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Investigation of the compatibility of tungsten and high temperature sodium

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Abstract

The compatibility of rotary swaged tungsten and sodium was investigated at 500, 600, 700 °C, and also at 600 °C of polished tungsten. The weight loss curves for the two kinds of W-specimens appear significantly different, however their weight losses approach constant values after testing for 400 h. The asymptotic change in sodium containing 30 μg/g oxygen at 600 °C are about 2.3 and 0.8 mg/cm^2 from 400 to 1500 h, respectively for the rotary swaging tungsten and the polishing tungsten. The corrosion products at the surfaces of two kinds of W-specimens after testing in high temperature sodium are different. The grains show significant growth after testing of both kinds of tungsten. The fracture stress of the rotary swaged tungsten at room temperature decreases considerably after testing with the effect slightly increasing with temperature from 500, 600 to 700 °C. A much smaller decrease of fracture stress is observed for polished tungsten at 600 °C, which already before testing has much smaller value. The micro-morphologies of the fracture surface indicate brittle inter-granular fracture in both kinds of tungsten. Embrittlement becomes much more notable for rotary swaged tungsten, while inter- and trans-granular fracture modes appear after corrosion tests in high temperature sodium for both kinds of tungsten.

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1. Introduction

An ADS verification facility will be proposed in the next phase of our ADS project. Tungsten and sodium or water are options for target and for sub-critical reactor coolant of ADS, respectively. Therefore investigations in our ADS project focus on compatibility studies of tungsten with sodium and with water. In this paper, some primary results about the compatibility of tungsten and sodium are presented.

2. Experimental method

2.1. Tungsten specimens

Rotary swaged W: The forging W was heated in a hydrogen furnace at 1450 °C, then shaped to a bar in rotary swaging machine.

Polished W: The rotary swaged W bar was turned for polishing in a emery pot at room temperature for about 20 h.

The tungsten specimens are cut from the rotary swaged W and the polished W bar, respectively. The purity for the two kinds of tungsten is 99.96%, and their size is ∅3 mm × 13 mm.

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2.2. Test facility

A high temperature stove system is used containing a special test section and the capsules.

2.3. Test conditions

The test conditions are listed in Table 1.

2.4. Preparation of the capsules containing samples and sodium

The specimens were put into a capsule, degassed under vacuum, then sodium was filled into the capsules in a glove box filled with high pure inert gas. Then the sodium inlet pipes on the capsules were welded by cold-welding pliers. Finally, the capsules were removed from the glove box and sealed by TIG welding. The prepared capsules (Fig. 1) were put into the special test section in the test facility to carry out the compatibility test.

3. Results and discussion

3.1. Chemical compatibility

3.1.1. Weight loss

The specimens tested for different periods were washed by alcohol and water, respectively, then were dried for weighing. The weight loss curves of the rotary swaged and polished W-specimens are showed in Fig. 2. It can be seen that the weight loss of the rotary swaged tungsten after a rise at 200 h decreases with increasing time, and approaches a constant of 2.3 mg/cm^2 after about 400 h. On the other hand, the weight loss of polished tungsten increases with increasing time, and approaches a constant value of 0.8 mg/cm^2 also after 400 h. Obviously, the weight loss curves for two kinds of tungsten are different, indicating that the different original surface condition resulting from the different processing technologies may influence the corrosion process of the tungsten.

The above results indicate that the chemical compatibility between tungsten and sodium is very good. The different original surface conditions resulting from the different processing technologies may influence the corrosion process of the tungsten.

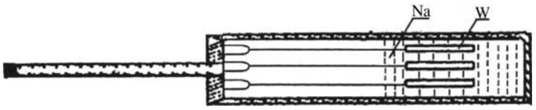

Fig. 1. Capsule containing samples and sodium.

