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Corrosion resistance of refractory metals in high-temperature water

Y. Ishijima [a], K. Kakiuchi [b], T. Furuya [b], H. Kurishita [c,*], M. Hasegawa [c], T. Igarashi [d], M. Kawai [e]

[a] *Tohoku University, Oarai, Ibaraki 311-1313, Japan*
[b] *Nuclear Fuel Industries, Ltd., Tokai-mura, Ibaraki 319-1196, Japan*
[c] *The Oarai Branch, IMR, Tohoku University, Oarai, Ibaraki 311-1313, Japan*
[d] *Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan*
[e] *High Energy Accelerator Research Organization, Tsukuba 305-0801, Japan*

Abstract

The high-temperature water corrosion resistance of refractory transition metals of group IVa, Va and VIa was studied. Corrosion tests were conducted for 17 kinds of tungsten, 12 kinds of molybdenum and other 9 kinds of metals in flowing water with a dissolved oxygen content of 400 ppb and pH 6–7 at 180, 260 and 320 °C for 200 h. It is shown that the corrosion rate of W and Mo depends strongly on temperature and material. W and Mo are not corroded severely at 180 °C, the corrosion rates are 0.001–0.047 mm/y for W and 0.022–0.029 mm/y for Mo. The heavy alloys are corroded severely at 260 °C, the corrosion rates are 0.141–0.214 mm/y. At 320 °C, significant corrosion attack occurs depending on the materials. CrN coated W shows excellent corrosion resistance, the rate is as low as $\simeq$0.004 mm/y. W–Re and Mo–Re alloys are corroded severely, with a maximum rate of 1.656 mm/y for W–2%Re and 0.405 mm/y for Mo–17.7%Re. Mo shows a considerably higher corrosion resistance than W. All group IVa and Va metals except Nb, as well as Cr, Re and SUS316 at 320 °C show better resistance than Mo.

1. Introduction

Refractory metals, especially tungsten, are candidate materials for fusion reactor structural and divertor applications and for spallation neutron source solid target applications because of their high melting point, high thermal stress factor, excellent compatibility with liquid metals, low sputtering yield, large mass number, high density, etc. These applications may require the use in a water coolant to minimize the damages arising from high heat fluxes and high-energy proton beam irradiations.

It is known that W and Mo exhibit good resistance to acidic solution due to the presence of passive oxide films of WO_3 and MoO_2, while they may corrode appreciably in a neutral aqueous solution containing dissolved oxygen [1]. However, very few data on the corrosion rates of W and Mo in high-temperature water are available [1,2]. Therefore, this study was undertaken to examine and compare the corrosion resistance of pure W and its alloys, pure Mo and its alloys, pure Cr, pure metals of group IVa and Va, pure Re and SUS316 in flowing water with a controlled dissolved oxygen content between 180 and 320 °C for 200 h.

2. Experimental

For corrosion tests, 17 kinds of pure W and its alloys, 12 kinds of pure Mo and its alloys, 7 kinds of other transition metals of group IVa, Va and VIa, pure Re and SUS316 were used. The designation, chemical

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[*] Corresponding author. Tel.: +81-29 267 4157/3181; fax: +81-29 267 4947.
E-mail address: kurishi@imr.tohoku.ac.jp (H. Kurishita).

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Table 1
Designation, composition, state and shape of specimens, measured weight gain, estimated corrosion rate, ratings and the occurrence of exfoliation or spalling of corrosion product films

