Deuterium permeation of low-activation vanadium alloys possible for reuse in a short time in fusion reactors

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Low-activation vanadium (V) alloys are alternative to reduced-activation ferritic/martensitic steels for the blanket structural material. To make the reusage of the alloys possible in a short time, new-design concepts of V alloy have been suggested in National Institute for Fusion Science. In the present study, the deuterium permeation properties of the new-designed V alloys were investigated.

The new-designed V-4Cr-4Ti alloy samples with high and low purity, named H44 and L44, respectively, were used. For comparison, the NIFS-HEAT-2 V alloy samples, named NH2 were also used.

It was found from the permeation experiments that deuterium permeability coefficient of L44 was smaller than that of NH2, while the permeability coefficient of H44 was comparable with NH2. These results suggest the permeation coefficient of D of the new-designed V alloy was similar to those of the conventional V alloy, if Ti and O content was the same. Estimated activation energies of diffusion and permeation indicated that the permeation behaviors significantly depended on titanium oxides at the surface and in the bulk. Data obtained by a microscope with Auger electron spectroscopy indicated that the concentration and the composition of the oxide must change with air exposure during the maintenance and with hydrogen isotope exposure during the reactor operation. The obtained results suggest these changes of the concentration and the composition result in the change in the permeation characteristics of hydrogen isotopes.

Keywords: New-design concepts of low-activation vanadium alloy, Reusage in a short time, Deuterium permeation, Titanium oxide

1. Introduction

Low-activation vanadium alloys (V alloys) are one of candidates for component materials in fusion reactors due to high-temperature strength, superior irradiation properties and non-magnetic characteristics [1-7]. V-4Cr-4Ti alloy has been selected as the most promising alloy composition with a level of interstitial impurities (C, N and O) of < 1000 wppm [8, 9]. High purity V alloys containing much lower interstitial impurities, < 300 wppm, have been developed at National Institute for Fusion Science (NIFS) in collaboration with Japanese industries [10-14]. Based on this development, a new design concepts of V alloy have been suggested in NIFS possible for reuse in a short time by impurity reduction processing and compositional changes [15, 16], especially for titanium minimized. The conventional vanadium alloy, NIFS-HEAT-2, incorporated high-activation impurities such as Co, that made the material reuse in a short time hard [15]. In addition, because Ti as one of the alloy elements must contribute the contact dose rate responsible for the reuse in a short time, the reduction of the Ti concentration is one of the strategies for the development of vanadium alloy possible for the reuse in a short time [15]. Irradiation-induced defects, cluster and/or precipitates lead to hardening and embrittlement of vanadium alloys containing interstitial impurities [16]. Impurity reduction in the vanadium alloy as one of the strategies would contribute to the irradiation damage resistance and the suppression of the hydrogen embrittlement.

Hydrogen isotope permeation of component material is one of the key concerns because they are strongly connected with the reactor safety and its feasibility. The permeation properties through V alloys have been investigated so far. Cherkez et al. have reported the deuterium permeation through V-4Cr-4Ti alloy under plasma irradiation [17]. Deuterium permeation flux after plasma discharge initiation increased and reached value, which was one or two orders in magnitude larger than those obtained at permeation from the gas phase. Hatano et al. have reported the surface segregation and its influence on surface reaction rates of hydrogen isotope for V-4Cr-4Ti [18]. The segregation of Ti at the surface, which proceed above 523 K, significantly reduced the surface reaction rate of hydrogen isotope. Hayakawa et al. have reported hydrogen ingress into NIFS-HEAT-2 V alloy after polishing and subsequent heat treatment [19]. The permeation rates of hydrogen after the heat treatment were radically smaller than those which have been reported so far. These results indicated the strong barrier effect of Ti oxide on hydrogen ingress. Kulsartov et al. have investigated hydrogen permeation thorough V-4Cr-4Ti at the conditions of reactor irradiation, namely under neutron irradiation [20]. The irradiation resulted in a

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decrease of the apparent diffusion coefficients and the permeation constants for the alloy.

The new-designed V alloy described above must result in change in properties of hydrogen isotope permeation. The present study represents deuterium (D) permeation properties of the new-designed V alloys at operating temperature such as permeation coefficient, diffusion coefficient and activation energy of permeation. This paper was focused on the effects of impurities on the hydrogen permeation for the new-designed V alloys. The effects of precipitates, oxide and surface condition on the permeation properties were discussed. Based on the material comparison and discussion, some suggestions for material designation and operation in the points of views of hydrogen isotope permeation were addressed.

