Ⅳ. 材料研究

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CNIC-01638/33
CNNC-0003

Investigation of the Compatibility Between ADS Target Material with Coolant

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Abstract: The compatibility tests for the forging tungsten with coolants are performed in sodium at 500, 600 and 700 ℃, and in water at 100 ℃. The results show : a compact W_xO_y film is formed at the surface of the tungsten, its thickness is about 1～2 μm. There are also corrosion product Na_xWO_y on the surface of the specimens, the amount of Na_xWO_y dependents on the temperature and the oxygen content in the sodium. After test for more than 400 h, the matrix of tungsten is not attacked further by sodium and oxygen resulting from the protection of the W_xO_y film, the thickness of W_xO_y film and the weight loss become a constant; for the corrosion of the tungsten in water, a W_xO_y film at the specimen surface is formed at the beginning of the test, its thickness is about 0.8 μm; This film is porous and loose, and they peels off after test for more than 100 h. The new oxide film does not form again because of the lack of the oxygen, the weight loss of the specimens is near a constant.

Key words: Target material, Sodium, Water, Compatibility

INTRODUCTION

At present, the program of the compatibility study in our ADS project is focused on the compatibility tests for the tungsten with water and sodium. An ADS verification facility is proposed in next phase of our ADS project, a swimming pool reactor will be repacked as the subcritical reactor system, and tungsten will be used as the target[1] . On the other hand, the LMFBR may be one of the options as the subcritical reactor system of ADS[2], thus, it is necessary to understand the compatibility characteristics between tungsten with water and sodium.

1 W-Na COMPATIBILITY TEST

1. 1 Experimental method

(1) Forging tungsten specimens: size: ϕ 3 mm×13 mm, purity: 99.96 %

(2) Facility for test: high temperature stove system containing a special test section

(3) Test conditions : temperature: 500, 600, 700 ℃
test periods: 200, 400, 600, 1000, 1500 h
oxygen content in sodium: 12.6 μg/g, 32.2 μg/g
carbon content in sodium: 7 μg/g
area to volume ratio: 0.05 cm^{-1}

(4) Preparation of the capsule containing specimens and sodium: The specimens was put into a capsule, degassed under vacuum, and then the quantitative sodium was filled into the capsule in a glove box with high pure inert gas. After this, the capsules were welded by a cold-welding pliers. Finally, the capsules were removed from the glove box and welded by argon arc. The prepared capsules are showed in Fig. 1, and the glove box in Fig. 2.

The prepared capsules were installed into the test section in the high temperature stove system with pure Ar (Fig. 3) for compatibility test.