Designation	Composition	State	Shape	Weight gain (mg/dm^2)/Corrosion rate (mm/year)/Ratings			
				180 °C	260 °C	320 °C	Exfoliation
W-P	99.95%W Poly	R	S	−122.40/0.028/B	−90.00/0.020/B	−907.46/0.206/C	O
HPW	99.999%W Poly	–	S	−125.00/0.028/B	–	−855.77/0.194/C	O
W-S	99.99%W Single	–	S	–	−141.50/0.032/B	−398.74/0.090/B	O
W-CVD	99.99998%W Poly	–	S	−101.60/0.023/B	–	−594.12/0.135/C	O
CrN/W	CrN (10 μm) coated W	–	S	−6.60/0.001/A	−1.40/0.000/A	−18.87/0.004/A	
W–2Re	W–2%Re	R	S	–	−167.40/0.038/B	−7296.37/1.656/C	O
W–3Re	W–3%Re	R	WI	−202.70/0.046/B	–	−6866.60/1.550/C	
W–5Re	W–5%Re	R	S	−121.70/0.027/B	−142.20/0.032/B	−5047.72/1.140/C	O
W–5Re	W–5%Re	R	WI	−155.20/0.035/B	–	−5213.30/1.177/C	
W–26Re	W–26%Re	R	WI	−212.20/0.047/B	–	−833.00/0.185/C	
W–2Ta	W–2%Ta	R	S	−99.90/0.023/B	−173.20/0.039/B	144.91/−0.033/B	O
W-10A	W–10%Cu (coarse grain)	–	S	−139.70/0.034/B	−349.60/0.084/B	−1191.37/0.286/C	
W-10B	W–10%Cu (fine grain)	–	S	−136.60/0.033/B	−371.00/0.089/B	−2138.23/0.513/C	
HM-7S	W–5% (Ni–Cu)	–	S	−112.20/0.026/B	−603.60/0.141/C	−2360.02/0.550/C	
HM-7ST	W–5% (Ni–Co)	–	S	–	−804.40/0.188/C	294.07/−0.069/B	O
HM-185	W–3% (Ni–Fe)	–	S	−145.30/0.034/B	−927.20/0.214/C	−1273.80/0.294/C	
W–50Mo	W–50%Mo	R	WI	–	–	95.02/0.028/B	
Mo-P-1	99.95%Mo Poly	R	S	−50.40/0.022/B	−45.80/0.020/B	−117.61/0.050/B	
Mo-P-2	99.95%Mo Poly	R	C	−55.50/0.024/B	–	−125.66/0.054/B	
Mo-S	99.99%Mo Single	–	S	−67.10/0.029/B	−49.80/0.021/B	−129.99/0.056/B	
Mo-P-3	99.99%Mo Poly	–	S	–	–	−65.49/0.028/B	
Mo–9.3Re	Mo–9.3% (5at.%)Re	–	S	–	–	−223.24/0.088/B	O
Mo–17.7Re	Mo–17.7% (10at.%)Re	–	S	–	–	−1105.48/0.405/C	O
Mo–20Re	Mo–20%Re	R	S	−65.30/0.023/B	−105.70/0.038/B	−972.98/0.350/C	O
Mo–32.7Re	Mo–32.7% (20at.%)Re	–	S	–	–	−243.16/0.079/B	
Mo–0.5Ti	Mo–0.5%Ti	–	S	–	–	−54.96/0.024/B	
Mo–1.5Ti	Mo–1.5%Ti	–	S	–	–	−56.67/0.024/B	
Mo–2Ta	Mo–2%Ta	–	S	–	–	−52.24/0.022/B	
TZM	Mo–0.5%Ti–0.07%Zr	R	S	–	–	−47.56/0.020/B	
Cr	99.9%Cr	R	S	–	–	3.70/−0.002/A	
Ta	99.95%Ta	R	S	−3.40/0.001/A	2.10/−0.001/A	16.70/−0.004/A	
Nb	99.9%Nb	R	S	−0.70/0.000/A	3.70/−0.002/A	299.93/−0.153/C	O
V	99.7%V	R	S	–	–	−2.17/0.002/A	

Hf	99.9%Hf	R	WI	–	–	24.85/−0.008/A
Zr	99.7%Zr	R	S	–	–	41.20/−0.028/B
Ti	99.5%Ti	R	S	–	–	0.75/−0.001/A
Re	99.97%Re	R	WI	–	–	−72.37/0.015/B
SUS316	Fe–Cr–Ni–Mo	R	S	–	–	104.63/−0.058/B

