



INEEL/CON-99-00078
PREPRINT

Hydrogen Release From Irradiated Vanadium Alloy V-4Cr-Ti

A. Kh. Klepikov
O. G. Romanenko
Y. V. Chikhray
I. L. Tazhibaeva
V. P. Shestakov
G. R. Longhurst

September 1999

5th International Symposium on Fusion Nuclear Technology

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint should not be cited or reproduced without permission of the author.

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, or any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use, or the results of such use, of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights. The views expressed in this paper are not necessarily those of the U.S. Government or the sponsoring agency.

HYDROGEN RELEASE FROM IRRADIATED VANADIUM ALLOY V-4CR-4TI

A.Kh.Klepikov, O.G. Romanenko, Y.V. Chikhray, I.L. Tazhibaeva, V.P. Shestakov

SRIETP of Kazakh State University, Tole bi 96a, Almaty, Kazakhstan, 480012

Phone: 7(3272)691917, Fax: 7(3272)503978, E-mail: klepikov@ietp.alma-ata.su

G.R. Longhurst^a

Idaho National Engineering and Environmental Laboratory

P.O. Box 1625, Idaho Falls, ID 83415-3860, USA

Phone 208 526 9950, Fax 208-526-2930, E-mail: gxl@inel.gov

Abstract

The present work is an attempt to obtain data concerning the influence of neutron and γ irradiation upon hydrogen retention in V-4Cr-4Ti vanadium alloy. The experiments on in-pile loading of vanadium alloy specimens at the neutron flux density 10^{14} n/cm²s, hydrogen pressure of 80 Pa, and temperatures of 563, 613, and 773 K were carried out using the IVG.1M reactor of the Kazakhstan National Nuclear Center. A preliminary set of loading/degassing experiments with non-irradiated material has been carried out to obtain data on hydrogen interaction with vanadium alloy. The data presented in this work are related both to non-irradiated and irradiated samples.

Key words

Hydrogen retention and release, irradiated materials, vanadium alloys

^a Support provided by U.S. Department of Energy, Office of Science under DOE Idaho Operations Office Contract DE-AC07-94ID13233

1. Introduction

The interest in the vanadium based alloy V-4Cr-4Ti for fusion application is connected with its excellent resistance to radiation swelling, low induced radioactivity and good thermal conductivity[1]. If we consider possible future application of this alloy as a DEMO breeder blanket material, its behavior with respect to hydrogen isotope retention will be very important, particularly at temperatures typical of those in a breeding blanket, which could be up to 800°C [2].

Numerous studies have been performed regarding activation, swelling, and mechanical properties of vanadium and vanadium alloys [3], but little work has been done on interactions with hydrogen isotopes. Abruzov et al. [4] injected pure vanadium and V-4Cr-4Ti with 700-keV deuterons at room temperature to a dose of $(0.01 - 2) \times 10^{22}$ D/m². They found a saturation effect in the amount of deuterium they could detect with D(d,p)T nuclear reaction analysis. The maximum deuterium concentration occurred at the location of the maximum number of vacancies predicted by TRIM 95. In pure vanadium, they found no migration of implanted deuterium during room-temperature storage, but pausing implantation led to a reduction in inventory in the alloy. They also observed a monotonically decreasing ion dose dependence on retained deuterium. They assumed deuterium traps in vanadium were vacancy-type defects that become saturated by self annealing and found the Ti content influences the amount retained (more Ti leads to lower retained D).

Röhrig et al.[5] found that hydrogen could be accommodated in V-4Cr-4Ti up to about 2.5 at.% but higher concentrations led to significantly weakening of the material, probably because of the formation and precipitation of hydrides. Pretreatment with

oxygen made the hydrogen threshold level for weakening less than 1 at.%. They confirmed Sieverts' law solubility and concluded that the alloy seems to behave like pure metal with respect to hydrogen solubility.

Saitoh et al.[6], using radioluminography, studied tritium distribution in vanadium. Tritium had been added to a vanadium sample by cathodic charging. They found that the tritium concentration evident depended on the grain orientation and related to variations in the amount of precipitated hydride.

The purpose of this work is to investigate uptake and retention issues in the V-4Cr-4Ti alloy, particularly those that may be associated with the radiation environment of a fusion blanket.

2. Experimental.

2.1 Samples

To perform preliminary experiments for non-irradiated material, a sample with dimensions 1×5×55mm was cut from a plate of V-4Cr-4Ti vanadium alloy (Russian production). The chemical composition of the sample is given in Table 1. Samples with the dimensions 1×3×55 mm were cut of the same plate of V-4Cr-4Ti vanadium alloy to be loaded with hydrogen in in-pile experiments.

2.2 Technique and results obtained

2.2.1 Out-of-pile experiments

In order to determine the hydrogen solubility in non-irradiated V-4Cr-4Ti material, preliminary experiments were carried out that involved loading a vanadium alloy sample

with hydrogen followed by degassing using thermal desorption spectroscopy (TDS). The experimental device “Orchideya” [7] was used to perform these experiments.

After positioning an as-received sample in the experimental chamber, a TDS spectrum was obtained. Figure 1 shows the thermodesorption spectrum of an as-received vanadium alloy sample without any pre-treatment. The rate of heating was uniform at 20 K/min. One can see the only peak at 750 K. Annealing at 1073 K alters the release characteristic, as will be shown later, but it can be restored by exposing the sample to air. Figure 1 also shows the TDS curve for such an air-exposed sample for comparison.

