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EXPERIMENTAL STUDY OF SWELLING OF IRRADIATED SOLID METHANE DURING ANNEALING

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Шабалин Е. и др. E13-2008-41
Экспериментальное изучение распухания облученного твердого метана
во время отогрева

Несмотря на низкую радиационную стойкость твердый метан широко используется как материал для холодных замедлителей нейтронов на импульсных нейтронных источниках. Одна из специфических проблем его использования — давление радиолитического водорода на стенки камеры замедлителя при облучении метана. Приводятся описание и результаты экспериментов по изучению этого феномена, которые были проведены на специально созданной низкотемпературной облучательной установке на реакторе ИБР-2. Пиковое значение давления на стенки экспериментальной ампулы после облучения метана при температуре 23–35 K составило 27 бар при поглощенной дозе 20 МГр и дальше падало с увеличением дозы. Это пиковое значение всегда достигалось при температуре метана 72–79 K. Анализ позволил выделить и объяснить три фазы распухания метана и выхода радиолитического водорода.

Результаты работы были использованы в проекте твердометанового замедлителя для второй мишени нейтронного источника ISIS, Англия.

Работа выполнена в Лаборатории нейтронной физики им. И. М. Франка ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна, 2008

Shabalin E. et al. E13-2008-41
Experimental Study of Swelling of Irradiated Solid Methane During Annealing

Solid methane, notwithstanding its poor radiation properties, is still widely in use at pulsed neutron sources. One of the specific problems is radiolytic hydrogen gas pressure on the walls of a methane chamber during annealing of methane. Results of experimental study of this phenomenon under fast neutron irradiation with the help of a specially made low temperature irradiation rig at the IBR-2 pulsed reactor are presented. Peak pressure on the wall of the experimental capsule during heating of a sample irradiated at 23–35 K appeared to have a maximum of 27 bar at the absorbed dose 20 MGy, and then falls down with higher doses. Pressure always reached its peak value at the temperature range of 72–79 K. Generally, three phases of methane swelling during heating can be distinguished, each characterized by proper rate and intensity.

Results of this study were accounted for in design of the solid methane moderator of the second target station of the ISIS facility (England).

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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INTRODUCTION

Solid methane, notwithstanding its poor radiation properties [1], is still widely in use at pulsed neutron sources as a cold neutron moderator [2, 3]. One of the specific problems is radiolytic hydrogen gas pressure on the walls of a methane chamber during annealing of methane. Hydrogen, both in atomic and molecular forms, is the main product of methane radiolysis. Four decomposed methane molecules give rise to about three molecules of hydrogen. Rate of hydrogen production RH_2 (mol/g of CH_4) is ruled by the relation [4, 5]:

$$\mathrm{RH}_2 = 3 \cdot 10^{-4} D'(t + D_0/D'(1 - \exp(-D't/D_0)),$$

where D' is the absorbed dose rate, MGy/h (1 W/g = 3.6 MGy/h), D_0 is a constant of ~ 8 MGy, and t is time of irradiation in hours. For low doses this is $6 \cdot 10^{-7}$ mol/J.

The usual temperature of methane moderator is 20–30 K, and radiolytic hydrogen being in the condensed state during irradiation does not cause any measurable internal pressure and swelling of methane [4]. But during heating of methane, gaseous hydrogen builds up internal pressure inside solid methane matrix, resulting in swelling of methane and pressure loads onto methane chamber walls. Many chambers of solid methane moderators were destroyed due to this effect [5–7, for example]. For 20 years of solid methane moderator use, no attempt was made to study quantitative characteristics of the phenomenon. This paper gives results of the only experimental study of pressure loads on the walls of a chamber with solid methane during its heating after fast neutron irradiation.

1. APPARATUS AND METHODS

This study was performed at the specially modified low temperature irradiation facility URAM-2 at the IBR-2 pulsed reactor [8, 9]. New irradiation rig and study programme were called the URAM-3M.