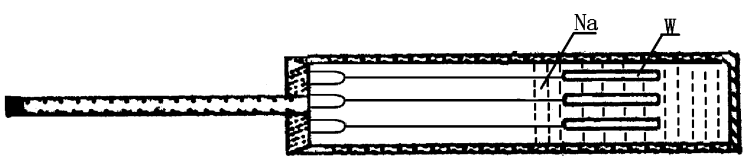


Fig. 1 Schematic diagram of the capsule

Fig. 2 Glove box system with inert gas

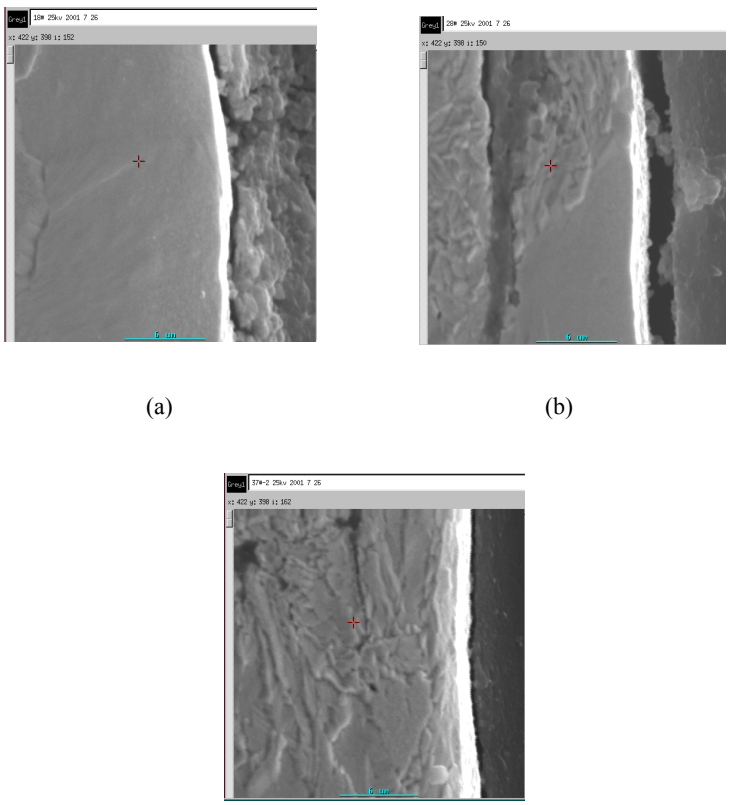
Fig. 3 W-Na compatibility test facility

1. 2 Results and discussion

1. 2. 1 Micro-morphology of the specimen surface

The SEM and optical-microscope observation for the specimens surface after compatibility tests at 600°C shows : there is a very thin and compact

film layer on the surface of the specimens, the thickness of these film layers is about 1～2 μm, and seems to be increase with the increasing of the test periods from 200 to 400 h , but nearly a constant after 400 h (Fig. 4 and Table 1).



(a) (b)

(c)

Fig. 4 Micro-morphologies of specimens surface

T = 600 °C w(O) = 32.2 μg/g

(a) 200 h (b) 400 h (c) 1000 h

Table 1 The thickness of the WxOy film after various test periods

Test period /h	Thickness of film/ μm
200	0.9
400	1.5
600	1.6
1000	1.6
1500	1.6

The compositions of the film may be W_xO_y and Na-W-O compounds. Due to the protection of the W_xO_y film after 400 h , sodium and oxygen penetrate difficultly into the matrix of the specimens further, therefore, the thickness of the film layer is nearly a constant after 400 h tests.

The X-ray diffraction analysis indicates that there are W_xO_y and Na-W-O compounds on the specimens surface (Fig. 5). Because the Na-W-O, such as the Na_xWO_y, can be dissolved in the water[3] when the specimens were cleaned by the water, therefore, there are no displaying of the Na-W-O peek at the X-ray diffraction spectrum. However, there is a displaying of the Na-W-O peek on the specimen surface when it is not cleaned by the water.

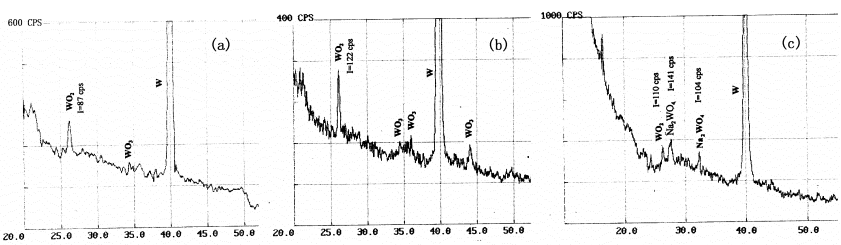


Fig. 5 X-ray diffraction spectrum of the reaction products

T = 600 °C, w(O) = 32.2 μg/g

(a) 200 h (b) 1500 h (c) 1500 h, not cleaned by water

1. 2. 2 Change of the specimen weight

The specimens after compatibility tests at 600 ℃ were cleaned with the alcohol and water respectively, in order to clean-up the sodium and reaction products on their surface. The weight of the specimen decreases after test and the weight loss appear to be a constant nearly after 400 h test (Fig. 6).

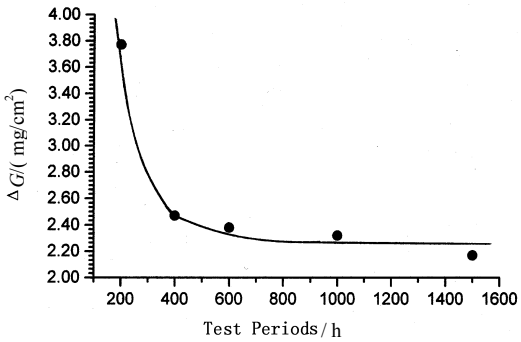


Fig. 6 Variation of the specimens weight versus test periods

T = 600 ℃, w(O) = 32.2 μg/g

The weight loss of the specimens may result from the formation of the W_xO_y and Na-W-O compounds dissolved in the water. As stated above, the thickness of the W_xO_y film is a constant nearly after 400 h test, therefore, the weight loss of the specimens seems also to be constant after 400 h.