2. Experiments

The samples used and their composition are summarized in Table 1. The sample was discoid with a diameter of 11.5 mm and a thickness of 0.25 mm. The new-designed V-4Cr-4Ti alloy samples with high and low purity, named H44 and L44, respectively, were used. For comparison, the conventional V alloy, NIFS-HEAT-2 V alloy samples, named NH2, were also used. It is noted that content of impurities such as N, Mo and Si were minimized for the new-designed V alloys compared to the conventional NH2. Before the permeation experiment, each sample was electropolished with H_2SO_4/CH_3OH solution and then degassed in a vacuum at 1273 K for 1 h. After the degassing followed by an air-ventilation, the sample was introduced into an experimental setup for an evaluation of D permeability explained below.

Figure 1 shows the schematic diagram of the experimental setup for the evaluation of D permeability. The inset shows an enlarged diagram in the vicinity of the sample fixed. The sample after the degassing was fixed between upstream and downstream sides using VCR joints. The permeation area was 3.17×10^{-5} m^2. After the evaluation of the permeabilities, we confirmed no deuterium leakage through the sealing ring at room temperature. There would be no leakage during the preceding permeation experiments, because the obtained permeation data were similar to those of the conventional V alloy reported in another literature [19] as mentioned below. It is noted that the samples after the degassing encountered an air-venting before the fixing. After the fixing, both the upstream and the downstream sides were pumped out using vacuum pump systems. The vicinity of the samples could be heated up to 973 K using an infrared furnace controlled by a temperature program controller

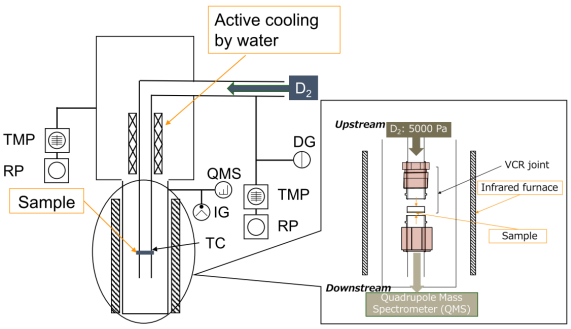

Fig. 1. Schematic diagram of the experimental setup for evaluation of deuterium permeability.

(TPC-5000, ULVAC) with an active water-cooling system placed above the sample.

Test temperatures for the evaluation of D permeation were taken in the range of 673 to 973 K, which was the operating temperature range in the reactor suggested in previous study [2]. The permeabilities of D were evaluated with elevating the sample temperature in steps and then lowering it in steps. Because the sample was exposed to the air before the installation into the setup for the evaluation of D permeability, the exposure developed a surface oxide layer. During elevating the temperature, the surface oxide condition must change. The permeability must be affected by the surface oxide condition. In fact, the hydrogen isotope permeation thorough vanadium [21] and V-4Cr-4Ti alloy [18, 19] significantly reduced with the surface oxide layer. On the other hand, the permeability must be affected a little while the subsequent evaluation with lowering the temperature, because the surface condition does not change during it in the present condition. Detail discussions on the surface condition are described below.

The permeation flux of D, J (mol m^{-2} s^{-1}), was quantitatively measured using a quadrupole mass spectrometer (M-431HG, ANELVA) on the downstream side. The spectrometer was calibrated with a D_2 standard leak (Vacuum Technology Inc.). If diffusion was rate-limited process on the D permeation, permeation coefficient, K (mol m^{-1} s^{-1} Pa$^{-1/2}$), was evaluated using the following relation,

$$J = DS\frac{\sqrt{P_{\mathrm{upstream}}}-\sqrt{P_{\mathrm{downstream}}}}{d} \sim K\frac{\sqrt{P_{\mathrm{upstream}}}}{d},$$

where D (m^2 s^{-1}) is diffusion coefficient, S (mol m^{-3} Pa$^{-1/2}$) solubility obeying Sieverts' law, K (mol m^{-1} s^{-1} Pa$^{-1/2}$) permeation coefficient, d (m) sample thickness, P_{upstream} and $P_{\mathrm{downstream}}$ (Pa) deuterium pressures in the upstream and the downstream side, respectively. Using a diagram vacuum gauge (WGI-470A S1-00,

Table 1. Atomic compositions of V alloy samples used in the present study.

