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# Corrosion of some V- and Nb-base alloys under irradiation in water

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**Abstract**

In the work, results of the irradiation influence in first circuit water of the SM reactor on the weight alteration, phase composition of corrosion products, and rupture type of some V- and Nb-base alloys are presented. The irradiation was carried out at 50–65°C in water and at 70–95°C in helium for comparison to neutron fluence of $\simeq 5 \times 10^{21}$ n/cm$^2$ ($E > 0.1$ MeV). Water rate was about 13.5 m/s and dissolved oxygen content was 550–720 ppb. As it is shown, V-alloys have undergone the strong corrosion in water under irradiation already at such low temperature as 50–65°C. The maximum corrosion rate occurs with V–3.0Ti alloy (about 900 μm/yr), and the minimal with the V–6.1Cr–5.3Ti–ZrC alloy (about 50 μm/yr). The corrosion products are oxides: $V_2O_5$ for pure vanadium, $TiO_2$ for V–3.0Ti alloy and TiO for V–4.4Cr–3.9Ti. The overwhelming majority of corrosion products are taken away by the water flow. These results compare with the data of the autoclave testings carried out in the Argonne National Laboratory. © 1999 Published by Elsevier Science B.V. All rights reserved.

## 1. Introduction

V–Cr–Ti alloys at chromium and titanium contents of 4–6 wt% are considered as most preferable structural materials of the thermonuclear reactor with lithium coolant [1–6]. Nevertheless, the possibility for their use with water coolant has not been excluded .

The investigations of V- and Nb-base alloys corrosion features in water have been carried out in the Argonne National Laboratory for a long time [7–9]. The tests are performed in an autoclave in the deaerated high pure water with dissolved oxygen contents of <12 ppb. The tests' temperatures are in the range 170–300°C, tests' time was upto 5000 h. It was demonstrated that more the chromium contents in V-alloys, the lesser the corrosion value which is <0.1 μm/yr for V–15Cr–5Ti alloy. However, these tests were fulfilled in the static conditions at the symbolic water flowrate of 4 cm$^3$/min ($6.7 \times 10^{-8}$ m$^3$/h).

The objective of this work was to test the performance in the first circuit water of the SM reactor core of some V-base alloys including reference composition V–4Cr–4Ti at the coolant's temperature. For conformation, the same tests were carried out for some Nb-base alloys as analogous on VA group of the Mendeleev's Table.

## 2. Experimental

Eight V- and six Nb-base alloys, the chemical composition and initial heat treatment of which are presented in Table 1, were investigated. Carbon contents was 0.0005–0.03%, nitrogen – 0.002–0.01%, oxygen – 0.03–0.06%, hydrogen $\leqslant 0.001$ wt%. The alloys were obtained as sheets of 0.5 and 0.7 mm thickness. Tensile specimens with working part sizes of $2 \times 15$ mm were manufactured by a punch. The sheets from V–4.4Cr–3.9Ti and V–5Cr–10Ti alloys were made by SSC RF RIIM.

Irradiation of specimens was carried out in the SM reactor core in two sub-capsules of 10 mm DIA from stainless steel. In one of them the specimens washed with the first circuit water at 13.5 m/s velocity. Another one was sealed and the specimens were irradiated in helium environment. In dependence from the height disposition

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Table 1
Alloys chemical composition and initial heat treatment

| Alloys chemical composition (wt%) | Temperature of 1 h anneal. (°C) |
|---|---|
| V–3.0Ti | 900 |
| V–3.1Fe | 900 |
| V–6.1Cr | 1100 |
| V–4.4Cr–3.9Ti | 1000 |
| V–6.3Cr–5.2Ti | 1000 |
| V–5Cr–10Ti | 1000 |
| V–5.4Cr–1.1Zr–0.09C | 1100 |
| V–6.1Cr–5.3Ti–0.6Zr–0.13C | 1000 |
| Nb–2.3V | 1350 |
| Nb–2.6Ti | |
| Nb–2.2Mo | |
| Nb-2.4W | |
| Nb–2.0V–1.0Zr–0.1C–0.04Y | |
| Nb–1.8Mo–1.1Zr–0.1C–0.03Y | |