1. 2. 3 Effect of the temperature and oxygen content in sodium

The tests results show that the temperature and oxygen content have a significant effect on the compatibility characters between the tungsten with sodium. Fig. 7 shows the different tendency of the weight loss for the test conditions of 12.6 and 32.2 μg/g oxygen at 500, 600 and 700 ℃. It can be seen that the weight loss decreases with the increasing of the temperature for the condition of 12.6 μg/g oxygen, this may results from the presence of the W_xO_y on the specimen surface, its thickness increases with the increasing of the temperature, and result in the decrease of the weight loss. Because the W_xO_y can be dissolved in the hot alkali solution[1], after the specimens were cleaned by hot NaOH solution, the weight loss of the them increases with the increasing of the temperature.

For the test condition of 32.2 μg/g oxygen, except for the formation of the W_xO_y, the formation of the Na-W-O compounds seems to be more easy than that of the W_xO_y. According to the free energy of the formation for Na-W-O and W_xO_y[4] and the corrosion characters of the materials in liquid sodium[5], the reaction of the W_xO_y with sodium and oxygen can be expressed as following:

$$A(W_xO_y)+B(Na)+Z(O) = X(Na_xWO_y)+Y(\ W\ )$$

Obviously, the increasing of the oxygen content in sodium will be favorable for the formation of the Na-W-O compounds.

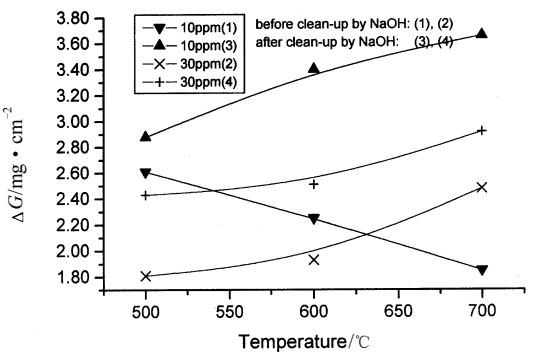


Fig. 7 Weight loss of the specimens versustemperature and oxygen content

(1) 1500 h, w(O) = 12.6 μg/g, (2) 1500 h, w(O) = 32.2 μg/g

(3) 1500 h, w(O) = 12.6 μg/g, (4) 1500 h, w(O) = 32.2 μg/g

Because the Na-W-O can be dissolved by the water and its amount increases with the increasing of the temperature, then the weight loss of the specimens increases correspondingly. After clean-up by hot NaOH, the W_xO_y dissolved in NaOH, the weight loss of the specimens greater than that before clean-up by NaOH (see Fig. 7). The X-ray diffraction analysis of the specimens surface reveals that the W_xO_y decreases with the increasing of the oxygen content (see Fig. 8), and the amount of the W_xO_y decreases and Na_xWO_y increases with the increasing of the temperature (see Fig. 9). It can be seen that the analytical results of the X-ray diffraction are in agreement with that of the weight loss.

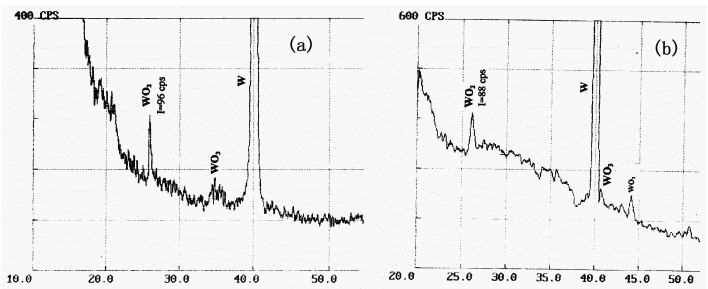


Fig. 8 X-ray diffraction spectrum of the specimens Surface under various oxygen content