Ref. ID	Cr	Ti	C	N	O	Mo	Al	Si
L44	3.93	3.91	0.006	0.006	0.036	<0.001	0.009	0.016
H44	4.11	3.89	0.008	0.003	0.018	<0.001	0.018	0.02
NH2	4.02	3.98	0.0069	0.0122	0.0148	0.0024	0.0059	0.027

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KYOWA), P_{upstream} was measured on the upstream side, and P_{upstream} was taken to be around 5000 Pa. It is noted that permeation coefficients were estimated in the present study under the assumption that D diffusion was rate-limited process on the D permeation.

A diffusion coefficient was evaluated by time-lag method [22], under an assumption that only diffusion process is responsible for initial and transient increase in the permeation flux.

Apparent activation energies of diffusion and permeation were estimated by the following relations,

$$D = D_0 \exp\left(-\frac{E_\mathrm{D}}{RT}\right)$$

$$K = DS = D_0 S_0 \exp\left(-\frac{E_\mathrm{D}+\Delta H_\mathrm{S}}{RT}\right) = D_0 S_0 \exp\left(-\frac{E_\mathrm{P}}{RT}\right),$$

where D_0 ($\mathrm{m^2\ s^{-1}}$) is frequency factor of diffusion, E_D (J $\mathrm{mol^{-1}}$) apparent activation energy of diffusion, R (J $\mathrm{mol^{-1}\ K^{-1}}$) gas constant, T (K) sample temperature, S_0 (mol $\mathrm{m^{-3}\ Pa^{-1/2}}$) solubility when the temperature goes to infinity, ΔH_S (J $\mathrm{mol^{-1}}$) enthalpy of solution, E_P (J $\mathrm{mol^{-1}}$) apparent activation energy of permeation, respectively.

For discussion, microstructures and compositional profiles inside and as-degassed samples were evaluated by Auger electron spectroscopy, JAMP-9500F(JEOL), after cross section polishing using SM-09010 (JEOL).

3. Results and discussion

Figure 2 shows Arrhenius plots of permeation coefficient of the new-designed V alloy evaluated in the present study. For reference, data of the conventional V alloy, NH2, were also shown. As described before, it is noted that the sample must have a surface oxide layer during the permeation experiment with elevating the temperature. The oxide layer must be developed during the air exposure prior to the installation into the permeation setup. On the other hand, the permeability must be affected a little while the subsequent evaluation with lowering the temperature. The permeation coefficients of H44 were similar to those of NH2, while the coefficients of L44 were smaller than other samples. In addition, permeation coefficients obtained during elevating temperature were smaller than those subsequently obtained during lowering temperature subsequently.

For the data during elevating temperature, the permeation coefficients of all samples had a linear relationship except those at 673 K. This indicates that all samples except 673 K would have similar surface and bulk condition. These are coincident with the facts that reduction of V oxide in NIFS-HEAT-2 occurs above 773K while reduction of Ti oxide does not occur below 973 K [17]. In addition, the coefficients of the new-designed V alloys increased with the sample temperature similarly to those of NIFS-HEAT-2 after the heat treatment, in which surface reaction was rate-limited process in the permeation [19]. This suggests that D permeation through all materials evaluated with elevating the temperature in the present study would be controlled mainly by surface reaction. This speculation is also consistent with the facts that Ti segregation at the surface occurs at (523-1023) K [18], and the permeation flux is controlled by Ti-enriched surface [23].

For the obtained data with lowering temperature after the temperature-elevation experiments, L44 sample had the same tendency with the sample temperature as the data with elevating temperature, namely the permeation coefficient decreased with a decrease in the temperature. This suggest that the surface reaction was rate-limited process for L44 sample during the evaluation of permeation coefficients with lowering temperature. On the other hand, diffusion would be mainly rate-limited process on D permeation for NH2 and H44 samples,