the specimens temperature was 50–65°C in water and 70–95°C in helium. Neutron fluences with $E > 0.1$ MeV were $(3.5 - 5.4) \times 10^{21}$ and $(3.2 \times 10^{21}$–$5.4 \times 10^{21}$ and $3.2 \times 10^{21}$–$5.6 \times 10^{21}$ n/cm$^2$. Duration of irradiation was 756 fph (862 calendar hours).

For the corrosion value estimation, the same set of specimens from 5, 6 or 3 samples were weighed. Mechanical tests were carried out on the tensile machines of MM-150D and 1236R types. Metallographic investigations were made on the optical microscopes of UMSD and MIM-15D types. Microhardness was measured on the distance-type microhardner of PMT-4D model at a load of 100 g. The surface investigations were performed with scanning electron microscope of REM-101 type. Surface phase composition was determined by means of KED-1 microdifractometer with X-ray beam diameter of 200 μm, using Cu–K$_\alpha$ radiation.

## 3. Results

The results of the weight alteration of irradiated specimens are presented in Figs. 1 and 2 for V- and Nb-base alloys, respectively. All of the V-base alloys indicated a loss of weight. The maximum value observed was for V–3.0Ti alloy, whose specimens were half dissolved. A loss of weight of V-alloys with 4–6% Cr is 2.7–5.1%. After irradiation in helium, the weight alterations are not large and fluctuate from −0.8% for V–6.1Cr to +0.5% for V–6.3Cr–5.2Ti. Quite another behaviour demonstrates Nb-base alloys at irradiation in water (Fig. 2). The maximum weight gain observed for Nb–2.2Mo alloy is +1.0%. The maximum loss occurred with Nb–2.6Ti alloy and was −0.6%.

Mechanical testings of irradiated specimens are carried out at 20, 400 and 800°C. In all cases, the increase in strength and decrease of ductility are observed. The differences in the irradiation effect in water and helium were not substantial, as a rule. An absolutely brittle rupture was not observed. For all alloys, excluding V–6.1Cr, V–5Cr–10Ti and Nb–2.2Mo, we observed the ductile instability at room temperature, when $\delta_{\mathrm{un}} \leqslant 1.0\%$ and all the strain was practically concentrated in a specimen neck only. As it is known, the ductile instability is a forerunner of the brittle rupture on the elastic section of tensile diagram $P - \Delta L$.

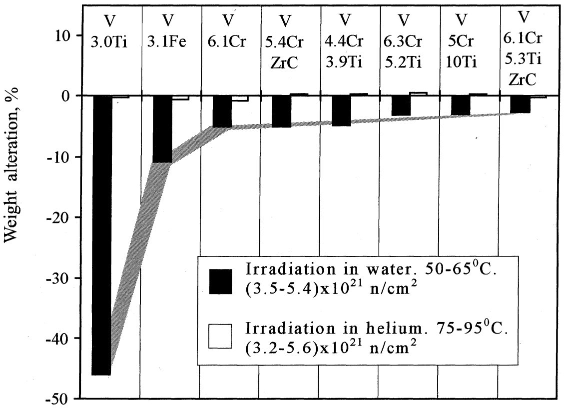

Fig. 1. Weight alteration of V-alloys after irradiation.