After the initial TDS measurement, the sample was annealed at 1073 K in high vacuum (10^{-7} Pa) for 1 hour. Then experiments to determine hydrogen solubility in vanadium alloy were implemented. In those experiments, the sample was heated to the loading temperature, hydrogen was admitted to the experimental chamber (10-100 Pa), the sample was exposed to hydrogen for the predetermined time, then the temperature was decreased to room temperature (average time of temperature decrease was about 90 s). After that, hydrogen was pumped out and the sample was ready for the TDS measurement.

To determine the time required for loading up to the equilibrium concentration, the set of loading experiments was carried out at fixed pressure and at several fixed temperatures for different times of charging. Figure 2 shows the thermodesorption spectra for the sample charged with hydrogen at fixed pressure (66Pa) and temperature (773K) but at different times of loading. One can see the fixed TDS peak position at 880K.

Figure 3 shows the dependence of released hydrogen on the time of loading. The amount of hydrogen dissolved was assumed to be equal to the amount released in the thermodesorption experiment and was calculated from the TDS spectra. Equilibrium

concentrations, calculated from the steady-state values of gas release (673-873 K), are given in Table 2.

Hydrogen solubility calculated on the basis of these data appears to follow Sieverts law in this range of temperature and loading pressures (10-100 Pa) and can be described by expression:

$$S\left(\frac{\text{mole}}{\text{m}^3 \sqrt{\text{Pa}}}\right) = 0.414 \exp\left(\frac{0.255 \text{ eV}}{kT}\right) \quad (1)$$

As shown in Figure 4, this compares well with the solubility for pure vanadium given by Smithels [8] and with that used by Röhrig et al. [9], which is effectively identical with Smithels' value.

Keeping in mind the loading times necessary to achieve equilibrium saturation at different temperatures, experiments on equilibrium charging followed by TDS experiments were implemented. Fig.5 represents the TDS spectra for the sample loaded with hydrogen at the fixed pressure of 66 Pa up to the equilibrium content at different temperatures. One can see again that the position of the TDS peak is the same (880K) for all curves.

To clarify the situation concerning the different positions of TDS peaks for the as-received sample (750K) and the after-annealing sample at the elevated temperatures, an experiment with a slightly oxidized sample was performed. Sample exposure to an air atmosphere at room temperature after a set of sorption/thermodesorption experiments resulted in the shift of the TDS peak to the same position as for the as-received sample. This was shown in Figure 1.

2.2.2 In-pile experiments

The experimental device “Liana” [10] was used to charge the samples of V-4Cr-4Ti vanadium alloy with hydrogen under the influence of reactor irradiation. Samples were inserted into three different containers made of stainless steel and having different wall thickness. Containers with the samples were pumped out and then filled with a high purity hydrogen admitted through a diffusion palladium-silver filter up to the pressure $P=80$ Pa. They were then positioned into the IVG 1M reactor core. The stainless steel containers were heated in the reactor core by gamma irradiation and cooled with gaseous nitrogen. Each container was at a different temperature because of different container wall thickness. Containers were designed after performing γ -neutron and thermal calculations to achieve the desired temperatures in the pile core. Temperatures achieved in the experiments (563K, 613K, 773K) were well consistent with the calculations previously performed.

Conditions of the samples while being charged with hydrogen under the influence of reactor irradiation are represented in Table 3.

TDS spectra for the V-Cr-4Ti4 samples charged with hydrogen under in-pile conditions and for the control samples charged at the same pressure, temperatures and within the same time of loading but otherwise under out-of-pile conditions, are represented in Figures 6 and 7. It is clearly seen that TDS peaks for the control samples have the same position for the different temperatures of loading and coincide with those for the as-received sample and for the sample exposed to air after loading with hydrogen. Hydrogen contents calculated from TDS spectra for both in-pile loaded samples and control samples are presented in Table 4.

3. Discussion of results obtained

There are two fundamental questions arising from this work. The first is an explanation for why the TDS peaks in the solubility measurements are all at the same temperatures and have the shapes they do. The second is what is different about the in-pile conditions that cause the TDS peaks to be different.

Figures 2 and 5 demonstrate that the position of the TDS peaks is the same (880K) for different initial hydrogen concentrations in the sample and different loading temperatures. Commonly, such a TDS peak behavior is typical for the case when the rate of hydrogen release is limited by a diffusion process. But attempts to describe the obtained experimental results in the framework of a simple diffusion driven model failed to replicate the TDS peak shape. It was possible to replicate the shape if one assumed the high diffusivity in vanadium alloy and limitation of release rate by the slow diffusion in the surface layer. The question is how to explain the observations.

The influence of the sample surface upon hydrogen release kinetics for the as-received and air-exposed samples is clearly seen from the abrupt leading edge of the desorption peaks in their TDS spectra (Figure 1). When compared with the shape of the TDS curves from previously hydrogen-exposed and annealed sample (Figures 2 and 5), it is obvious that there is a different process controlling release in the 600 – 800 K range. Therefore, it seemed reasonable to apply a recombination-limited model for experimental results. Conformance to Sieverts' law suggested it be second order.