A: Attack <0.0125 mm/y. The material is regarded as suitable for use where little dimensional change can be tolerated.
B: Attack between 0.0125 and 0.125 mm/y. The material may be suitable for use provided that some corrosion is permissive.
C: Attack >0.125 mm/y. The material is ordinary considered unsuitable.

composition, state and shape of the specimens are listed in Table 1. Here, S represents a sheet with the typical dimensions of 25 mm × 25 mm × (1–2) mm and a hole of 2 mm in diameter at a corner to suspend the specimen, and WI represents a wire of about 1 mm in diameter and 100 mm long. R stands for the rolled state. The sheet specimens with the hole were mechanically polished with emery paper of #240 to 2000 and the wire specimens were used in the as-received conditions.

Corrosion tests were conducted in flowing water with a dissolved oxygen content of 400 ppb and pH 6–7 at 180, 260 and 320 °C for 200 h under 8.5 and 13 MPa using an autoclave. Before and after each test, weight measurements, X-ray diffraction (XRD) and surface appearance observations were performed.

3. Results and discussion

All data on the weight gain, corrosion rate, ratings and the occurrence of exfoliation or spalling of corrosion product films are listed in Table 1. The corrosion rate was estimated assuming that the measured value at 200 h may hold in a longer test period.

3.1. Tungsten

Fig. 1 shows the weight gain and corrosion rate as a function of the test condition. It is obvious that a weight loss occurs in most cases and the magnitude of the weight loss strongly depends on test temperature and material. In the case of pure W (W-P), at 180 and 260 °C the weight loss remains almost constant, ≃100 mg/dm^2, while at 320 °C it increases rapidly to ≃900 mg/dm^2, which correspond to 0.022 and 0.2 mm/y, respectively. The value of 0.022 mm/y belongs to class B (0.0125–0.125 mm/y: medium corrosion resistant and judged usable) and 0.2 mm/y to class C (above 0.125 mm/y: poor corrosion resistant and judged unusable) [3]. Therefore, we can say that pure W may be used in flowing water with a dissolved oxygen content of 400 ppb and pH 6–7 at and below 260 °C, although data on the corrosion rate at much longer time than 200 h are required.

It is seen from the figure that at 180 °C, there is no significant difference in weight loss between W-P and the other materials except for CrN/W. At 260 °C, only the heavy alloys (HM-7S, HM-7ST and HM185) show a significant increase in weight loss: one order larger than W-P, indicating that the heavy alloys cannot be used at 260 °C. At 320 °C, the corrosion attack is promoted for most W grades, with a significant difference in corrosion rate between the materials. It should be noted that even at 320 °C CrN/W shows a small weight loss, ≃20 mg/dm^2, which corresponds to ≃0.004 mm/y. This value belongs to class A (less than 0.0125 mm/y: good corrosion resistance).