The conceptual scheme of the irradiation facility is shown in Fig. 1. It consists of four principal parts:

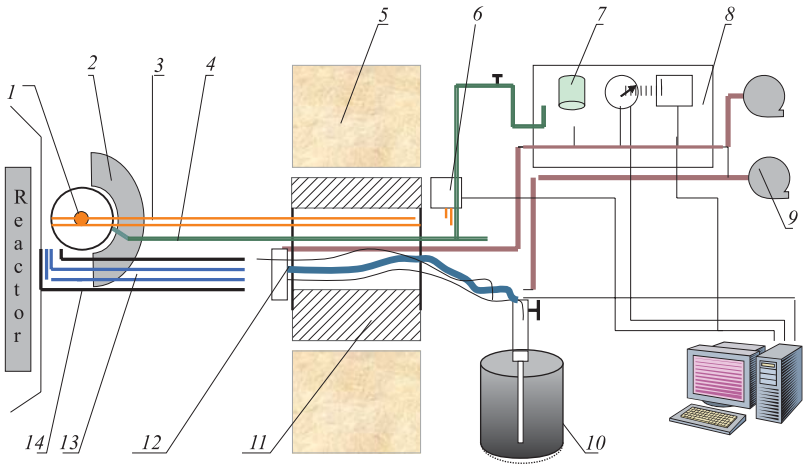

Fig. 1. The URAM-3M irradiation facility: *1* — chamber with a sample; *2* — beryllium reflector; *3* — coaxial cables of displacement gauges; *4* — methane supply pipe; *5* — biological shield of the reactor; *6* — electric adapters and amplifiers; *7* — methane and hydrogen bottles; *8* — technology console; *9* — vacuum pumps; *10* — liquid helium 200 l Dewar; *11* — movable shielding plug; *12* — flexible helium pipeline of 12 m long; *13* — straight helium pipeline; *14* — evacuated and holding tube

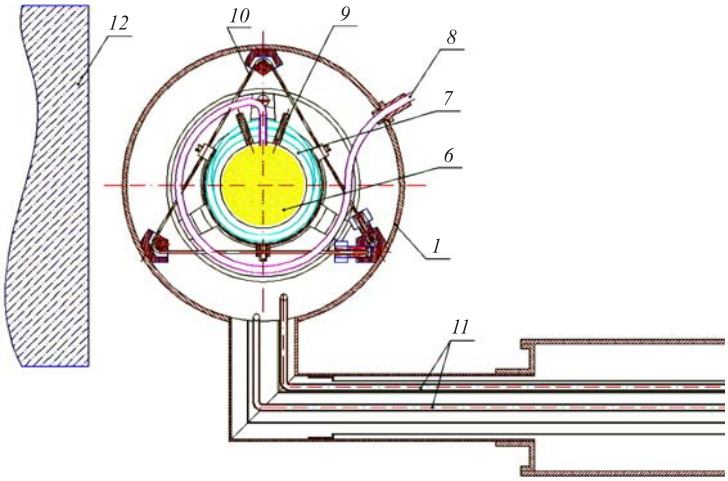

Fig. 2. Front-end of the irradiation rig, elevation through central plane of the sample. *1* — cylindrical shell of the chamber; *6* — aluminium foam filled with solid methane; *7* — coils of copper tube; *8* — steel tube for filling and evacuation gases; *9* — pockets for temperature sensors; *10* — steel string suspender of the sample chamber; *11* — helium pipes inside an evacuated 3-m-long tube; *12* — reactor

