuum system were measured based on the method of gas expansion (of the given pressure) from the calibrated volume into the measured volume that is pumped to a high vacuum beforehand.

4. Metrological certification of He content measurement techniques

Standard monocrystal encapsulated samples with a given content of ^4He isotope, which were made and certified in the Center of Expert Examination, Certification and Quality Issues of Ural State Technical University, were used as standard samples for metrological certification of techniques. They were made of potassium bromide crystals because of the requirements for high homogeneity of the specimens. The samples were made using saturation of initial monocrystals in the gas phase at given temperatures and pressures. Helium thermal desorption was used to measure helium in the standard

samples of each batch. A source sample was heated up to the melting temperature to measure the amount of the extracted helium using the mass-spectrometer that had been subjected to volumetric calibration and operated under static pump-down conditions.

The comparison of measurement data with the passport values using two different methods of helium content measurement in standard samples (Fig.2) reveals that the measurement data are in good agreement with the passport values and between each other in the whole measurement range in both cases. A difference between measurement results N_{meas} and passport values N_{pas} is no more than 15% in absolute value but the difference in measurement results, which have been obtained using two different techniques for one batch of specimens, is no more than 10% in absolute value.

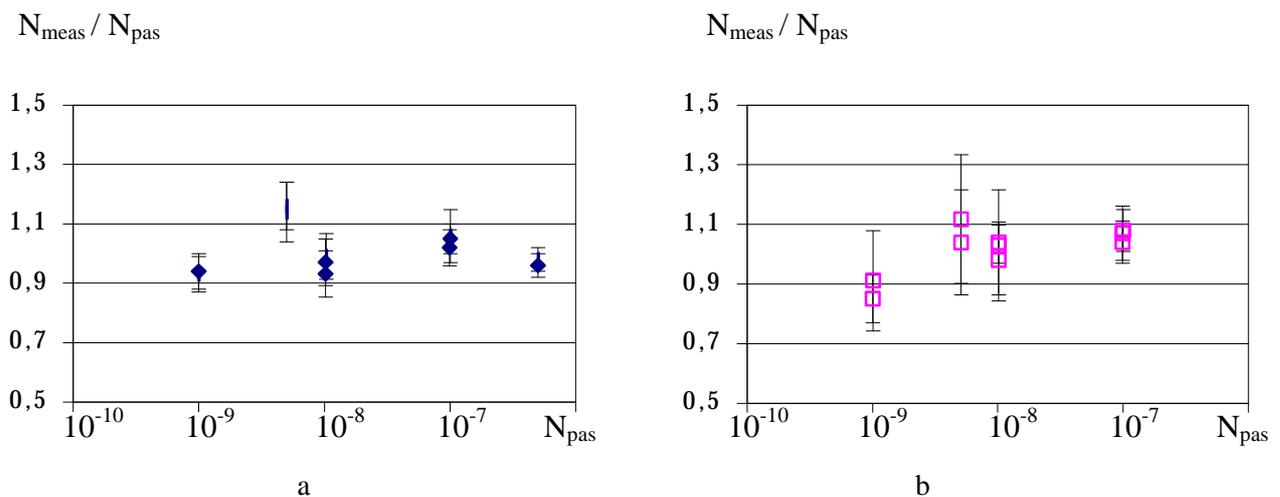


Fig.2. Mass-spectrometer comparison of measurement results with passport values of helium quantity in the standard samples using isotopic dilution (a) and volume calibration (b)

Low values of measurement errors (Table 1) in combination with high sensitivity proves the availability of this set of techniques in the reactor material science to measure the helium content in irradiated reactor materials. The field of application for the described set of techniques can be the study of spectrum, neutron flux density and neutron fluence effects on helium accumulation in materials under irradiation.

Table 1. Confidence bounds of relative measurement errors

Ranges of helium content in specimen			Relative measurement error is less than, %	
Quantity, mole	Mass fraction, (ppm)	Molar fraction, (appm)	Isotopic dilution	Volume calibration
$1 \cdot 10^{-9} \div 1 \cdot 10^{-8}$	0.4 ÷ 5	12 ÷ 150	9	19
$1 \cdot 10^{-8} \div 1 \cdot 10^{-7}$	5 ÷ 11.5	150 ÷ 340		7
$1 \cdot 10^{-7} \div 5 \cdot 10^{-7}$	11.5 ÷ 24	340 ÷ 725	6	-

CONCLUSIONS

1. There is a pilot facility to measure helium content in the irradiated structural materials having a melting temperature up to 2000°C. The range of absolute helium quantity measurement inside the specimen is $(10^{-12} \div 10^{-5})$ mole and it allows the molar fraction of helium to be measured in the range of (1- 10 000) appm according to the specimen matrix mass and material.

2. Mass-spectrometer techniques of helium content measurement using isotopic dilution and volumetric quasistatic methods were developed and certified. The confidence bounds of relative measurement errors depend on the measured value and are in the range of 6 to 9% for the method employing isotopic dilution and of 7 to 19% for the volumetric quasistatic method.
3. The results of comparative certification of two measurement procedures using the same standard specimens demonstrate a good agreement of helium measurement results, which were obtained with the help of two techniques.

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