T = 700 ℃, t = 1500 h (a) 12.6 μg/g, (b) 32.2 μg/g

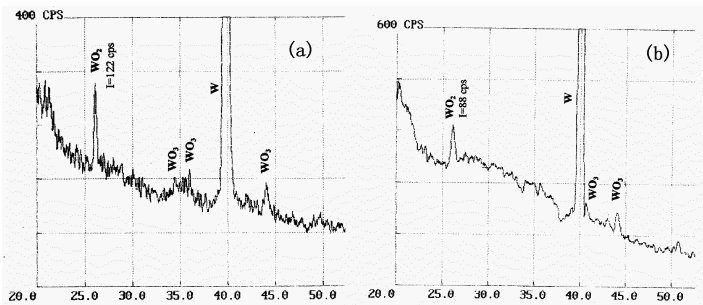


Fig.9 X-ray diffraction spectrum of the specimens Surface at various temperature

w (O) = 32.2 μg/g, t = 1500 h (a) 600 ℃ (b) 700 ℃

2 W-H_2O COMPATIBILITY TEST

2. 1 Experimental method

(1) Forging tungsten specimens: size, ϕ 4 mm×46 mm; purity, 99.96 %.

(2) Facility for test: autoclave system made of stainless steel (see Fig. 10).

(3) Test conditions:

temperature: 100 ℃

test periods: 100, 200, 500, 800, 1500, 2500, 3000 h

water quality: pH 5.9～6.8, conductivity＞1.00 μs /cm

SO_4^{-2}＜80 μg/kg, Cl^-＜20 μg/kg , Cu^{+2}＜0.2 μg/kg.

bubbling with N_2 for 5 h to remove oxygen
area to volume ratio: 0.05 cm^{-1}

2. 2 Results and Discussion

2. 2. 1 Weight loss

The weight loss of the tungsten specimens after tests indicates that the weight loss is the maximum during 200～500 h test periods, then it is a constant nearly after 500 h (see Fig. 11 (a)). The rate of the weight loss decreases with the increasing of the test periods gradually after 200 h test period (see Fig. 11 (b)). This may results from the formation accompanied with the dissolution of W_xO_y film on the surface of the specimens at the beginning of the test, and the film break down after 100 h. Because the test temperature (100 ℃) and the part pressure of the oxygen in the water is not high enough to form the compact W_xO_y film. The film is porous and loose; they peeled off and resulted in the increasing of the weight loss. Due to there are no enough oxygen in the water to form W_xO_y further with the increasing of the test periods, therefore, the weight loss of the tungsten is a constant nearly after longer test periods. The X-ray diffraction results of the tungsten specimens surface show that there are WO_3 peeks in the spectrum, and the WO_3 amount on the specimens surface decreases with the increasing of the test periods, there are no WO_3 film on the surface nearly in 3000 h test period (see Fig. 12). It indicated that the WO_3 film break down after 100 h test period, and peeled off fully at 3000 h. These results consist with that of the weight loss.

2. 2. 2 Micro-morphology of the specimen surfaces

The SEM observation of the specimens surface show that there is a very thin film on the surface of the specimen after for 100 h test. Its thickness is about 0.8 μm; the film is broken for 200 h test period (see Fig. 13); and there are no film on the specimen surface after tested for 3000 h.

It can be expected that the mechanism of the corrosion for tungsten in the water may be to form the W_xO_y film on the surface at first, then the film breaks down; and due to the part pressure of the oxygen in water is very low after longer test periods, the further corrosion of tungsten specimens is little.