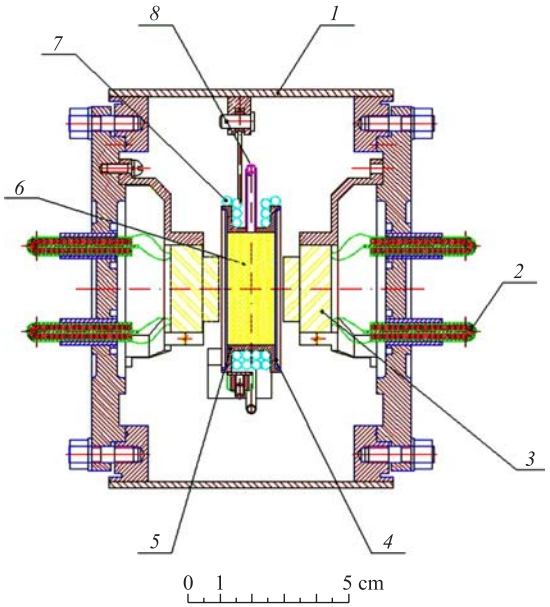

Fig. 3. Evacuated chamber with a sample, elevation along diameter. *1* — cylindrical shell of the chamber; *2* — coaxial cables of displacement gauges (3); *4* — steel membrane; *5* — steel shell of a sample chamber; *6* — the sample (aluminium sponge filled with solid methane); *7* — coil of copper tube (heat exchanger); *8* — steel tube for filling and evacuation of methane and hydrogen gases

— irradiation rig head with supporting parts (see Figs. 2 and 3),
— cooling system, based on using liquid helium as a coolant material,
— vacuum-gas technology system,
— and control equipment.

It enables to irradiate solid methane condensed inside aluminium foam at 25–35 K for 35–40 h at dose rate of either 0.23 or 0.5 W/g. Solid methane samples were prepared by condensing methane gas into the chamber as liquid, and freezing it afterwards.

Both the irradiation chamber and aluminium foam inside it, have cylindrical shape. All walls of the chamber are made of stainless steel 12X18H10T (Russian standard), which has high resistance to radiation and good mechanical properties at low temperature. Two faces of the chamber represent plates of steel of 1.5 mm thick and serve as membranes to follow methane expansion during hydrogen release (see characteristics in Fig. 4).

Displacement of the membranes was measured with two gauges of induction type (sensitivity — 0.63 V/mm). Inside an evacuated jacket of polished stainless

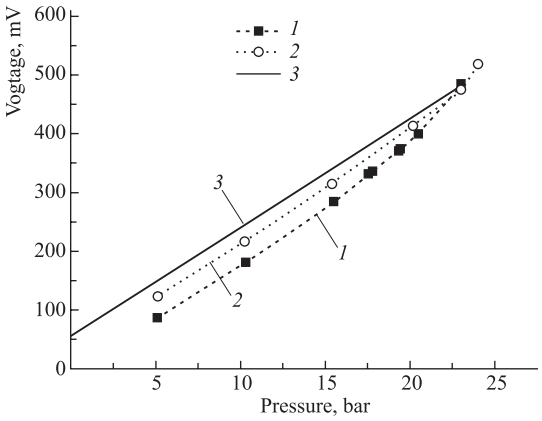

Fig. 4. Response of the displacement gauge to the gas pressure load on the membrane at 70–80 K. Curve *1* is for the first load after heating up to room temperature, curve *2* is for the second load, and curve *3* — for the third load and the following

steel, the chamber is kept strongly space oriented with a steel string in tension. Nevertheless, position of the irradiation chamber with respect to the displacement gauges depended on temperature. This temperature effect was compensated by estimation of displacement of the membranes as an average of indications of two gauges. Because $P-X$ diagram (pressure on the membranes versus its displacement) at the first load after heating up to room temperature appeared to be nonlinear, «training» of membranes at 70–75 K was done each time before new irradiation run, that is, triple loading up to 25 bar. Such a procedure guaranteed linear character of the $P-X$ diagram.

To prevent overfilling of the aluminium foam with methane, a capillary tube made of copper was placed inside the methane feeding tube and welded into the steel walls of the vacuum chamber. Due to high thermal conductivity of copper, the temperature of the capillary tube was near 300 K everywhere preventing freezing of methane at the neck of the chamber.

Temperature nonuniformity in the foam filled with solid methane was calculated with 3D-heat transfer code and expected to be near 3 K.

Temperature of the chamber walls was measured by thermocouples welded between copper tube coils. Dose rates were measured in advance with a purposefully arranged test bench; moreover, dose rate in methane was checked every time by measuring amount of hydrogen gas released since hydrogen output per unit of absorbed dose is well known. Gas pressure monitoring was arranged with two gauges: 0–400 mbar and 0–25 bar, both of 0.1% accuracy at full scale.