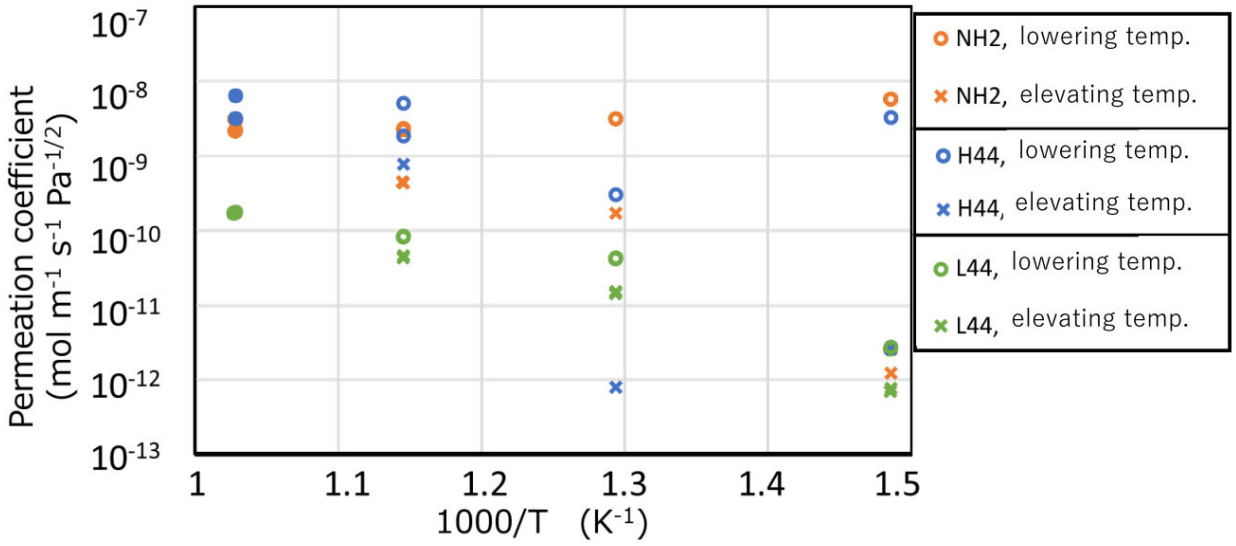

Fig. 2. Deuterium permeation coefficient of the new-designed V alloys, H44 and L44. The data of the conventional V alloy, NH2, were also shown for comparison. It is noted that permeation coefficients were obtained in the present study under the assumption that D diffusion was rate-limited process on the D permeation.

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because NH2 and H44 had very weak temperature dependencies, which were similar to the mechanically polished V alloy, in which diffusion was rate-limited process [19]. In addition, the increase of permeation coefficient for NH2 with a decrease in the sample temperature suggests that diffusion is rate-limited process on the permeation [24]. In other words, the reduction of Ti oxide would proceed for NH2 and H44, while Ti oxide still exists for L44 at 973 K because of large oxygen content.

We have obtained the permeation data at every permeation experiment, until the permeation flux was almost constant. So, we have not obtained the permeation coefficient during the transient regime at 973 K. The reduction of Ti-O would proceed at 973 K, so that the permeation flux might increase compared to the case in the existence of TiO. However, the linearities of Arrhenius plots for the data with elevating temperature indicated that the contribution of the reduction to the increase of the permeation flux at 973 K was small.

Evaluated apparent activation energies of permeation and diffusion are summarized in Table 2 and 3, respectively. Minus values in the activation energy of diffusion resulted from effects of enthalpy of solution. The apparent activation energies of permeation and diffusion varied with the surface condition. The energies for H44 were similar to those for NH2 obtained during lowering temperature. These results suggest that the permeation behavior of the new-designed V alloy was similar to NH2, if Ti and O content was the same. It is noted that the activation energy for H44 during lowering temperature was quite similar to that of tritium diffusion in NIFS-HEAT-2 [25]

Element map inside as-degassed L44 sample are shown in Figure 3. TiCON precipitates were formed after the degassing. TiCON [26, 27] must influence deuterium permeation/diffusion properties because they could re-trap deuterium. Evolution of surface condition and their effects on D permeation of V alloy are summarized in Figure 4. It is noted that the surface conditions in fig. 4 are speculation from other literatures.

Table 2. Apparent activation energy of permeation, $E_P(=E_D + \Delta H_S)$ (kJ mol^{-1}), in V alloy estimated in the present study.

	NH2	H44	L44
Elevating Temperature	156	194	98
Lowering Temperature	-25	43	75

Table 3. Apparent activation energy of diffusion, E_D (kJ mol^{-1}), in V alloy estimated in the present study.

