



Investigation of palladium alloy properties degradation during long-time tritium exposure

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Abstract

The investigation of life-time properties of Russian industrial Pd-membrane alloy V-1, as a material for a palladium diffuser of the ITER Fuel Clean-Up System, has been continued. The saturation experiment with duration up to 2004 h has been performed. The calculated helium-3 concentration in the samples was 466 appm. Investigation of the samples after exposure showed that mechanical properties were slightly changed. The lattice parameter was slowly decreased. Positron annihilation treatment showed that simple defect concentration was slowly decreased, and that the helium-3 bubble sizes and He-3 concentration were significantly increased during the exposure. Microstructures of the specimens showed a uniform distribution of helium-3 bubbles inside the grains. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Employment of palladium/silver (Pd/Ag) membrane permeators (PMP) for purification of tritium (T) has a lot of advantages compared with other methods. PMP is attractive, for example, in thermonuclear experimental facilities and reactors. The following processes make use of PMP: recovery of unburnt fuel from exhaust gases in the Fuel Clean-Up (FCU) system; processing of the tritiated gas impurities in FCU; T recovery from purge gas in the Breeding Blanket System (BBS).

The investigation of degradation probability of PMP properties during long-time exposure to T at ITER conditions was started in the Tritium Laboratory of A.A. Bochvar All-Russia Research Institute of Inorganic Materials (VNIINM) in 1994. Experience with PMP in such conditions was absent, and the problems of reliability and safety of PMP needed to be solved. The experimental results after 385 and 1460 h of tritium exposure were published earlier [1,2]. Now we

present experimental results for 2004 h tritium exposure.

2. Experimental

T experiments were prolonged with Russian industrial Pd/Ag alloy V-1 (Pd15Ag0.6Pt0.6Ru1.0Au0.2Al). The experimental device was described earlier [1]. He-3 accumulation in V-1 tube specimens ($\varnothing 1.2 \times 0.1$ mm) was achieved by immersion in D–T gas mixture at the following conditions: immersion temperature 350°C; immersion pressure 0.8–0.9 MPa; immersion medium D–T (1:1) gas mixture; whole exposure duration 2004 h.

The following investigations were done using tritium exposure specimens: stress–strain tests; electron microscopy; positron annihilation spectroscopy; X-ray structure analysis.

He-3 accumulation in the alloy during T exposure was estimated, under the assumption that no He-3 escape from the alloy took place, using the following values of the parameters: tritium solubility of the alloy at 350°C: 2.9 cm³ (T) per cm³ (V-1) per kPa^{1/2}; He-3 formation rate: 6.4 appm/h; V-1 density: 11.9 g/cm³. The results are presented in Table 1.

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Table 1
He-3 concentrations in V-1 alloy

T exposure (h)	385	938	1458	2004
He-3 concentration (appm)	73	205	330	466

3. Experimental results

3.1. Tensile properties

The influence of deuterium (D) and tritium exposure on tensile properties of the V-1 samples is presented in Table 2. The data show that, after slight decrease of σ_u and $\sigma_{0.2}$ values due to annealing of the alloy, further slow strengthening and elasticity decrease took place.

3.2. X-ray structure

The results of X-ray investigations are presented in Table 3. The data show that, after the initial increase of the lattice parameter, its subsequent decrease of took place, approaching the initial value. No large He-3 containing clusters were found (no line widening), and no texture changes after T exposure were found (no intensity change of diffraction maximum).

3.3. Positron annihilation properties investigation

Positron spectroscopy was used for the investigation of microdefect behavior in the crystal lattice of the alloy. Measurements of positron life-time distributions for

Table 2
Tensile properties of the V-1 samples before and after T exposure

Conditions	σ_u (MPa)	$\sigma_{0.2}$ (MPa)	Elongation, δ (%)
Initial, $T=20^\circ\text{C}$	730	570	8.2
5 h D exposure	700	560	11.8
T exposure (h)			
385	690	530	19.7
938	710	480	22.5
1458	710	490	22.5
2004	725	510	20.5

Table 3
Lattice parameter of the V-1 alloy before and after T exposure

Conditions	Lattice parameter, a (nm)	$\Delta a/a$ (%)
Initial	0.39131	—
T exposure (h)		
385	0.39155	0.07
938	0.39150	0.05
1458	0.39150	0.05
2004	0.39140	0.02

initial and T exposure specimens were carried out with the ORTEC device with a time resolution of ~ 330 ps.

The investigation showed that single vacancy (V) concentration in the initial alloy was 10^{17} cm^{-3} and it grew up to $1.6 \times 10^{17} \text{ cm}^{-3}$ after deuterium annealing during 5 h.

After tritium exposure for 385 h, positron spectroscopy revealed such helium–vacancy clusters as 2V–2He, 2V–3He ($3.7 \times 10^{16} \text{ cm}^{-3}$) and more complex: 5V–4He ($1.3 \times 10^{17} \text{ cm}^{-3}$). Total He-3 content in the clusters was not more than 7 appm.