Separately taken TDS spectra from Fig. 5 could be rather easily described in the framework of common second order recombination desorption model with reasonable values for recombination coefficients. But when describing the set of TDS spectra using a

common second order desorption model , there was a visible shift of the peak to the side of higher temperatures with the decreasing of the initial hydrogen concentration in the sample. Such a shift in TDS peak temperature is a known fact for the mechanism of recombination when two atoms recombine from similar sites. It can be shown that the TDS peak will not shift with initial concentration in the sample if the release rate is diffusion limited rather than recombination limited. The differences in TDS spectra for the as-received and air-exposed samples and the annealed one (Figs.1 and 2) convinced us that it is necessary to take into account the possible changes in the elemental compositions both of surface and subsurface regions of the samples.

Another possibility was that recombination was dominant at lower temperatures and diffusion was dominant at higher temperatures. That could be accomplished with a high activation energy for recombination as compared with a lower activation energy for diffusion. As an example Fig. 8 shows that observed TDS peak behavior could be moderately well explained when using the values:

$$K_R \left(\frac{\text{m}^4}{\text{s}} \right) = \frac{4.214 \times 10^{-22}}{\sqrt{T}} \exp \left(- \frac{1.4 \text{ eV}}{kT} \right) \quad (2)$$

$$D \left(\frac{\text{m}^2}{\text{s}} \right) = 6.4 \times 10^{-8} \exp \left(- \frac{0.35 \text{ eV}}{kT} \right), \quad (3)$$

where K_R is a recombination coefficient; D is a diffusivity; k is Boltzman's constant and T is temperature. For comparison, Völkl and Alefeld [11] gave diffusivity in pure vanadium as

$$D \left(\frac{\text{m}^2}{\text{s}} \right) = 3.1 \times 10^{-8} \exp \left(- \frac{0.045 \text{ eV}}{kT} \right). \quad (4)$$

A further assumption was that there was a surface film that was impervious until a temperature of 680 K was reached. This was suggested by the observation that essentially no hydrogen was seen coming out of the samples until that temperature had been reached even though conventional diffusion and trapping theory would have it leaving at lower temperatures. It also corresponds approximately to phase transition temperatures of slightly oxidized (5 – 30 at.%) vanadium [12].

The results for in-pile experiments and corresponding control experiments demonstrate that equilibrium saturation with hydrogen was not achieved in these experiments in spite of the fact that according to Fig.3 it should occur approximately in an hour of exposing the samples to hydrogen at any of the specified temperatures. Because the TDS curves in Figures 6 and 7 exhibit the abrupt low-temperature edge characteristic of as-received and air-exposed samples, it is probable that a contaminating film inhibited uptake in the samples. Without knowing the equilibrium concentration of hydrogen in the samples, little could be deduced about the effects of the irradiation environment on solubility. To clarify the influence of neutron and gamma irradiation upon hydrogen retention in V-4Cr-4Ti vanadium alloy additional in-pile experiments are needed.

4. Conclusions

The experiments on in-pile loading of vanadium alloy specimens at the neutron flux density 10^{14} n/cm²s, hydrogen pressure of 80 Pa, and temperatures of 563, 613, and 773 K were carried out using the IVG.1M reactor of the Kazakhstan National Nuclear Center.

A preliminary set of loading/degassing experiments with non-irradiated material has been carried out in the temperature range 673-1073K and loading pressures (10-100 Pa). Hydrogen solubility in non-irradiated V-4Cr-4Ti alloy appeared to follow Sieverts' law within this range of temperatures and loading pressures and to be similar to solubility in the pure metal.

Based on the experimental data obtained possible mechanisms of hydrogen release from the V-4Cr-4Ti alloy have been discussed. While it appears that diffusion dominates release at higher temperatures, at lower temperatures there appears to be a strong surface effect. That could be due to a film that is impermeable at temperatures below about 680 K.

The results for in-pile experiments and corresponding control experiments for that demonstrate that equilibrium saturation with hydrogen was not achieved in these experiments. That could be due to surface film development. To clarify the influence of neutron and gamma irradiation upon hydrogen retention in V-4Cr-4Ti vanadium alloy additional in-pile experiments are needed.

Acknowledgements

Authors would like to express especial acknowledgements to E.A. Kenzhin, A.V. Zvonarev, D.I. Zelenskiy and B.O. Korshiev for assistance in implementation experiments.

References

1. E. E. Bloom, The challenge of developing structural materials for fusion power systems, J. Nucl. Mater. 258-263 (1998) 7-17.

