STUDIES ON TRITIUM PERMEATION INTO VARIOUS MATERIALS AS A FUNCTION OF GAS COMPOSITION, PARTIAL PRESSURE AND TEMPERATURE

S. Brad, I. Stefanescu, A. Bornea, L. Stefan, M. Zamfir, A. Lazar, F. Vasut, N. Bidica, N. Sofalca, M. Vijulie
The National Institute for Cryogenics and Isotopes Technology, Ramnicu Valcea, Romania

General information

Considering this interest in hydrogen isotopes permeation, the reported research has been structured to be developed in a two general directions. Starting from our experimental knowledge into mechanical properties analysis at cryogenic temperatures, we followed a previously-expressed idea, which intend to eliminate the cryostat equipment from the mechanical toughness machine, by using a polystyrene foam like a thermal protection envelope. The general setup of this experimental part of the research was based on comparing the experimental results using the common previously-designed system and the new version with the polystyrene jacket. The main part of the research was focused on the hydrogen isotopes permeability into metallic materials as is expressed in the title. An important comment has to be made at the beginning. Due to the internal problems related to the Tritium operation license approval by the National Commission for Nuclear Activities, we decided to continue the experiments with the other isotopes of Hydrogen and at the moment that we will receiveapproval to work in the right conditions we will repeat the same experiments with Tritium. Also, we tried to develop experiments for the tritium permeation at concentrations admitted for normal environment, but unfortunately we could not achieve data with high accuracy. An experimental stand for hydrogen isotopes permeability has been designed and built and different metallic materials has been tested for various experimental conditions.

Experimental setup

Test stand modification by the elimination of the cryostat used for cooling, design of the sample specific polystyrene foam like a thermal protection envelope and the cryogenic liquid, make tension test at a specialized laboratory.

Concerning the first objective of this reported research, we have to emphasise that the general experimental works has been developed onto the previously-designed equipment used for metallic toughness measurements in a large range of temperatures between 4 K until 500 K. In order to increase the accuracy of the testing and also to simplify the system, new polystyrene foam has been used as a thermal protection envelope instead of the complicated and hard-to-be-used cryostat.

Study of Hydrogen isotopes permeation into various materials as a function of gas composition, partial pressure and temperature

The second important objective was to design and build an experimental stand dedicated to the hydrogen isotopes permeability investigation for metallic samples, used generally as materials for fusion facilities. A few general requirements have been considered when we started to design this new facility. One was related to the sample geometry and had to allow using both plate and tube samples. The used plate samples were thin discs with a 25 mm

diameter and 0.1-0.5 mm thickness. Also, an integrated system for acquisition of testing parameters has been provided. The sample membrane is squeezed by two cooper gaskets between knife-edge-sealed vacuum flanges. The assembly is connected to a vacuum system and before each experiment we will determine the leakage and pump the entire stand for several hours. Also there is the possibility to change the gas feeding system of the experimental stand in a continuous or an intermittent way. In the case of joints or welded materials the reactor is different and will be mounted in the same assembly. The reactor is made of stainless steel and isolates the sample from the exterior, the permeated gas will be recovered in the same stocking recipient. The samples will be prepared in tubular geometry. The principle of the measurement is the same as for the disc samples described above but the tube geometry is more suitable for investigating hydrogen-tritium permeation phenomena. All the samples will be prepared at 20 mm diameter and 100 mm length, and the joint or weld zone will be polished at very thin dimensions. All the samples will be cleaned with sequential washes of detergent, distilled water, acetone, and distilled water again. A heat lamp will be used to dry the cleaned discs. In order to explain easily the experimental system, we can design a schema, in which we consider two different chambers with the permeability device, surrounded by a thermal furnace. Chamber l is used for the input of hydrogen isotopes through a valve. The purification system is based on a cold trap and charcoal sieves and is used to prepare the hydrogen before the experiment. Chamber 2 is provided with a specially prepared gas chromatograph, which measures the hydrogen or deuterium flux permeated through the sample. The sample is heated by an electric heater. A specially designed control system connected to the membrane-sealing unit adjusts the heater to maintain the desired temperature. All parameters of the installation are regulated, treated and stored in a controlling computer. During the experiment, the following parameters were measured and controlled: sample temperature, hydrogen isotopes partial pressure over membrane inlet surface, the flow rate of hydrogen isotopes permeated through the sample. The zone of diaphragms can be changed with another vessel tank in order to determine the permeation rates for tubes and also metallic tubes joints obtained by friction welding procedure.