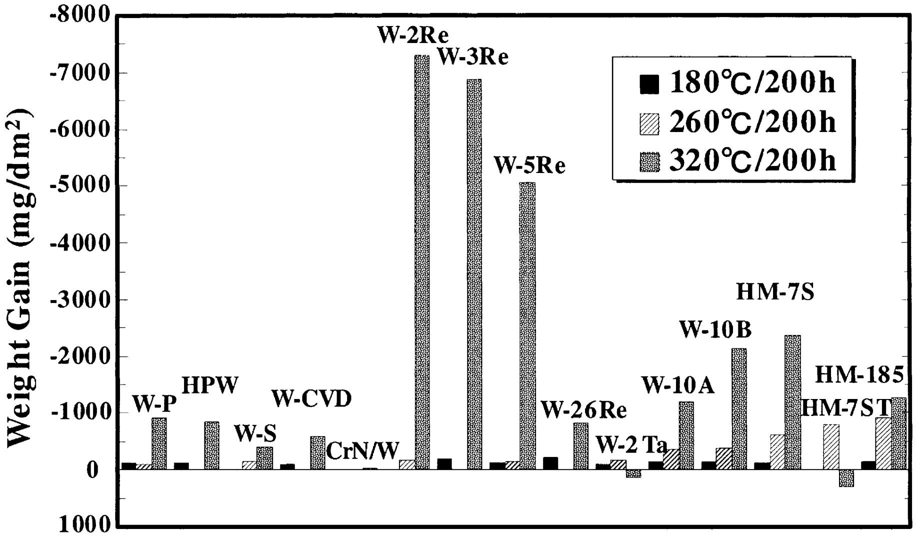

Fig. 1. Weight gain of W as a function of testing temperature.

The worst corrosion-resistant material is the W–(2–3)%Re alloy. Fig. 2 shows the Re concentration dependence of the weight loss at 180 and 320 °C for the sheet and wire specimens of W-Re alloys. At 180 °C the weight loss remains almost constant over the entire Re concentrations, while at 320 °C it rapidly increases and takes a maximum at around 2 wt%Re and then gradually decreases toward the level of pure Re. It is surprising that the addition of only 2–3 wt%Re to W remarkably increases the weight loss, ≃7000 mg/dm^2, although pure Re shows fairly good corrosion resistance (≃70 mg/dm^2, see Table 1). The electronegativities of W and Re are 1.7 and 1.9, respectively, which are not very different. Further studies will be needed to explain the observed effect of Re addition.

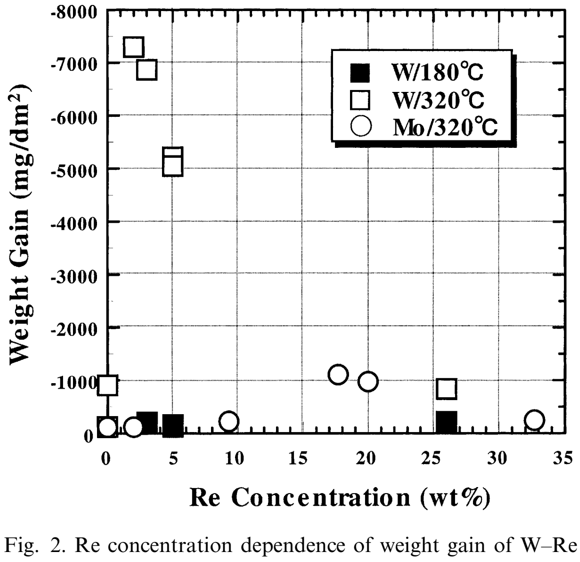

Fig. 2. Re concentration dependence of weight gain of W–Re and Mo–Re alloys.

In addition, only at 320 °C the single crystal (W-S) shows less weight loss compared with W-P, and the coarse-grained W–10%Cu (W-10A) shows less weight loss compared with the fine-grained one (W-10B). This indicates that the detrimental effect of grain boundaries promoting corrosion attack occurred at 320 °C. It is also interesting to note that CVD-W, which has a very high purity and fairly fine grain size of ≃5 μm or less, shows a weight loss between single- and poly-crystals and that W-2Ta and HM-7ST show the change from weight loss at and below 260 °C to weight gain at 320 °C. In W-2Ta and HM-7ST, exfoliation of corrosion product films occurred, indicating that the films are not stable.