	NH2	H44	L44
Elevating Temperature	-97	71	93
Lowering Temperature	-28	11	86

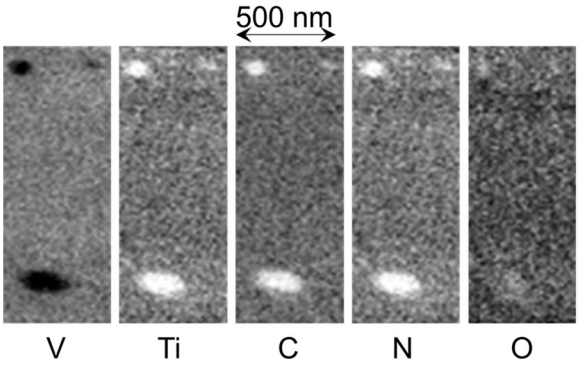

Fig. 3. Element map inside as-degassed L44 sample.

4. Conclusion

The new-design concepts of V alloy have been suggested in NIFS to make the reusage of the alloys possible in a short time. In the present study, D permeation properties of the new-designed V alloys at operating temperature such as permeation coefficients and activation energies of permeation.

The permeation coefficient of D of the new-designed V alloy was similar to those of the conventional V alloy, if Ti and O content was the same. The surface oxide layer and TiCON segregate formed during degassing (heat treatment) and air-ventilation significantly affect D permeation behaviors in this alloy.

The concentration and composition of the oxide must change with air exposure during the maintenance and with hydrogen isotope exposure during the reactor operation.

In the new design concept, Ti content would be reduced if impurities of C, N and O would decrease in the alloy. The obtained results suggest that the new-designed V alloy with low Ti and O content would show stable permeation characteristics for hydrogen isotopes because of the absence of TiCON segregate. A coating of stable permeation barrier film might be necessary to suppress the change in hydrogen isotope permeation during operation/maintenance.

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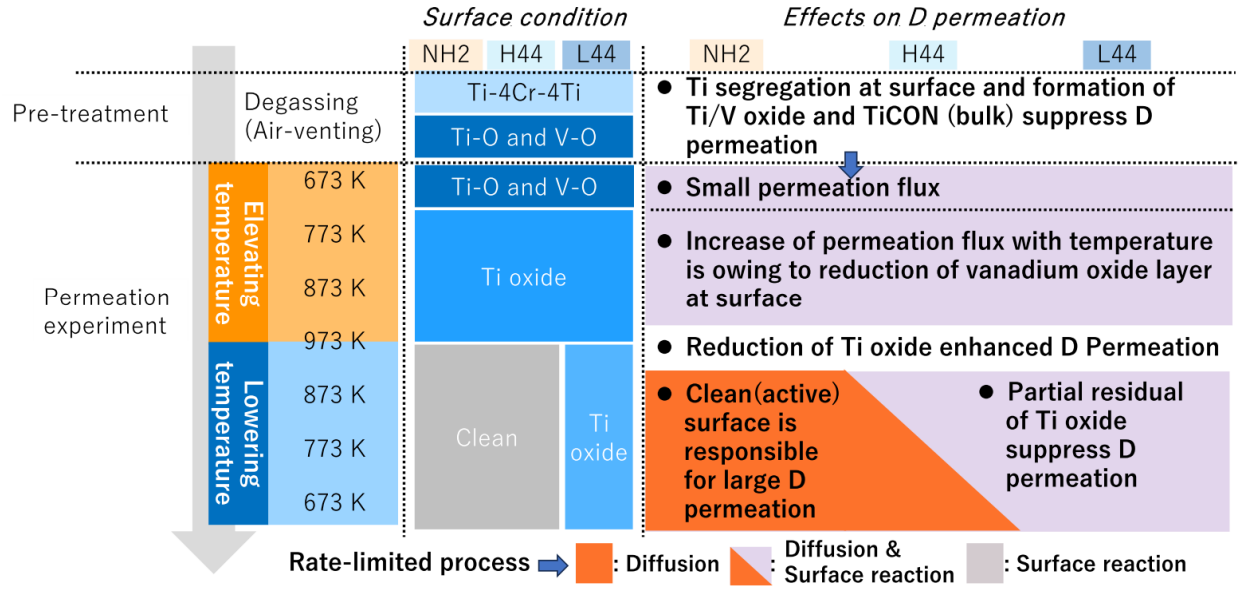

Fig. 4. Evolution of surface condition and their effects on D permeation of V alloy evaluated in the present study.

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