Fig. 10 Autoclave system for W-H_2O compatibility test

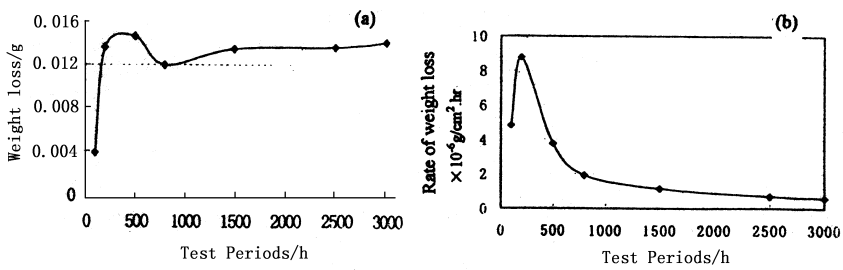


Fig. 11 Weight loss of tungsten specimens verses test periods

(a) weight loss (b) rate of the weight loss

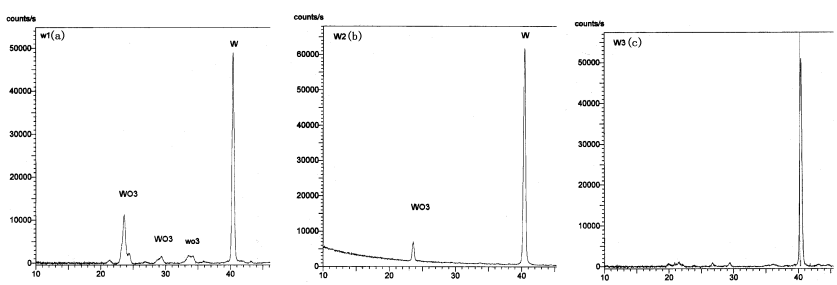
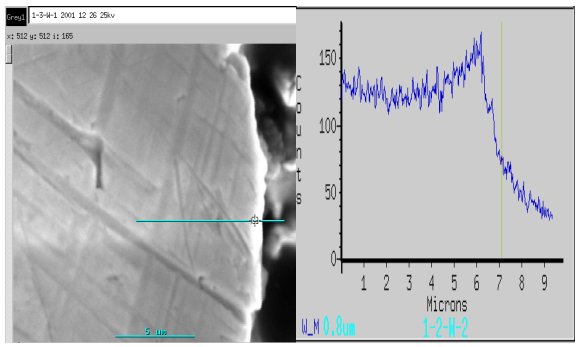
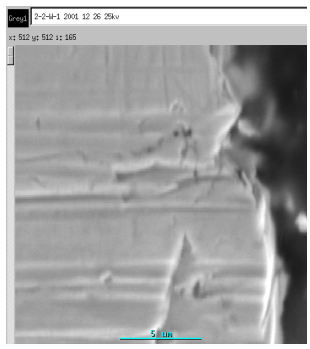


Fig. 12 X-Ray diffraction spectrum of W specimens surface

(a) 100 h (b) 200 h (c) 3000 h



(a) 100 h test



(b) 200 h test

Fig. 13 Micro-morphology of the specimen surfaces

3 CONCLUSION

(1) Under the test conditions of 600 ℃ and 32.2 μg/g oxygen content, the interaction between the tungsten and sodium forms a W_xO_y film layer; and the W_xO_y reacts with oxygen and sodium further to form the Na_xWO_y compound which can be dissolved by water. The W_xO_y protects the matrix of the tungsten from the attack further by oxygen and sodium; the weight loss of the tungsten specimens is a constant nearly after 400 h.

(2) The effects of the oxygen content in sodium and temperature on the compatibility character between the tungsten and sodium is significant. Under the test conditions of the 12.6 μg/g oxygen, the W_xO_y film and Na_xWO_y are

formed on the specimen surface. The thickness of the W_xO_y film increases with the increasing of the temperature, and the Na_xWO_y amount increases with the increasing of the temperature under the test condition of the 32.2 μg/g oxygen. The formation of the Na-W-O compounds are more easy when the oxygen content is higher.

(3) There are a porous and loose film on the tungsten specimens surface at 100 ℃ water and in test period of 100 h, they peeled off with the increasing of the test periods, resulting in the increasing of the weight loss. The mechanism of the corrosion for tungsten in the water may be to form the W_xO_y film on the surface at first, then the film break down. And due to the part pressure of the oxygen in water is very low after longer test periods, the further corrosion of the tungsten specimens is little.

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ADS 靶材和冷却剂的相容性研究

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摘　要：分别在 500，600 和 700 ℃的高温钠和在 100 ℃的堆用水质条件下进行了 ADS 靶材锻造纯钨与钠及水的相容性试验。研究结果表明：经钠侵蚀后的钨样品表面生成厚度约 1～2 μm 的致密膜和可溶于水的 Na_xWO_y 腐蚀产物，它们的量与钠温及钠中氧含量密切相关。经 400 小时相互作用后，由于所形成的 W_xO_y 的保护作用，钨基体免受钠和氧的进一步侵蚀，使 W_xO_y 膜的厚度及失重量趋于稳定；在本试验条件下，在钨和水相互作用初期，钨试样表面生成了厚度约 0.8 μm 的 W_xO_y 膜，该膜疏松多孔，100 h 后开始破碎脱落。因此时水中氧分压很低，不足以再与钨作用生成新的 W_xO_y 膜，使钨试样的失重量趋于稳定。

关健词：靶材 钠 水 相容性