Fig. 3 gives a typical example of an XRD pattern taken from W-P tested at 320 °C. Large peaks of WO_3 and $WO_{2.9}$ and small peaks of WO_2 occur together with

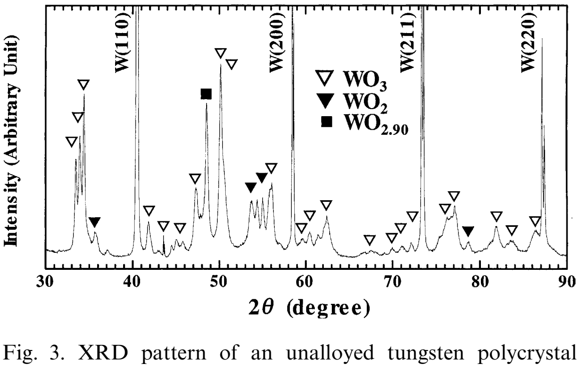

Fig. 3. XRD pattern of an unalloyed tungsten polycrystal (W-P).

Table 2
Structure of corrosion products determined by XRD

	Corrosion products
W-P	W, WO_3, WO_2, $WO_{2.90}$ mainly: WO_3
W-CVD	WO_3, WO_2, $WO_{2.90}$ mainly: WO_3
CrN/W	CrN, Cr, W mainly: CrN
W–5Re	WO_3, WO_2, $WO_{2.90}$ mainly: WO_3
W–2Ta	WO_3, WO_2, $WO_{2.90}$ mainly: WO_3
W-10B	Cu_2O, WO_3, $WO_{2.90}$, Cu, Cu_3N
HM-185	W, $NiWO_4$
Mo-P-1	Mo, MoO_2
Mo–20Re	Mo, MoO_2, ReO_2 mainly: MoO_2
Ta	Ta, Ta_2O_5, TaO_x mainly: Ta_2O_5
Nb	Nb_2O_5, NbH, NbO, $NbO_{1.1}$

strong peaks of W. Similar results were obtained for 320 °C-tested specimens of HP-W, W-S, CVD-W and W–5Re. The structure of corrosion product films determined by XRD is shown in Table 2.

3.2. Molybdenum and other metals

Fig. 4 shows the weight gain for pure Mo and its alloys, pure Ta and pure Nb. All Mo grades show a weight loss which is considerably smaller than that of W: in the pure-metal case, approximately one half of W at 180 and 260 °C and approximately one tenth at 320 °C. At 320 °C, dilute alloys of TZM, Mo–0.5Ti, Mo–1.5Ti and Mo–2Ta show almost the same weight loss, which is slightly smaller than pure Mo. These corrosion rates belong to class B, suggesting that pure Mo and dilute alloys containing transition metals may be used even at 320 °C.

The Re concentration dependence of weight loss in Mo–Re alloys is also shown in Fig. 2. It is seen that as compared with W–Re alloys, Mo–Re shows a much less dependence on the Re concentration and takes a maximum at higher Re concentrations. These results indicate that the effect of alloy addition on the corrosion rate is much smaller in Mo than in W. An appreciable difference in weight loss between Mo-P-1 or -2 and Mo-P-3 is observed. The observation is probably due to the difference in residual strain because Mo-P-1 and -2 are in the as-rolled condition, while Mo-P-3 is in the as-sintered condition.

Fig. 5 gives a comparison of weight gain among unalloyed metals of group IVa, Va and VIa, pure Re and SUS316 tested at 320 °C. Except for Nb, the other metals show better corrosion resistance than W and Mo.

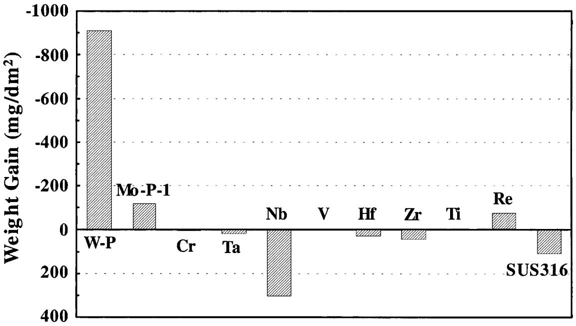

Fig. 5. Comparison of weight gain of unalloyed transition metals of group IVa, Va and VIa, unalloyed Re and SUS316 tested at 320 °C for 200 h.