Principal procedure of an experiment:

1. Before condensation of methane, the chamber is cooled down to 70–80 K, and filled with helium under pressure varying from 0 to 25 bar for calibration of the displacement gauges and training of the membranes.

2. Methane cavity is evacuated, heated up to 105–115 K and connected to a bottle of 5.73 l capacity charged with methane gas of 99.99% purity to a pressure between 1.9 and 2.3 bar (two irradiations were performed with methane doped with 0.65 mol% BF_3 gas enriched with B^{10}up to 83%, which increased dose rate up to 0.5 W/g, not decreasing time of irradiation). After condensation of 1.4–1.5 bar, the bottle is chipped off the methane filling tube. Until condensation completed, temperature of methane is kept above 90.6 K to prevent solidification of methane before sample chamber is filled with liquid methane. Then methane is cooled down to 25–30 K.

3. Continuous irradiation of the solid methane sample for some predetermined time at the maximal temperature of the methane from 26 K up to 35 K proceeds.

4. Temperature of the methane sample is increased up to 90 K with definite rate (from 0.3 to 5 K/min) by switching helium heater on and depressing helium flow rate. In the process 3 and 4, temperature of the methane chamber, and outgoing gas pressure, and displacement of steel membranes (faces of the chamber) are recorded.

5. After saturation of gas pressure in the bottle (that means that all hydrogen released) the temperature goes up for evaporation of methane, and cavity of the chamber is pumped out at 355 K to remove partly high boiling products of methane radiolysis.

6. Cavity of the chamber is filled with helium under pressure close to that observed in the experiment, for calibration of the displacement gauges.

7. Helium is pumped out, temperature goes up, methane is evaporated, chamber cavity is evacuated and the next experiment begins.

2. EXPERIMENTAL RESULTS

Main characteristics of experimental runs are summarized in the Table.

Lower limit of value in the column H reflects more or less exactly beginning of hydrogen release; upper limit is the temperature corresponding to the peak of

Experimental data (titles of the columns see in the note)

No of run	A	B	C	D	E	F	G	H	I
1	430	6.0	25–27	18.8	2.5–3	13.7	24	81–87	$\sim 3\%$
2	406	5.7	25–30	17.1	1.5–2	13	24	83–85	$\sim 10\%$
3	450	9.16	30–35	28.3**	4–5	21.5	10	86–88	$\sim 10\%$
4	400	15.5	25–26	37.3	~ 0.5	21	21	67–72	3%
5	400	6.7	27–30	19.3	−***	20.5	~ 20	> 85	$\sim 10\%$
6	406	24.2	30–35	51.4	0.6–1.4	24	24	66–74	6%
7	400	29.5	30–39	60.0	1–2	24.5–25	20	64–72	$\sim 11\%$
8	391	9.8	30–31	23.4	0.3	13	21	69–79	0.7 %
9****	383	7.5	85	39	–	–	–	–	–
10	367	18	23	80	10–15	19.7	16	68–74	28%

Note: A — charge of methane, mmol; B — irradiation time*, h; C — temperature of irradiation, K; D — amount of H_2 accumulated, mmol; E — heating rate, K/min; F — peak pressure on the membrane, $P_{\max}$ bar; G — fraction of H_2 released before pressure reached $P_{\max}$%; H — temperature range of hydrogen release, K; I — maximal rate of hydrogen release, min^{-1}.

*1 h of irradiation $\equiv 0.81$ MGy (for experiments Nos. 1–8).

** Calculated value.

*** Heating by filling the chamber with the warm methane gas.

**** Experiments No. 9 and No. 10 were made with methane doped with boron; No. 9 was assigned to check the boron doping effect on amount of hydrogen.

the pressure (column F). Typical temporal behavior of parameters during heating of irradiated samples is given in Figs. 5 and 6.