He-3 containing bubbles were found after prolonged tritium exposure. He-3 density, n (nm^{-3}), in the bubbles was calculated from the following equations: $n_{\text{He}} = 3.71 \times 10^4 / \tau_{\text{He}}$ [3] and $\tau_{\text{exp}} = 500 - 2.35 n_{\text{He}}$ [4–6], where $\tau_{\text{He}} = 500 \tau_{\text{exp}} / (500 - \tau_{\text{exp}})$ and τ_{exp} is the experimental positron life-time, ps. The bubble sizes and He-3 amounts in the bubbles were calculated by using the “hard spheres” state equation: $P = ZnkT$, where Z is the compressibility factor [7]. It was suggested that the bubbles were in an equilibrium state and He-3 pressure could be defined from the equation $P = 2\gamma/r$, where γ is the surface tension and r is the bubble size. The assumption of bubble equilibrium state was supported by microstructure investigations (no strain fields around bubbles were found). The results of these calculations are presented in Table 4.

3.4. Microstructure

No He-3 bubbles were found in the recrystallized structure of the material after T exposure for 385 h [1]. Some rare He-3 bubbles (diameter ~ 1 nm) were found after T exposure for 938 h [2]. With He-3 content growth, the size and concentration of bubbles were increased. Microstructures of the specimens after T exposure for 2004 h exhibited larger bubbles (1–3 nm) with uniform distribution over the grain volume; no primary bubble concentration growth along grain boundaries and dislocations was observed, but the bubble size on dislocations and grain boundaries was greater than inside the grains.

The bubble concentration distribution in correspondence with bubble size during T exposure is given in Table 5. These values must be considered as approximate ones. He-3 content was calculated by using the “hard spheres” state equation (see previous item).

Alloy swelling was insignificant (about 0.025%).

4. Discussion

The recrystallization of the alloy was really completed after 385 h of annealing in tritium at 350°C .

Table 4
He–V cluster and He-3 bubble parameters during tritium exposure

T exposure (h)	He–V clusters concentration, 10^{16} cm^{-3}	He-3 bubble concentration, 10^{16} cm^{-3}	He-3 bubble diameter (nm)	He-3 content in bubbles (appm)
938	3.6	2.7	2.4	140
1458	3.4	2.4	2.8	280
2004	3.1	1.8	3.8	480

Table 5
He-3 bubble size and concentration distribution during T exposure

T exposure (h)	He-3 bubbles concentration, 10^{16} cm^{-3} , corresponding to bubble size						He-3 content in bubbles (appm)
	$\leq 1 \text{ nm}$	1–2 nm	2–3 nm	3–4 nm	4–6 nm	Total	
938	0.7	0.3	0.06	–	–	1.1	24–30
1458	–	0.13	0.7	–	0.08	0.9	~204
2004	5.6	1.5	2.5	–	–	9.6	240–500

Simultaneously, a slight elasticity increase was observed. As microstructure investigations showed, no He-3 containing bubbles were formed at this stage. Positron spectroscopy revealed such helium–vacancy clusters as 2V–2He, 2V–3He and more complex: 5V–4He. Helium–vacancy cluster growth was favored by high concentration and high migration rate of vacancies at temperatures greater than $0.3 T_m$ (T_m indicated the melting point of alloy). The main part of the He-3 formed (~90%) was in solid solution and produced the largest lattice deformation at this stage (Table 3).

Helium bubble formation in Pd–0.25Ag alloy was first observed by Penzhorn and co-workers [8] as a result of alpha-particle implantation at 300°C. The 3.3–5.5 nm bubbles were observed at Helium concentrations higher than ~500 appm. In our investigations, He-3 bubble formation (mainly ~1 nm diameter fraction) was just observed at He-3 concentration of ~200 appm although radiation-induced vacancies were not created. In the consequence of Pd-alloy exposure to T, it was observed that He-3 bubbles grew and new bubbles formed from helium–vacancy complexes. Nucleation of elementary defects such as 2V–2He and 2V–3He was continued. Decrease of lattice-distributed He-3 (Table 3) was indicated by relaxation of the lattice parameter at this stage. He-3 bubbles were uniformly distributed throughout the grain volume; no primary bubble concentration growth along grain boundaries and dislocations was observed. Average bubble size increased from ~1 nm at He-3 concentration of ~200 appm to ~3 nm at He-3 concentration of ~500 appm during tritium exposure.

The alloy elasticity remained high, but its slow decrease was observed after 2004 h T exposure. Some strengthening of the alloy took place.

5. Conclusion

Investigations performed revealed that palladium alloy V-1 did not lose its strength properties after tritium exposure at 350°C for 2004 h. It may be recommended as a material for palladium filters in ITER technology with appropriate working capability at 350°C.

However, it was observed that exposure causes structure changes such as He-3 containing bubbles formation occurred. These structure changes may cause the material properties degradation in the case of filter capacity increase.

Furthermore, degradation effects will be strengthened in the case of an unforeseen temperature rise or working temperature increase up to 400°C. Therefore, it is necessary to prolong the investigations to solve the following questions:

- investigation on capacity increase up to ~6000 h;
- investigation on temperature increase up to 400°C;
- investigation of rapid temperature decrease accident;
- investigation of other palladium alloys.

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