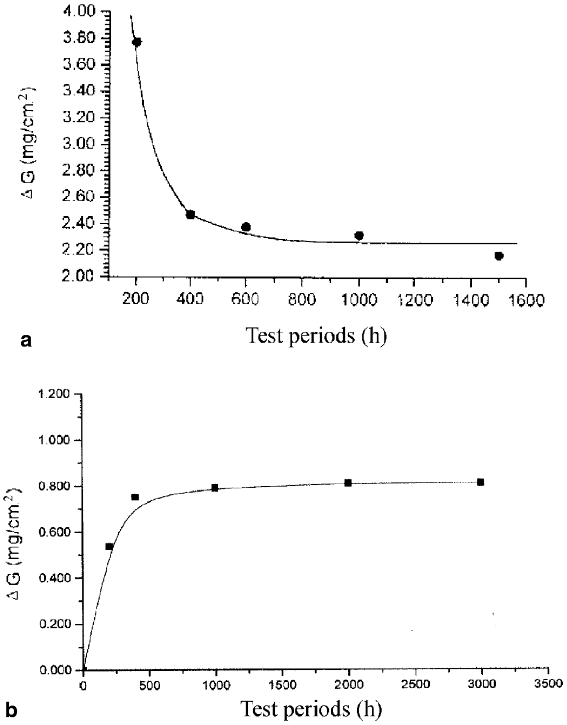

Fig. 2. Weight loss ΔG of tungsten after test in sodium with 30 μg/g oxygen at 600 °C (a) rotary swaged W; (b) polished W.

The weight loss of the rotary swaged W-specimens tested in sodium for 1500 h at various temperature is shown in Fig. 3. There is a little effect at low temperatures on the weight loss, and with an increasing at 700 °C.

Table 1
Test conditions

Temperature (°C)	500, 600, 700
Test periods (h)	200, 400, 600, 1000, 1500 h (for rotary swaged W) 200, 400, 600, 1000, 1500, 2000, 3000 h (for polished W)
Oxygen content in sodium (μg/g)	12.6, 32.2, using vacuum distillation at 10^{-3} Pa, 400 °C, capacity method
Carbon content in sodium (μg/g)	7, using vacuum distillation at 10^{-3} Pa, 400 °C, then burn at 1100 °C, gaseous chromatograph method
Ratio of specimens area to sodium volume (cm^{-1})	0.05

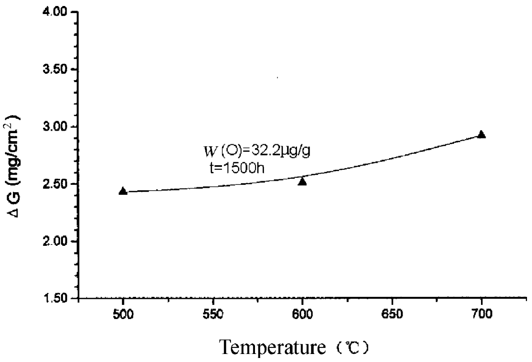

Fig. 3. Weight loss of the rotary swaged W-specimens tested at various temperature.

3.1.2. Surface micro-morphology

SEM observation for the surface of the two kinds of W-specimens shows that there is a very thin oxide film (about 2 μm thickness) on the original surface of the rotary swaged W-specimens (arrows), its thickness decreases after testing for 200 h, then it increases again and approaches a constant value after 400 h (Fig. 4(a)–(d)). The original surface of the polished tungsten is very smooth and there is no oxide film on it, even after testing (Fig. 4(e) and (f)).

The thickness of the oxide film (arrows) on the rotary swaged W-specimens shows only slight variation with temperature (Fig. 5), and is in accord with the behavior of weight loss. The scan analyses show that there is no sodium penetration at the grain boundaries for both kinds of W-specimens (Fig. 4(g)).