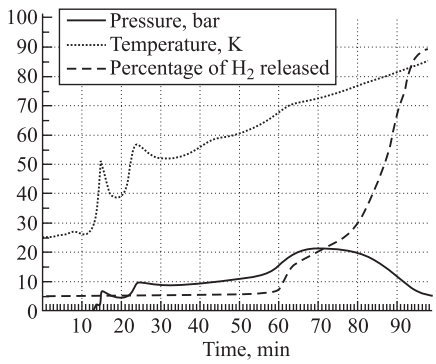

Fig. 5. Record of parameters during heating, experiment No. 4

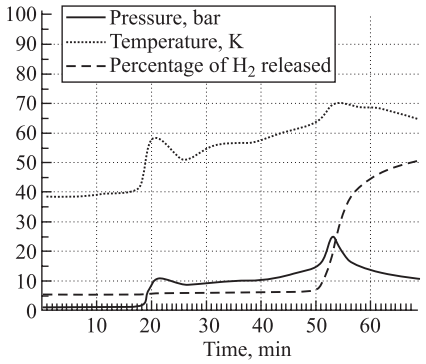

Fig. 6. Record of parameters during heating, experiment No. 7

2.1. Effect of the Heating Rate. In Fig. 7, maximal pressure on the membranes versus amount of accumulated hydrogen is given. Six out of nine ex-

perimental points lie strictly on the smooth curve, which can be approximated with a polynome of the third order. All of these experiments are characterized by similar conditions (the chamber is not overfilled and rate of heating is in the range 0.5–15 K/min), except for different temperatures of irradiation. Three other points differ either in filling of the chamber (No. 3), or in the way of heating (in experiment No. 5 methane was heated by bleeding of a portion of warm methane gas), or by very low heating rate (No. 8). The last circumstance is not significant for practice — to gain about 20% in pressure on the membrane, one needs one hour extra time for heating. So that, the rate of heating is not critical factor for pressure on the membranes.

2.2. Effect of Temperature of Irradiation. As is clear from Fig. 7 and the Table, there is no visible evidence of the irradiation temperature effect on maximal displacement of membrane.

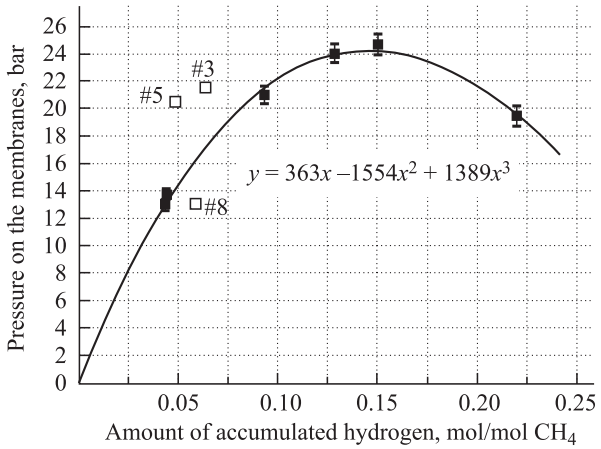

Fig. 7. Peak value of pressure during heating of irradiated methane versus amount of hydrogen accumulated. Black squares — experiments with the normal amount of methane in the chamber and with medium or high rate of heating; hollow squares — experiments with different parameters of heating

2.3. Maximal Value of Pressure. For dose > 20 MGy the peak of pressure on the membrane during heating reaches the maximum of about 25 bar with amount of accumulated hydrogen (displacement of the membrane is 0.4 mm accordingly), and then falls down, not depending on the rate of heating. Since the diameter of the membrane is greater than the diameter of the aluminium sponge, the maximal pressure on the membrane was really 10% more, that is, about 27 bar.

2.4. Effect of Burping. In experiments No. 1, No. 4, and No. 10 induced burps were indicated. They did not affect markedly value of the peak pressure on membranes.

3. DISCUSSION AND INTERPRETATION OF THE RESULTS

Following regularities in the behavior of pressure on the membrane during heating of methane samples, it is worth to note that:

- Pressure on the membrane always reaches peak value at temperature in the range of 72–79 K (after long irradiation

  ), and, which is most intriguing, just up to this moment about 20% of the stored hydrogen is released in all the experiments.