2. M. I. Solonin, Materials science problems of blankets in Russian concept of fusion reactor, J. Nucl. Mater. 258-263 (1998) 30-46.
3. See, for examples: D.L. Smith, M.C. Billone, S. Majumdar et al., Materials integration issues for high performance fusion power systems, J. Nucl. Mater. 258-263 (1998) 65-73; T. Muroga, S. Ohnuki, F.A. Garner et al. The influence of neutron spectrum and irradiation history on microstructural evolution in fusion structural materials, J. Nucl. Mater. 258-263 (1998) 130-139; S. J. Zinkle, H. Matsui, D.L. Smith et al., Research and development on vanadium alloys for fusion applications, J. Nucl. Mater. 258-263 (1998) 205-214; H. D. Röhrig, J. R. DiStefano, L. D. Chitwood, Effect of hydrogen and oxygen on the tensile properties of V-4Cr-4Ti, J. Nucl. Mater. 258-263 (1998) 1356-1360; T. Shibayama, I. Yamagata, H. Kayano, et al., Effect of small additional elements on DBTT of V-4Cr-4Ti irradiated at low temperatures, J. Nucl. Mater. 258-263 (1998) 1361-1368; R. J. Kurtz, M. L. Hamilton, H. Li, Grain boundary chemistry and heat treatment effects on the ductile-to-brittle transition behavior of vanadium alloys, J. Nucl. Mater. 258-263 (1998) 1375-1379; D.S. Gelles, P. M. Rice, S. J. Zinkle et. al., Microstructural examination of irradiated V-(4-5%)Cr-(4-5%)Ti, J. Nucl. Mater. 258-263 (1998) 1380-1385; and many more in that volume.
4. V. L. Abruzov, G. A. Raspopova, and V. B. Vykhodets, Radiation-induced segregation of deuterium in austenitic steels and vanadium alloys, J. Nucl. Mater. 271-272 (1999) 340-344.
5. H. D. Röhrig, J. R. DiStefano, L. D. Chitwood, Effect of hydrogen and oxygen on the tensile properties of V-4Cr-4Ti, J. Nucl. Mater. 258-263 (1998) 1356-1360.
6. H. Saitoh, T. Hishi, T. Misawa et al., Quantitative visualization of tritium distribution in vanadium by tritium radioluminography, J. Nucl. Mater. 258-263 (1998) 1404-1408.
7. I. L. Tazhibaeva, A. K. Klepikov, V. P. Shestakov et al., Hydrogen release of reactor irradiated RGT graphite, J. Nucl. Mater. 233-237 (1996) 1198-1206.
8. C. J. Smithells, Ed., Metals Reference Handbook, 5th Ed., Butterworths, London (1976) 846.
9. H. D. Röhrig et al., Effect of hydrogen and oxygen on the tensile properties of V-4Cr-4Ti, J. Nucl. Mater. 258-263 (1998) 1356-1360.
10. I.L. Tazhibaeva, V. Chikhray, O. G. Romanenko, A. Kh. Klepikov, Hydrogen permeability measurements of 08Cr18Ni10Ti stainless steel in fission reactor irradiation conditions, *Plasma Devices and Operations*, Vol.5, No.1 (1996) 71-76.
11. J. Volkl and G. Alefeld, in: G. Alefeld and J. Volkl Eds, *Hydrogen in Metals, Basic Properties*, Springer-Verlag, Berlin (1978) 333.

12. T. B. Massalaski, Ed., *Binary Alloy Phase Diagrams*, 2nd Ed, Vol 3 ASM International, Materials Park, Ohio, (1990) 2931.