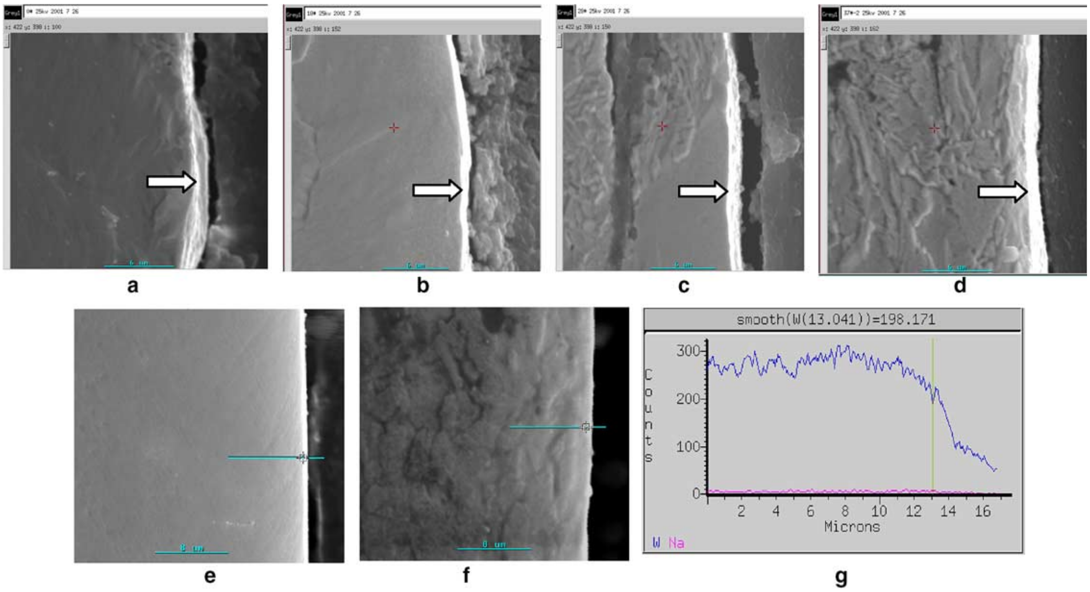

Fig. 4. Surface oxide film of rotary swaged W-specimens and the surface micro-morphology of polished W-specimen tested in sodium $w(\mathrm{O}) = 32.2$ μg/g; $T = 600$ °C rotary swaged W: (a) original; (b) 200 h; (c) 400 h; (d) 1000 h; polished W: (e) original; (f) 1000 h; (g) sodium scan line for 1000 h.

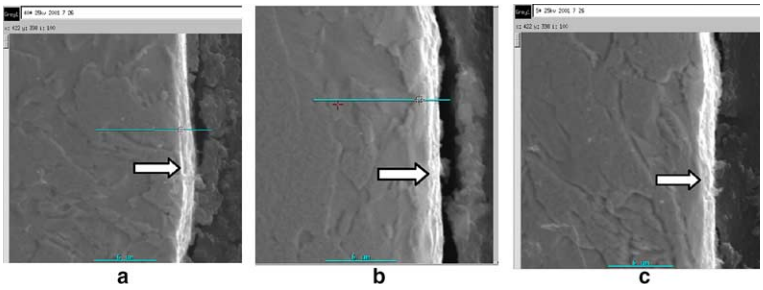

Fig. 5. Surface oxide film of rotary swaged W-specimens tested in sodium $w(\mathrm{O}) = 32.2$ μg/g; $t = 1500$ h (a) 500 °C; (b) 600 °C; (c) 700 °C.

3.1.3. Corrosion products

The results of the X-ray diffraction of the surfaces of W-specimens shows that there are W_xO_y and Na_xWO_y on the surface of rotary swaged W-specimens without water-washing (Fig. 6(a)). On the surface of the polished W no W_xO_y, but only $Na_xW_zO_y$ is observed (Fig. 6(b)). It is quite evident that the X-ray diffraction for the corrosion products, the SEM observation for the micro-morphologies and the weight loss curves are related to each other.

As stated above, the different original surface conditions resulting from the different processing technologies may influence the corrosion process of tungsten. The reaction between tungsten and high temperature sodium may be as following [1,2]:

$$W_xO_y + Na + O \rightarrow W + Na_xO_y \tag{1}$$

$$W + Na + O \rightarrow W_xO_y + Na_xWO_y \tag{2}$$

$$W + Na + O \rightarrow Na_xWO_y. \tag{3}$$

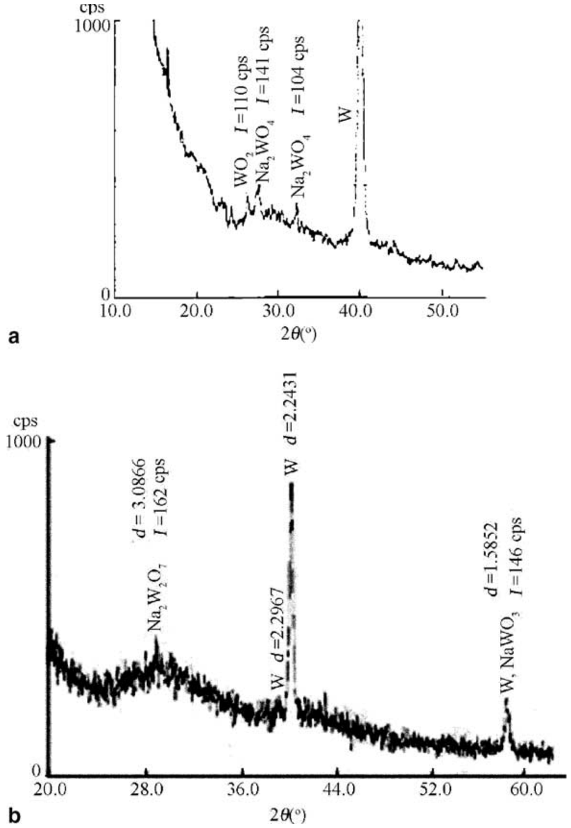

Fig. 6. X-ray diffraction spectra of W-specimen surfaces without water-washing $w(O) = 32.2$ μg/g; $T = 600$ °C; $t = 1500$ h (APD-10, PHLIPS, Cu K_α, 40 kV, 40 mA) (a) rotary swaged W; (b) polished W.