- Rate of hydrogen release depends on temperature not monotonically: in the range of 64–72 K (for high doses of radiation) it sharply intensifies, and returns to exponential (Arrhenius type) growth afterwards (see Figs. 5 and 6 and Figs. 8 and 9).

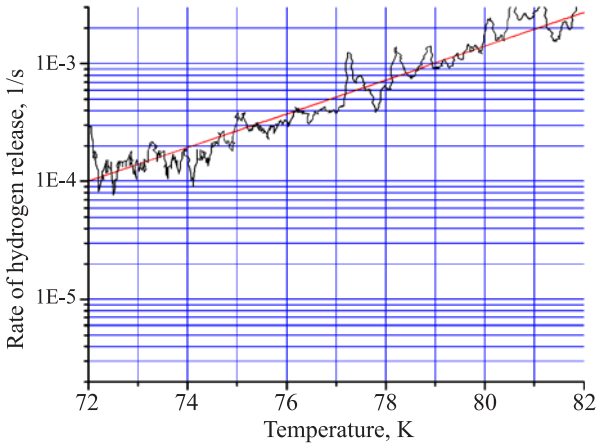

Fig. 8. Rate of hydrogen release (relative to the amount of hydrogen unreleased)

- Before hydrogen starts to escape at $T > 64$ K, membranes exhibit displacement. This swelling of methane, which is about half of the peak value, follows a jump of temperature from 40 to 60 K. Balance of the heat in the chamber showed (Fig.10) that at this moment the additional energy, released in the methane sample, is about 60 J/g.

These regularities and other characteristics of the process of radiolytic hydrogen release can be explained if one suggests that the process of hydrogen release goes on through three phases:

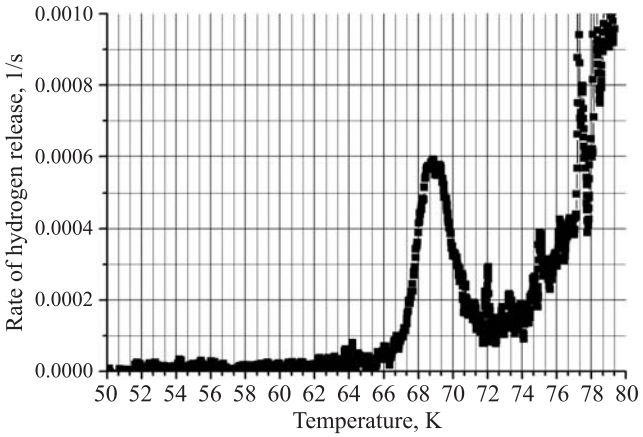

Fig. 9. The same as Fig. 7, for broader temperature range

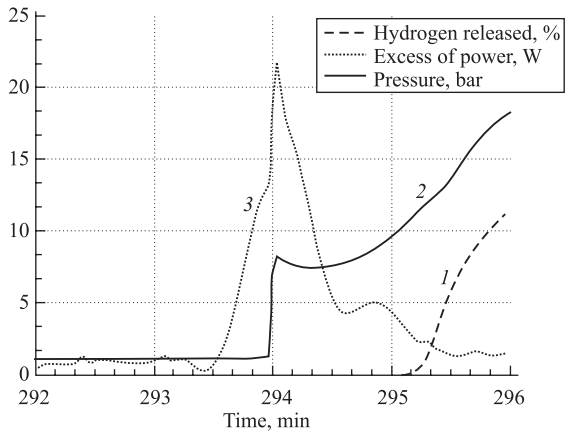

Fig. 10. Internal heat release (curve *3*, W) at the first stage of heating of irradiated methane. Curve *1* — hydrogen release, %; curve *2* — pressure on the membranes, bar

First phase — swelling of methane without releasing hydrogen. When solid methane sample is cooled down to lower temperature after solidification, a lot of unpercolated pores and grains inside bulky methane are formed because of strong adhesion of methane to metallic walls (aluminium sponge enhances this effect). During heating, pressure inside hydrogen gas bubbles goes up, until it becomes large enough to crack methane grains. Hydrogen is released partly (probably, 15–

20%) out of grains into pores, building up an internal pressure that causes in turn expansion of the sample (the sponge, in our case) which then follows temperature. The process of methane grain disintegration and release of the compressed gas is favoured by fast heat release due to the recombination of radicals, which are partly (around 1%) still «alive» at $\mathrm{T} > 35$ K (see Figs. 5 and 10).