The interaction layer is not observed by means of metallographic investigation, however, the surface state is different for various alloys. The signs of selective types of the corrosion process development were noted for V–6.1Cr alloy only, in which the grain boundary corrosion was observed. Probably, corrosion has preferably a frontal character with continued removal of the corrosion products by the strong water flow with 13.5 m/s velocity at 50 atm pressure and at 67 m$^3$/h flowrate. For V–5Cr–10Ti and V–6.1Cr–5.3Ti–ZrC–Y alloys,

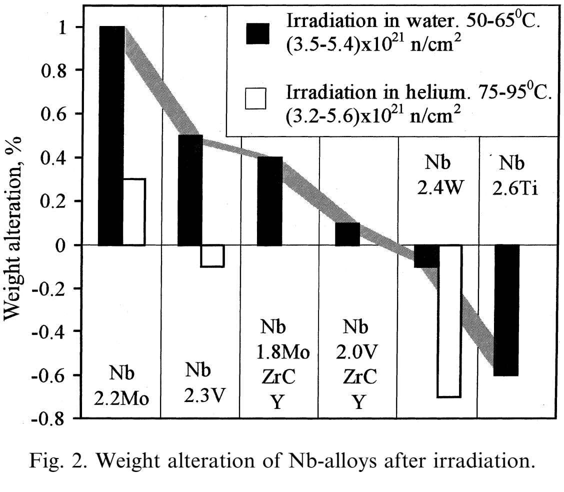

Fig. 2. Weight alteration of Nb-alloys after irradiation.

demonstrating the minimal loss of weight of 3.1% and 2.7%, the specimen surface remains smooth.

After irradiation of V-base alloy specimens in helium, and Nb-base ones in water and helium, the specimens surface are smooth when the weight alterations do not exceed 1% on one or the other side analogous to the initial state.

So far as we did not observe, the absolutely brittle rupture over the tensile diagrams and the strain was basically concentrated in the specimen neck. Therefore we observed the ductile rupture type only with typical tearing off dimples for all the alloys. At the near-by surface layers on the separate sections, we sometimes observed the fields with brittle transgranular cleavage. During the specimens surface investigation by SEM, the corrosion products sometimes remained as separate crystallites or agglomerates. If the particle size was 8–18 μm for vanadium, then for V–4.4Cr–3.9Ti alloy it was over an order less, 0.7–1.9 μm.

X-ray investigation evidences that the main corrosion process during irradiation of V-alloys in water is an oxidation. In the dependence of the alloy chemical composition the formation of oxides of different types takes place: $V_2O_5$ is for pure V, $TiO_2$ is for V–3.0Ti, TiO is for V–4.4Cr–3.9Ti alloy. Probably, $TiO_2$ oxide is taken away by water flow most easily.

## 4. Discussion

It is expedient to compare the presented results with analogous ones received in the autoclave tests in high pure deaerated water [7–9]. For the convenience of comparison it is advisable to present data not in a loss of weight but in the form of the corrosion rate in g/m$^2$ and μm/yr (Table 2). The conditions of confronted tests are in Table 3. The results of comparison presented in Table 4.

As it is seen from Table 3, the test conditions during irradiation and in the autoclave tests were quite different. The basic difference was that the reactor tests were carried out with high speed water flow at the large oxygen contents with 67 m$^3$/h flowrate. For decrease of PH due to radiolization, a few cubic metres of hydrogen were introduced each day. As a result of this, water contained about 2–5 cm$^3$/kg dissolved hydrogen continually. The autoclave tests were performed at higher temperature and up to longer time at the symbolic flowrate of $6.7 \times 10^{-8}$ m$^3$/h.

It follows from Table 4 that pure vanadium indicates lesser corrosion rate under irradiation than during the autoclave tests. It may be bound up with radiation-induced segregation of transmutated chromium on the specimen surface even at low temperatures of 50–65°C. In the irradiation conditions, not one of the investigated V-alloys indicated such low corrosion rate as V–15Cr–5Ti in the autovlave tests (≃0.1 μm/yr). The best in-