The original oxide film on the rotary swaged W-specimen may be reduced by sodium (reaction (1)), then, W and Na may react according to reaction (2) and (3) to form W_xO_y and Na_xWO_y. It can be expected from Fig. 2 that the reaction rate is large early in the test, the oxygen is depleted and the reaction rate becomes lower with prolongation of the test. It is clearly that the higher original oxygen content in sodium is in favor of the formation of the compound Na–O–W which can be solved in water, but the depletion of oxygen due to corrosion may enhance the growth of new oxide film based on the remaining oxide film. Therefore, it is suggested that the sodium and oxygen react with the oxide film on the surface for the rotary swaged W-specimens, and form both the compound Na–O–W and a new oxide film which becomes a barrier against penetration and attack by sodium and oxygen. For the polished tungsten, the sodium and oxygen react directly with the matrix to form the compound Na–O–W according to reaction (3).

3.2. Fracture characteristic

3.2.1. Fracture stress

The fracture stress for rotary swaged and the polished W-specimens was determined using the miniature disk bend method [3]. The size of the specimen is ∅3 mm × 0.3 mm, and the results are showed in Table 2. It can be seen that the fracture stress of the tested rotary swaged W-specimens decreases significantly under sodium exposure. There is nearly no effect of temperature on the fracture stress under higher oxygen content, and a slight decrease with increasing temperature under lower oxygen content. The fracture stress is higher under lower oxygen content than that under higher oxygen content at the same temperature. For the polished tungsten, fracture stress is already low before testing and is almost not effected by sodium exposure.

3.2.2. Fracture surface morphology

The fracture surface morphology of rotary swaged tungsten is showed in Fig. 7.

The fracture surfaces of the rotary swaged W show brittle fracture (Fig. 7), which becomes much more notable after high temperature sodium corrosion with inter- and trans-granular fracture morphologies. There is a clear effect of temperature on the fracture characteristic of the rotary swaged tungsten. Higher temperature exposure for a long time may enhance embrittlement of tungsten.

The fracture surface morphology of polished tungsten is shown in Fig. 8. It can be seen that the fracture surface morphologies show inter-granular brittle fracture for the original specimens, and inter- and trans-granular brittle fracture modes after test in high temperature sodium.

Table 2
Fracture stress of W-specimens before and after testing in sodium (at room temperature)

Material	Test conditions	Fracture stress (MPa)
Rotary swaged tungsten	Before testing	600 (1 ± 2.8%)
	500 °C, 10 µg/g (O), 1500 h	143 (1 ± 7.5%)
	500 °C, 30 µg/g (O), 1500 h	106 (1 ± 12%)
	600 °C, 10 µg/g (O), 1500 h	129 (1 ± 16%)
	600 °C, 30 µg/g (O), 1500 h	105 (1 ± 2.8%)
	700 °C, 10 µg/g (O), 1500 h	115 (1 ± 14%)
	700 °C, 30 µg/g (O), 1500 h	101 (1 ± 21%)
Polished tungsten	Before testing	140 (1 ± 4.7%)
	600 °C, 30 µg/g (O), 1500 h	134 (1 ± 7.6%)

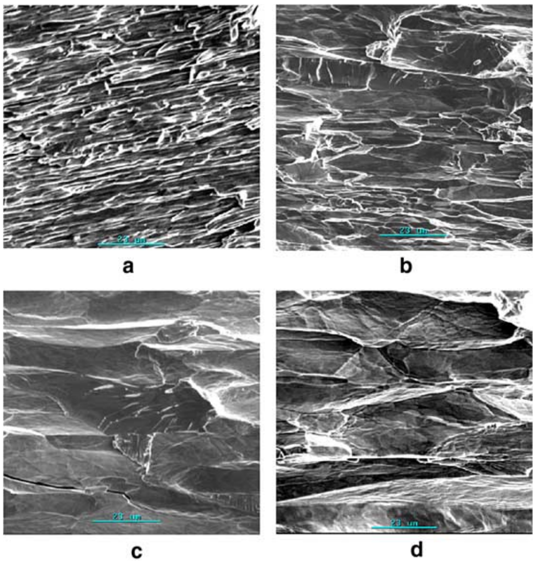

Fig. 7. Fracture surface morphologies of rotary swaged W-specimens $w(\mathrm{O}) = 32.2$ µg/g; $t = 1500$ h (a) original; (b) 500 °C; (c) 600 °C; (d) 700 °C.