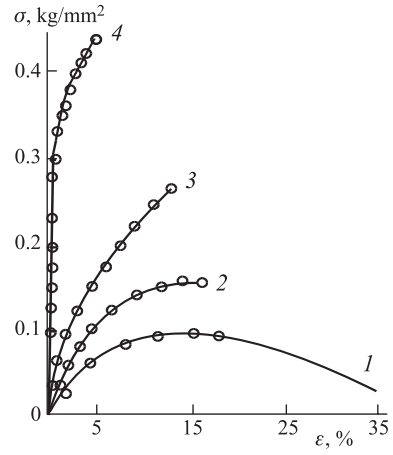

Fig. 11. Uniaxial tensile stress-strain curves σ at the deformation rate $d\varepsilon/dt = 3.3 \cdot 10^{-4}\mathrm{s}^{-1}$ on a polycrystal CH_4: *1*) $T = 77$ K; *2*) $T = 64$ K; *3*) $T = 20$ K; *4*) $T = 4.2$ K

Second phase. When temperature of methane becomes large enough (about 64 K after long irradiation) to cause plastic deformation of methane under pressure of gas inside pores, the hydrogen gas escapes fast now that the cavities are percolated (the peak in Fig. 9). At this phase, swelling of methane reaches the maximum because the remaining gas cannot press methane having free paths for escape. Methane at this stage is viscous-plastic, that is why its deformation decreases slow after hydrogen gas in bubbles escaped. After the second phase, most part of hydrogen is still kept dissolved in the methane matrix as isolated molecules.

Temperature and pressure of gas at the first and second phases of the process of hydrogen release are determined by stress-stain diagram of solid methane, Fig. 11 [10]. The diagram for irradiated methane is unknown but analysis showed that if one uses that of fresh methane, experimental facts more or less agree with this theory. Really, at low dose of irradiation (6 h of irradiation, 4.9 MGy) temperature of the beginning of hydrogen release (81 K) corresponds to strength yield for uniaxial tension ~ 10 bar, and experiment gives 13 bar pressure on the membranes. At high dose of irradiation (30 h of irradiation, 27 MGy) temperature of the beginning of hydrogen release (64–67 K) corresponds to strength yield 16–17 bar, and about 20 bar was observed in experiment.

The presence of the maximum of the peak displacement of the membranes with absorbed dose is evident because decomposition of methane at doses 20–35 MGy reaches 20–30%. At such a grade of decomposition, the remaining substance has mechanical property totally different from that of methane, and it seems to be more pliable. As a result, hydrogen escapes at lower pressure.

From experimental phenomena, it is possible to make estimation of volume of pores at temperature of irradiation (low temperature) — about 9–10%. During heating, this volume decreases down to $5.5 \div 6.5\%$ at 60–65 K. Adding to that a volume of maximal swelling of methane, we have $11 \div 12\%$. This value is close

to elongation of methane at ultimate strength on stress-stain diagram of fresh methane, which confirms hypothesis of a cracked methane.

Third phase. When all hydrogen, accumulated in gas bubbles, is released, the remaining hydrogen molecules diffuse through fragments of grains of methane, which is now in the viscous-plastic state, following Arrhenius law (see Fig. 8). Then, they come out fast along percolated passes. A temperature increase of 2.1 K gives two-fold rate of hydrogen release. For solid methane in the IBR-2 moderator, this was 1.4 K for two-fold rate. In this manner, the presence of the sponge defines distinctions in hydrogen release from bulky methane.

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