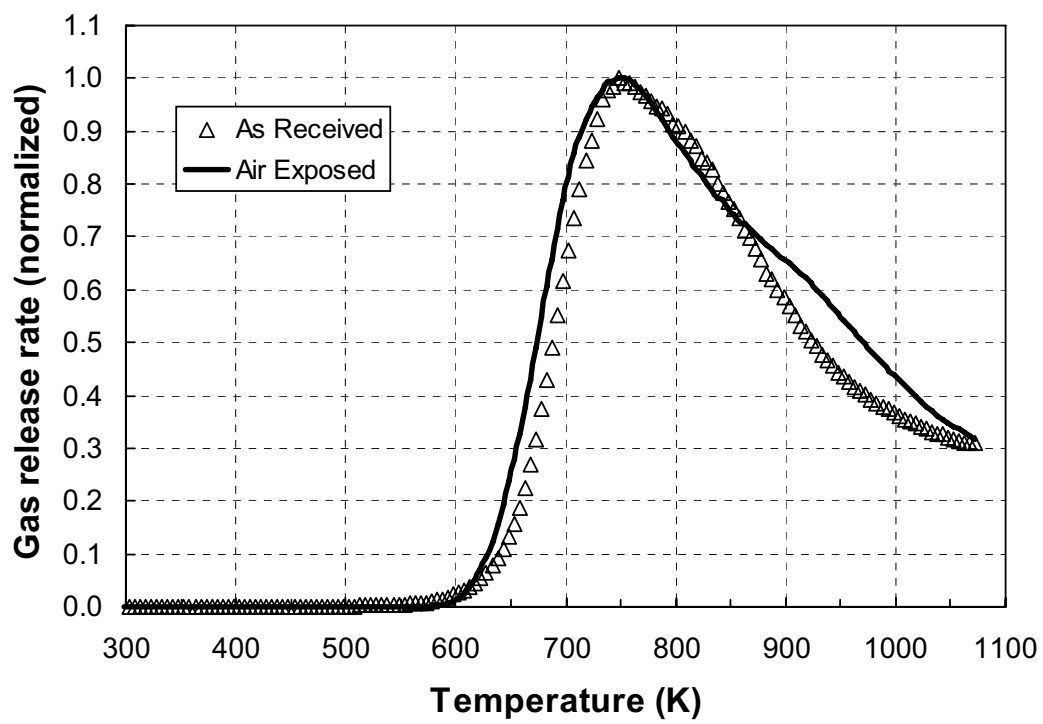


Fig.1 A.Kh.Klepikov

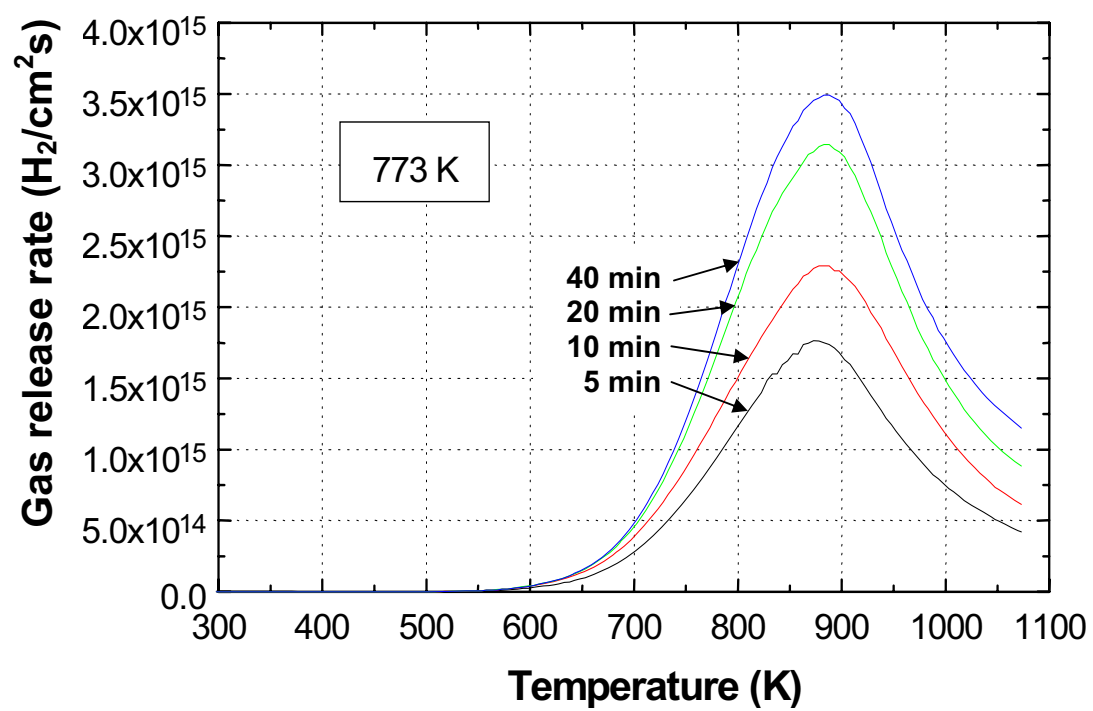


Fig. 2. *A.Kh.Klepikov*

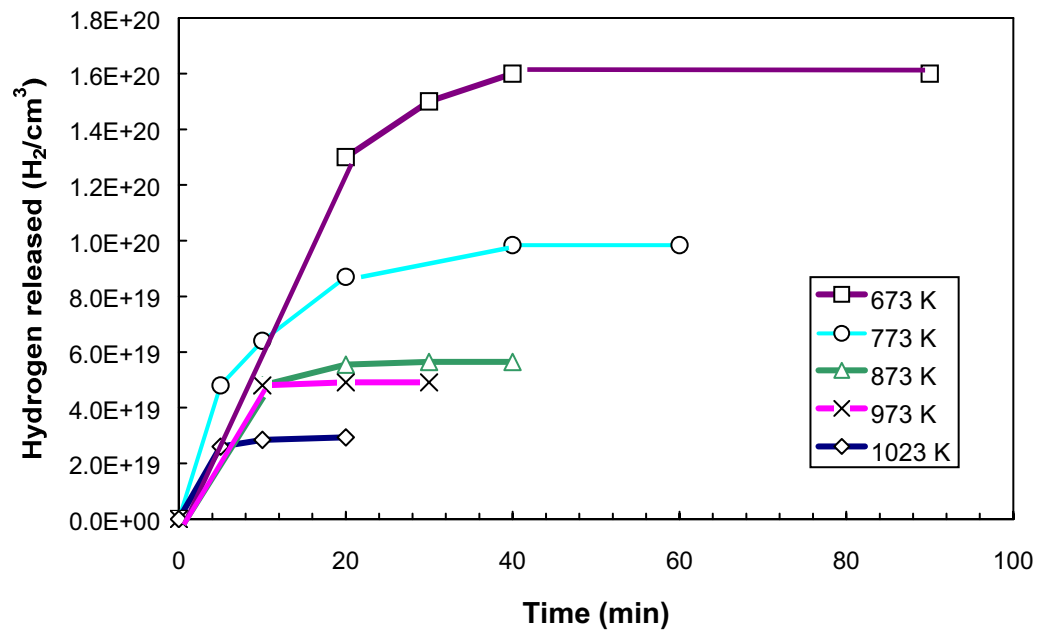


Fig. 3. A.Kh.Klepikov

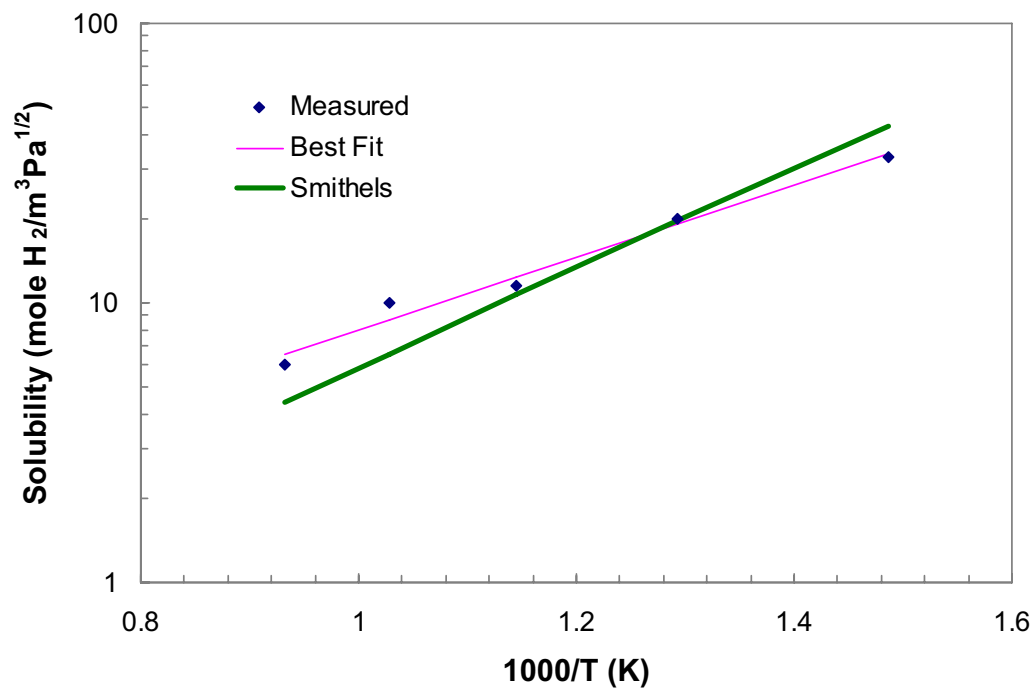


Fig.4 A.Kh.Klepikov

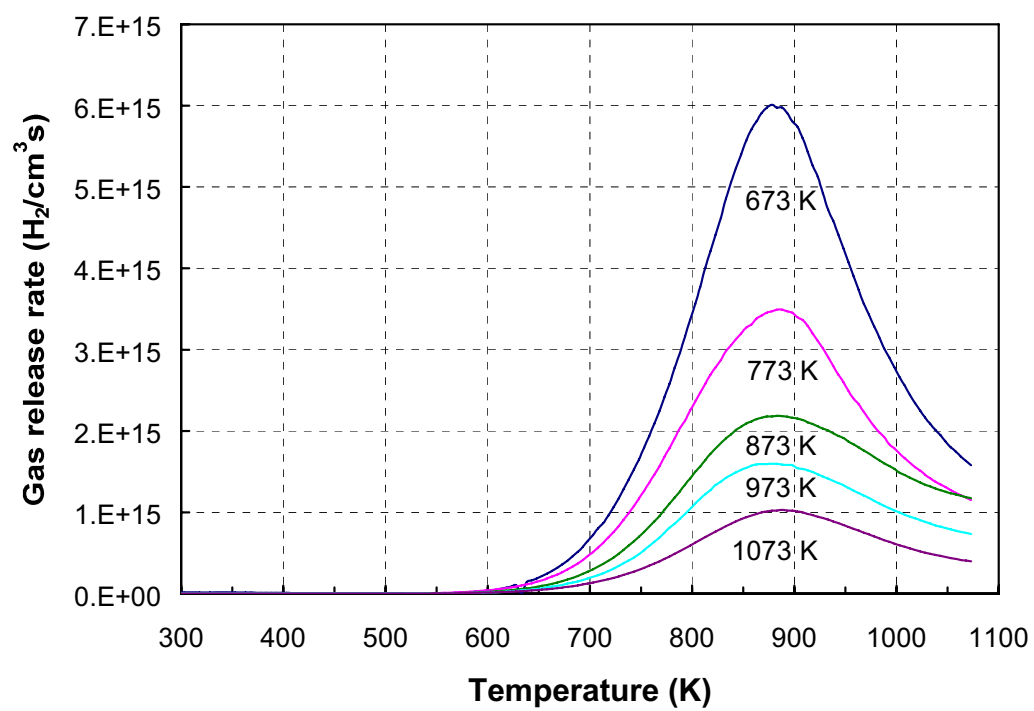


Fig. 5. *A.Kh.Klepikov*

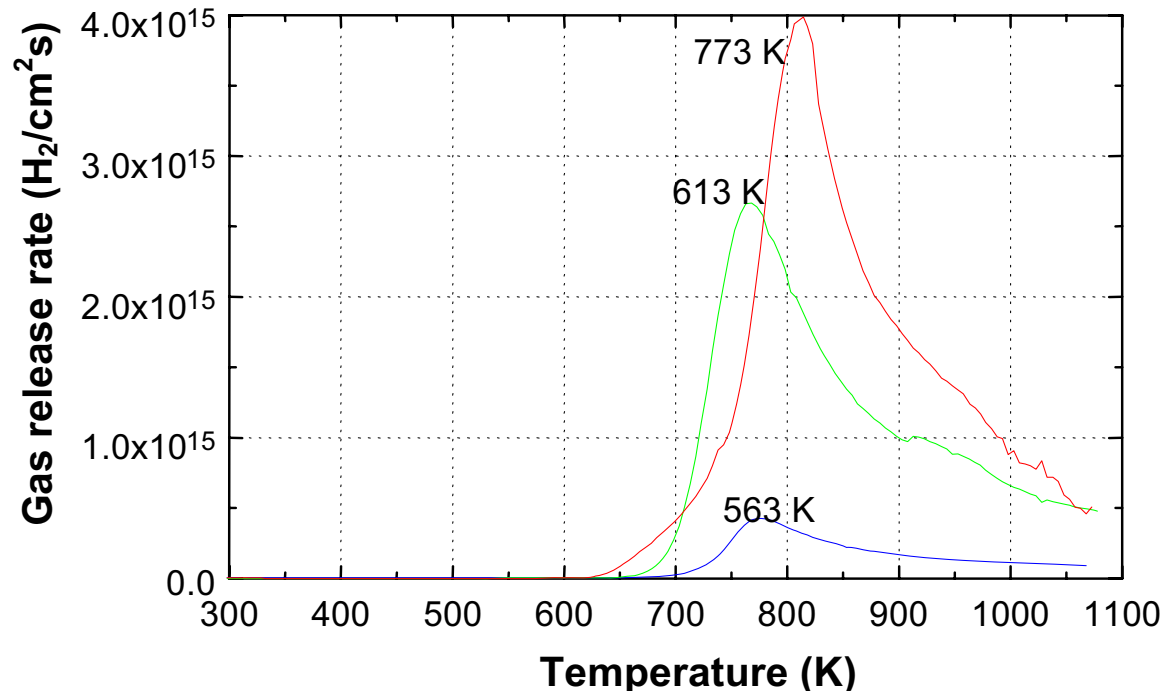


Fig. 6. *A.Kh.Klepikov*

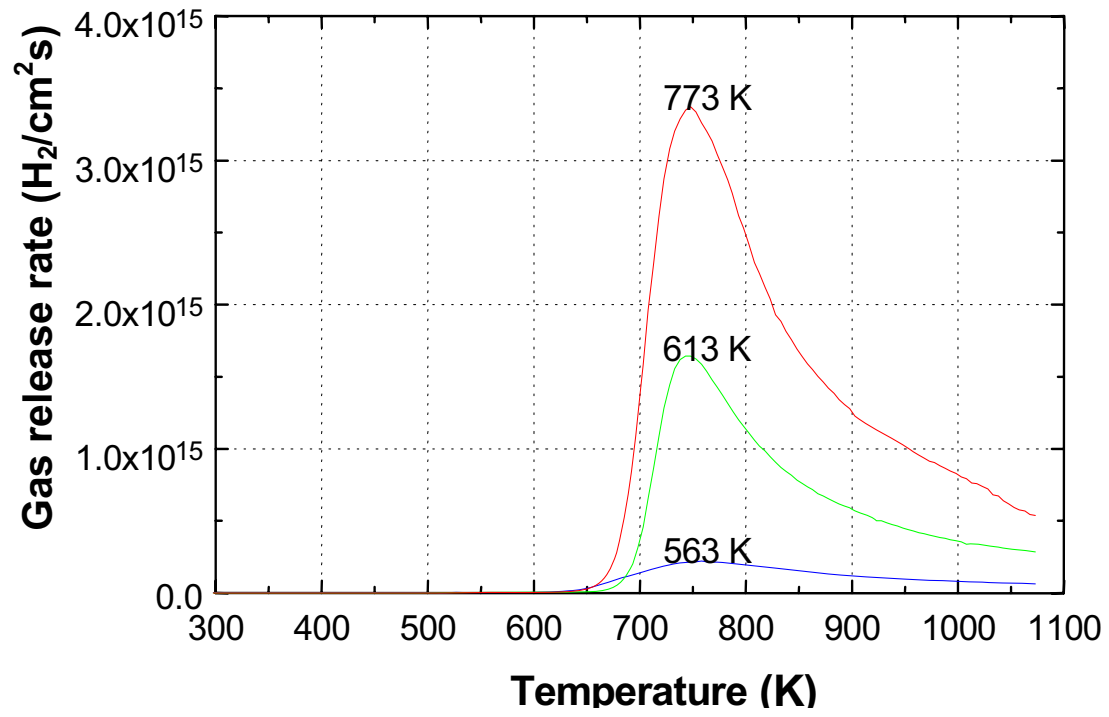


Fig. 7. *A.Kh.Klepikov*

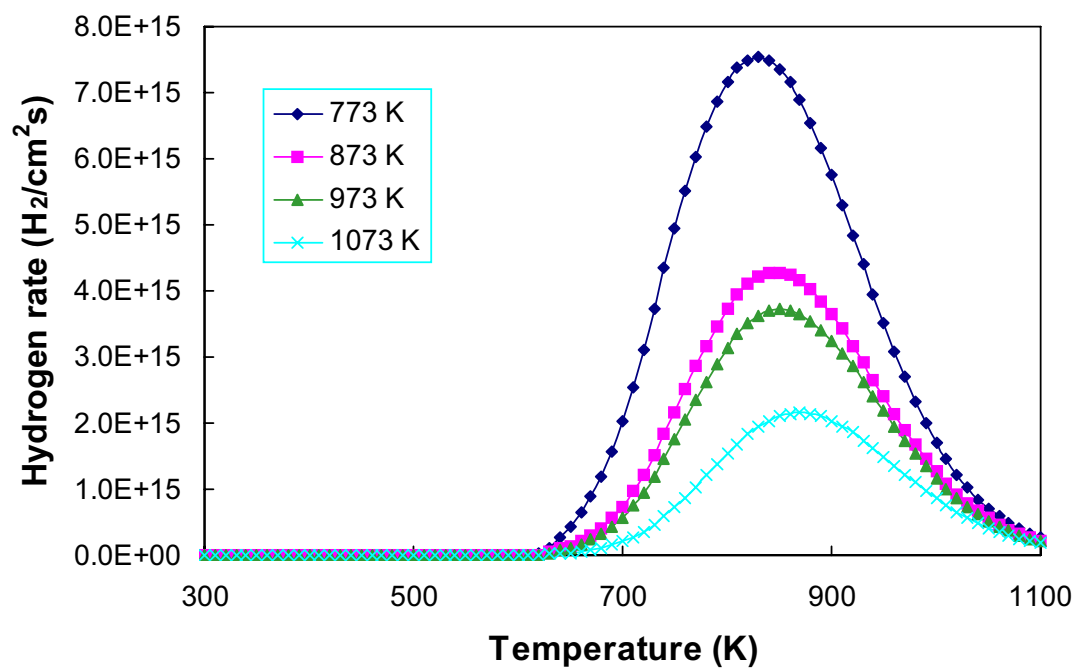


Fig.8 *A.Kh.Klepikov*

Table 1. Chemical composition of V-4Cr-4Ti vanadium alloy according to the data of manufacturer (Russia production)

Element	V	Cr	Ti	C	O ₂	N ₂	Fe	Si	Al	Nb	Mo	Zr
Content (%)	balance	4.1-4.2	3.9-4.2	0.01	0.025	0.01	0.01	0.03	0.05	<0.04	0.03	0.003