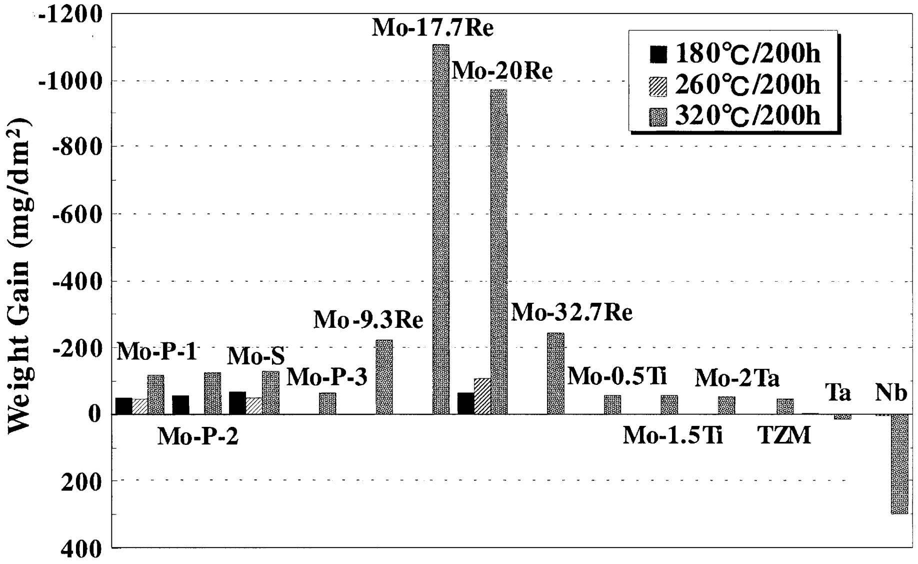

Fig. 4. Weight gain of pure Mo and its alloys, pure Ta and pure Nb as a function of testing temperature.

Only V and Re show weight loss, while the others show weight gain. Among all materials tested at 320 °C, Ti shows the highest resistance to water corrosion. The structure of the corrosion product films in Mo and other metals is also shown in Table 2. In pure Mo only MoO_2 is observed.

4. Conclusion

In order to examine the corrosion resistance of refractory metals in high-temperature water, 17 kinds of W, 12 kinds of Mo, 7 kinds of other unalloyed transition metals, Re and SUS316 were tested in flowing water with a controlled dissolved oxygen content of 400 ppb and pH 6–7 at 180, 260 and 320 °C for 200 h.

For W tested at 180 °C, except for CrN/W, there was no significant difference in weight loss due to corrosion attack, the weight loss being $\simeq$100 mg/dm^2 ($\simeq$0.022 mm/y). At 320 °C, the corrosion attack was promoted and a significant difference in the corrosion rate occurred between the materials: CrN/W still showed an excellent resistance ($\simeq$20 mg/dm^2, 0.004 mm/y), but the addition of only 2–3 wt% Re to W remarkably increased the weight loss, $\simeq$7000 mg/dm^2 ($\simeq$1.656 mm/y) although pure Re showed fairly good corrosion resistance ($\simeq$70 mg/dm^2, $\simeq$0.015 mm/y). Detrimental effects of grain boundaries were observed at 320 °C.

For Mo the weight loss was considerably smaller than that for W at all temperatures. The Re concentration dependence of weight loss was much smaller, with a maximum at a higher concentration ($\simeq$18 wt%Re) than W. Mo alloys of TZM, Mo–0.5Ti, Mo–1.5Ti and Mo–2Ta showed almost the same weight loss ($\simeq$50 mg/dm^2, $\simeq$0.024 mm/y) which was slightly smaller than for pure Mo.

All group IVa and Va metals except Nb, as well as Re and SUS 316 tested at 320 °C showed a higher corrosion resistance than W and Mo. Only V and Re showed weight loss, while the others showed weight gain.

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