Experimental details

Considering the general structure of the research divided into two parts, we will refer in this section separately to these two scientific objectives.

Test stand modification by the elimination of the cryostat used for cooling, design for the sample specific polystyrene foam like a thermal protection envelope and the cryogenic liquid, make tension test at a specialized laboratory.

It is well known that the main parameter for materials used for designing and building the cryogenic installation is toughness, which is the absorbed energy at breaking. Therefore, the toughness measurements have been made at three temperature levels, shown in the results tables. Three types of materials have been investigated using a Charpy machine, both with the old toughness measurement system and the improved one. The measuring conditions have been kept the same during both experimental systems. Also, the data acquisition automatic line has been used for both measurements sets.

Study of Hydrogen isotopes permeation into various materials as a function of gas composition, partial pressure and temperature

The permeability measurement has been performed using the before discussed experimental stand, using the gas-chromatograph analysis for the gas sampled from both sides of the membrane (or tube) sample investigated. Two different materials have been investigated for

Hydrogen isotopes permeation – 304 L stainless steel and AL- High purity Aluminum. The chemical composition is shown in Table 1.

Specimen	*Diameter (mm)*	*Chemical composition*							
		Cr	*Ni*	*Mo*	*Mn*	*Si*	*C*	*P*	*S*
304L	*20*	*18*	*8*	*-*	*2*	*1*	*<0.08*	*<0.05*	*<0.03*
AL (99.9%)	*25*	*-*	*-*	*-*	*-*	*-*	*-*	*-*	*-*

Table 1. The chemical composition of the two d materials investigated.

The experiments have been performed for only two (due to the long time necessary to complete a given measurement) different working pressure – 300 Pa and $5*10^3$ Pa and for two input gas compositions: High purity Hydrogen and High purity Deuterium. The working temperature was kept constant at 700 K based on the known low dependence of permeability with temperature in such range of temperature.

It is necessary to mention that the first material investigated – 304 L, was measured with tube geometry and the second one – Aluminum with plate geometry. The investigated samples have been prepared before experimentation by polishing at very thin dimensions. All the samples have been cleaned with sequential washes of detergent, distilled water, acetone, and distilled water again. A heat lamp was used to dry the cleaned discs.

The second part of this task was to investigate the crystalline structure of the tested materials by SEM(for tube sample) and X-ray diffraction (for plate sample) analysis techniques. The SEM analysis has been performed onto a REM 100 instrument using a magnification factor of 2000. XRD analysis system used was a Diffractometer type DRON-UM1 with an automatic data acquisition system. The measuring parameters were CuK - 1.54 A, U = 40 KV, I = 30 mA.

Experimental results and considerations

Test stand modification by the elimination of the cryostat used for cooling, design for the sample specific polystyrene foam like a thermal protection envelope and the cryogenic liquid, make tension test at a specialized laboratory.

As we before mentioned, the measurements have been performed on three different materials, both for the older version of the system and for improved one. The measured toughness values for the system with cryostat are shown in the Table 2.

Material type	*Temperature (K)*	*KCV (J)*	*Material type*	*Temperature (K)*	*KCV (J)*
8 Cr 170	*300*	*80*	*8 Cr 170*	*300*	*75*
	77	*45*		*77*	*20*
	20	*5*		*20*	*5*
20 Cr 130	*300*	*90*	*20 Cr 130*	*300*	*90*
	77	*55*		*77*	*45*
	20	*20*		*20*	*10*
2 Cr Ni 18 9	*300*	*217*	*2 Cr Ni 18 9*	*300*	*210*
	77	*163*		*77*	*159*
	20	*67*		*20*	*52*

Table 2. The measured toughness values for the system with cryostat.

The second measured values set has been performed for the same material types but for the improved version of the toughness testing system. The results are shown in the second table. From these reported data, it could be easily observed that the KCV(J) values measured on the improved system (which use the polystyrene jacket) are smaller than the first values set. The direct conclusion which could be drawn is that using the polystyrene new system the temperature measuring system is more accurate and the testing temperatures measured are more appropriate to the real ones. Also, we wish to emphasize that the new system could be considered as a significant simplification of the entire installation, which could be used for further design of such equipment.

Study of Hydrogen isotopes permeation into various materials as a function of gas composition, partial pressure and temperature

In order to define the mechanical properties of materials investigated in the Hydrogen isotopes permeability measurement system, we used the Charpy machine to measure the KCV(J) for 304L and AL.