Table 2
Corrosion rate of vanadium and its alloys under irradiation in water

| Alloy | Corrosion rate | |
|---|---|---|
| | g/m$^2$ (862 h) | μm/yr |
| V–3.0Ti | 530 | 883 |
| V–3.1Fe | 139 | 232 |
| V | 99 | 166 |
| V–4.4Cr–3.9Ti | 80 | 133 |
| V–5.4Cr–ZrC | 62 | 103 |
| V–6.1Cr | 58 | 97 |
| V–5Cr–10Ti | 51 | 85 |
| V–6.3Cr–5.2Ti | 39 | 65 |
| V–6.1Cr–5.3Ti–ZrC | 31 | 52 |

Table 3
Conditions of carrying out of autoclave [8,9] and under irradiation testings

| Parameter | Under irradiation | In autoclave [8,9] |
|---|---|---|
| Test temperature (°C) | 50–65 | 230 |
| Test duration (h) | 862 | up to 4508 |
| Water specific resistance (MΩ × cm) | 0.7–1.0 | > 10 |
| Contents of dissolved oxygen (ppb) | 550–720 | < 12 |
| Water flow velocity (m/s) | 13.5 | 0 |

Table 4
Comparison of corrosion rate W of vanadium and some its alloys in water under irradiation and in autoclave testings

| Under irradiation | | | In autoclave [8,9] | | |
|---|---|---|---|---|---|
| Vanadium or vanadium alloy | W (g/m$^2$) (862 h) | W (μm/yr) | W (g/m$^2$) (4508 h) | W (μm/yr) | Vanadium or vanadium alloy |
| Vanadium | 99 | 166 | 350[a] | 246 | Vanadium |
| V–4.4Cr–3.9Ti | 80 | 133 | 63 | 20 | V–5Cr–5Ti |
| V–6.3Cr–5.2Ti | 39 | 65 | | | |
| V–6.1Cr–5.3Ti–ZrC[b] | 31 | 52 | 0.35 | 0.1 | V–15Cr–5Ti |

[a] Test duration is 2046 h.

[b] Alloy with minimal corrosion rate under irradiation.

vestigated under irradiation V–6.1Cr–5.3Ti–0.6Zr–0.13C alloy had a corrosion rate of 52 μm/yr (about three orders more) and, probably, the corrosion product was TiO oxide.

As regarding Nb-base alloys, it was shown after the autoclave tests in water with the same parameters at 170°C for 3052 h that Nb–1Zr, Nb–5Mo–1Zr, Nb–5V–1Zr alloys indicated a gain of weight of $\leqslant 1$ g/m$^2$ only [10]. By the X-ray investigations, it was shown that the corrosion products are preferably NbO with possible presence of $Nb_2O_5$. After irradiation at 50–65°C in water flow the weight alterations of Nb-base alloys are not too large, but we observed both a gain and a loss of weight. Probably, in that case the weight alterations of the specimens would be made with more accuracy.

## 5. Conclusions

1. V-base alloys have undergone strong corrosion in water under irradiation. The tests were carried out in water with high oxygen contents (550–720 ppb) at a flow speed of 13.5 m/s at 50–65°C. The maximum corrosion rate was observed for V–3.0Ti alloy (883 μm/yr), the minimal one was for V–6.1Cr–5.3Ti–ZrC (52 μm/yr). The alloy of V–(4.4–6.3)Cr–(3.9–10)Ti type indicated a corrosion rate of 65–133 μm/yr.

2. It was revealed that the corrosion products are basically oxides of $V_2O_5$ type in pure vanadium, $TiO_2$ – in V–3.0Ti alloy, TiO – in V–4.4Cr–3.9Ti alloy. The corrosion has both the preferably frontal (V–3.0Ti) and mixed frontal and selective types (vanadium). The overwhelming majority of the corrosion products are taken away by the water flow.

3. Comparing the results under irradiation with the autoclave tests, carried out in Argonne National Laboratory [7–9], it can only be said that on the whole, the irradiation effects are substantially stronger in spite of the lesser test temperature.

4. Nb-base alloys under analogous irradiation conditions indicated minimal weight alteration.

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