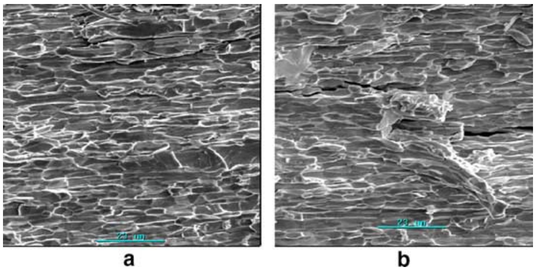

Fig. 8. Fracture surface morphologies of polished W-specimens $w(\mathrm{O}) = 32.2$ µg/g; $t = 1500$ h (a) original; (b) after testing at 600 °C.

3.2.3. Microstructure

The microstructure of the rotary swaged W-specimens and the polished W-specimens before and after tested are shown in Fig. 9. All specimens are etched in mixed solution of 10 g $CuSO_4 \cdot 5H_2O$ + 40 ml H_2O + 20 ml NH_4OH at 25 °C for 40–50 s.

It can be seen that the grains of the original rotary swaged tungsten are compact (Fig. 9(a)), while the grains of original polished tungsten are more strongly attacked by etching (Fig. 9(c)).

Obviously, the different processing technology results in different microstructures. This may be the reason that the fracture stress of the original rotary swaged tungsten is different from that of the original polished tungsten.

The grains grow significantly after corrosion test in high temperature sodium for both kinds of tungsten (Fig. 9(b) and (d)).

The reasons of grains growth and the reduction of the fracture stress for the tungsten specimens tested under above conditions should be investigated further.

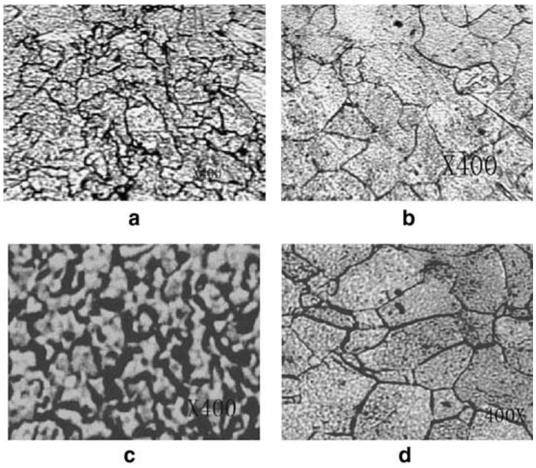

Fig. 9. Microstructure of rotary swaged and polished W-specimens before and after testing $w(\mathrm{O}) = 32.2$ µg/g; $T = 600$ °C; $t = 1500$ h (a) original rotary swaged W; (b) rotary swaged W after testing; (c) original polished W; (d) polished W after testing.

4. Preliminary conclusions

(1) The different original surface states which are due to the different processing technology may cause different corrosion behavior, microstructure, and fracture characteristics.

(2) The corrosion resistance to high temperature sodium of rotary swaged and polished tungsten are good under the present test conditions. After about 400 h, the weight loss becomes on finally constant for both materials (at least up to 1500 h) with asymptote weight losses of 2.3 mg/cm^2 and 0.8 mg/cm^2, respectively. No sodium penetration was observed at the grain boundaries for both kinds of W-specimens.

(3) The grains grow significantly after testing in high temperature sodium for both kinds of tungsten. For the rotary swaged tungsten, the fracture stress decreases significantly after test. For the polished tungsten, the fracture stresses before and after testing are similar, these phenomena and their mechanism should be investigated further.

(4) Both original W-specimens show inter-granular brittle fracture mode before, and inter- and trans-granular brittle fracture mode after the test. Higher temperature exposure for long time may enhance embrittlement of tungsten, increasing with higher temperature.

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