Table 2. Hydrogen equilibrium concentrations and solubility in the temperature range 673-873 K for loading pressure 66 Pa.

Loading temperature, K	Hydrogen released, H ₂ /cm ³	Solubility, S, mole/(m ³ *Pa ^{1/2})
673	1.62×10 ²⁰	33.07
773	9.84×10 ¹⁹	20.12
873	5.65×10 ¹⁹	11.55
973	4.91×10 ¹⁹	10.04
1073	2.94×10 ¹⁹	6.02

Table 3. Conditions of samples while being charged with hydrogen in the IVG.1M reactor.

Duration of loading, hours	Loading atmosphere	Flux/fluence of fast neutrons ($E > 0.1\text{MeV}$)	Flux/fluence of thermal neutrons ($E < 0.1\text{MeV}$)	Total flux/fluence
3	hydrogen	$1.0 \times 10^{13} \text{ n/cm}^2\text{s}$	$0.6 \times 10^{14} \text{ n/cm}^2\text{s}$	0.7×10^{14}
	P=80Pa	$1.1 \times 10^{17} \text{ n/cm}^2$	$6.0 \times 10^{17} \text{ n/cm}^2$	7.1×10^{17}

Table 4. Hydrogen contents calculated from TDS spectra for both in-pile loaded samples and control samples. Hydrogen pressure during loading was 80 Pa.

Loading temperature, K	Hydrogen released, H ₂ /cm ³	
	control samples	in-pile loaded samples
563	0.7×10^{18}	0.9×10^{18}
613	0.4×10^{19}	0.6×10^{19}
773	1.1×10^{19}	1.0×10^{19}

Fig.1 TDS curves of an as-received V-4Cr-4Ti sample and one exposed to air following hydrogen absorption and thermal desorption.

Fig. 2. TDS curves of hydrogen gas release from the vanadium alloy sample, that was loaded at the same pressure (66 Pa) and temperature ($T=773$ K) for different periods of time.

Fig. 3. Amount of released hydrogen depending on the loading time.

Fig.4 Temperature dependence of hydrogen solubility in V-4Cr-4Ti alloy compared with Smithels' value for pure vanadium.

Fig. 5. TDS curves of hydrogen gas release from the vanadium alloy sample that was loaded up to equilibrium concentration at different temperatures but a constant hydrogen pressure of 66 Pa. The rate of temperature ramping is 20K/min.

Fig. 6. TDS spectra for V-4Cr-4Ti vanadium alloy samples loaded with hydrogen for 3 hours at pressure 80 Pa and temperatures 563, 613, and 773 K under in-pile conditions. Temperature ramp rate was 20 K/min.

Fig. 7. TDS spectra for V-4Cr-4Ti vanadium alloy samples loaded with hydrogen for 3 hours at pressure 80 Pa and temperatures 563, 613, 773 K under out-of-pile conditions. Temperature ramp rate was 20 K/min.

Fig.8 TDS flux rates calculated by TMAP4 for assumed recombination –limited release at low temperatures and diffusion-limited release at high temperatures with a surface film that became permeable at 680 K.