Material	***Temp (K)***	***Energy (J)***
304L	*293*	*144*
304L	*293*	*152*
304L	*77*	*80*
304L	*77*	*92*
Al	*300*	*112*

Table 3. The KCV(J) values for the two materials investigated.

The values of measured diffusivity for the two material types are presented in the Table 4. In order to make clear and analyze these measured data, a plot of dependence of these values on temperature, reported in the literature (permeability is obviously obtained by the relation: P=D*Ks).

Material	*Diffusivity*	*Solubility*	*Temperature*
	Do(m^2/s)	*Ks($mol/m^3P^{1/2}$)*	*T(K)*
H_2-Al	*$1.8x10^{-5}$*	*7.9*	*700*
H_2-Al	*$1.0x10^{-5}$*	*0.9*	*700*
D_2-Al	*$1.1x10^{-7}$*	*1.9*	*700*
H_2-304L	*$1.01x10^{-7}$*		*700*

Table 4.The values of measured diffusivity for the two material types.

The first sample – 304 L has been examined by SEM technique. It could be seen the many nuclear cavities from which ridges emanate. The morphology of internal voids and cracks, in hydrogen embrittled steels, leaves little doubt that growth commonly occurs by the development of new surface progressively at the roots of notches because broad expanses of relatively smooth surface are exposed.

Fracture studies using scanning electron microscopy seem to place the sites of cavity nucleation too far apart in relation to the height of the ridges of final rupture. For an aluminum sample, we investigate the possibility of Hydrides formation. The phase analysis performed with a

diffractometer system using a Powder Diffraction File database, do not reveal any Al-H bonds, as could be seen in the bellow diffraction spectra.

The work developed at FZK was conducted to achieve the experimental results on the hydrogen isotopes permeation through different materials types and to compare it with the results obtained. (The results obtain at FZK was based on the experimental setup developed on metallic permeation membranes and also on polymeric membranes.) The behavior of hydrogen isotopes permeation through samples are observed and compared with the values from the model calculation. The permeability of H_2 and D_2 through materials tested is quantified and they agree well with previously reported values. On the other hand, an important database was achieved on the mechanical comportment of metallic materials in a tritium atmosphere. Also connected with the activity from other experiments fields tensile strength membranes measurements with a ZWICK tensile strength machine were made. The tests were made for polymeric membranes used in an electrolyser, in order to determine if there are important modifications of mechanical proprieties for these membranes after long-time use in a hydrogen isotopes atmosphere. After a program of tests on the original membranes and also on membranes put to work in a high deuterium concentration a decreasing of strain of these membranes in a range of 2 to 10 N/mm^2 was observed. The HOGEN electrolyser which will be used in the WDS plant at FZK had practically the entire pipelines made of plastic materials and with different seals and joints made also of plastic materials. That means, we can have a higher risk of leakage of tritiated gas or water inside of the electrolyser, because the plastic materials can be easily deteriorated not only for radioactive reasons but also for technological one's. Therefore the pipelines system was redrawn in isometrics views for the HOGEN electrolyser and recommended a list of spare parts which must be achieved in order to have also an entire system of draining hold-up. Another important problem was to draw and prepare a project of a catalyst treatment device in order to apply the sintering process for the catalyst type Pt/C/PTFE at proper temperature and in a heated nitrogen atmosphere conditions. The importance of this treatment was revealed in several studies and our task was to draw a leak-free- and safe treatment device, a very good convection in the reactor for the heated nitrogen flow, an easer recharging system of the reactor with different samples quantity and the project also of this reactor was finished. An important aspect which was discussied at FZK was the possibility to use in the future the stand for permeability in order to determine new data for different alloys and also the stand for toughness also because this last stand can determine resilience in a very great temperature range from high temperature to cryogenic level for different tests of the new WDS plant.

Final remarks

The reported research has been structured along these two directions mentioned above. Generally it follows to accomplish the scientific objectives mentioned in the work programme. The improvement of our toughness testing system and the more accurate results obtained for the KCV(J) values are the main result of the first point of our scientific programme. Also, a few modifications for tritium measurement, for isotopes permeation equipment has been defined and built and the adequate testing procedure has been elaborated. The results indicated the validity of our system and testing methods and could be considered as a good basis for an extended permeation investigation for a longer period of time.