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The research on improving the anti-oxidation of tungsten rhenium alloy wires

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Abstract: The research compared the stability of EMF (Electromotive Force) though the same electrode testing method. Oxidation, morphology and composition of Tungsten Rhenium alloy thermocouple wire was characterized by Zeiss scanning electron microscope (EV018)and XPS (X-ray Photoelectron Spectroscopy) . The results showed that a small amount of rare earth elements droping tungsten rhenium alloy Wire can keep stable at a longer period of time in high temperature oxidation environment. Through the analysis of the SEM (Scanning Electric Microscopy) and XPS (X-ray Photoelectron Spectroscopy), the oxide film dopping rare earth is much denser, as well as lower valence oxide content. In a word, the rare earth droping in the tungsten rhenium alloy wire stabilize the EMF with specific films.

1. Introduction

Tungsten Rhenium thermocouple have been widely used in aviation, iron and steel smelting, petrochemical and other high-temperature test field because of its advantage in high melting point, high strength, high thermoelectric force, fast response speed and large signal output. Tungsten Rhenium thermocouple is quite susceptive at oxidizing atmosphere ,which restrict its range of application and storage method. Concerning on the effect of heat treatment on mechanical property[1] and failure analysis[2], the thermocouple of anti-oxidation generally include filament surface treatment and packaging technology with surface dip coating material[3] and package isolating oxygen[4]. Through the study of Tungsten Rhenium alloy wire oxidation behavior, the Kuihan Wang[5] and Ming Dai[6] found that the oxidation film grow radially under 800℃ at oxidation atmosphere. meanwhile, the J.R. Distefano[7] studied the oxidation behavior of Mo-Re alloy at different temperatures and pressures ,they found that the materials with larger oxygen solubility are brittle at low oxygen pressure. Our experiment research the anti-oxidant properties by adding Rare Earth Lanthanum elements in the Tungsten Rhenium alloy.

2. Experiment

2.1. Materials Preparation

In the test, the alloy with the composition of（97.5%～96.5%）W-（2.5%～3.5%）Re-（0.01%～0.1%）La in weight was prepared. To be noted that the purity of Tungsten powder - diameter 1～8μm

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–is equal or greater than 99.9%.Rhenium added in form of Rhenium acid ammonia with purity not less than 99.99%; La added in form of analytical reagent Lanthanum Nitrate Hexahydrate . The preparation of W-Re-La alloy which have uniform composition and microstructure by metallurgic method containing weighing, high energy dispersion, low temperature roasting, high temperature deoxidize, adding forming agent, hydraulic pressure molding. Pre-sintering, sintering, density test, rotary forging, straight pulling, pull in the turntable and small turntable,500MM & 300MM fine drawing, electrolytic polishing and cleaning process, heat treatment.

2.2. Test method
The high precision digital multi-meter 8846A was used to measure and monitor the change of relative EMF (Electromotive Force) of the thermocouple wire which oxidize under 800℃; Using NETLSCH DIL449C thermo-gravimetric experiment equipment to test the oxidation process of WRe3 alloy (DSC/TG); The morphology and composition of oxidation film was characterized by Zeiss scanning electron microscope (EV018)and XPS (X-ray Photoelectron Spectroscopy) .

3. Analysis and discussion

3.1. The research of Rare Earth effect on EMF (Electromotive Force)
To improve the stability of thermocouple, the thermocouple should maintain the EMF (Electromotive Force) through standard index. The EMF (Electromotive Force) of WRe3 thermocouple wires（1#:La0.08%，2#:La0.1%）were tested in same polar method and found the non-uniformity is no more than 13μV (As shown in Table 1), which illustrate WRe3 alloy wires tolerance of temperature measurement under 0.125%.

Table1. The relative EMF of single Tungsten Rhenium thermocouple wire

Sample number	1#-1	1#-2	1#-3	2#-1	2#-2	2#-3
Relative EMF/μV	-4	3	5	1	-5	8

3.2. The stability testing of EMF in the air condition
Connecting two groups of K-type thermocouple wire with diameter 2.5mm as anode . In addition, the cathode separately used W-Re3 couple wire with diameter 0.5mm. The thermocouple wires were heated to 800±1℃ by electric heating tube furnace in the air. The FLUKE8846A digital multi-meter was used to measure the EMF of thermocouple, and record the data every 10 minutes, the results as shown in Figure 1.

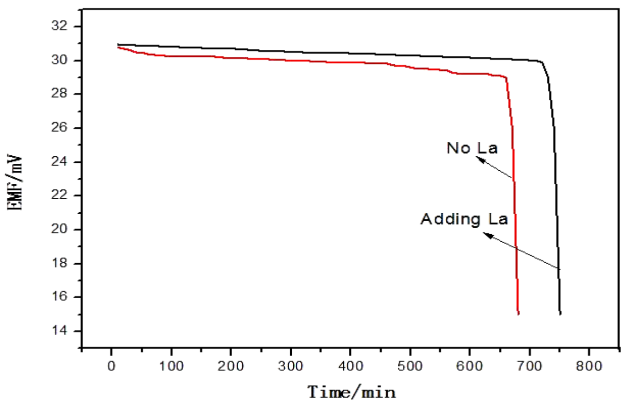

Figure 1. The EMF (Electromotive Force) of thermocouple at 800℃

The study found that the EMF (Electromotive Force) adding La perform more stable at 800℃ oxidation atmosphere, contrasting no La thermocouple wire. With time going on, EMF (Electromotive Force) sharply decrease, but the thermocouple doping La element works longer, just as shown in figure 1.

3.3 The analysis of oxidation process

Figure2 show the DSC/TG curves of W/Re alloy wires with Rare Earth La and without La element, respectively.

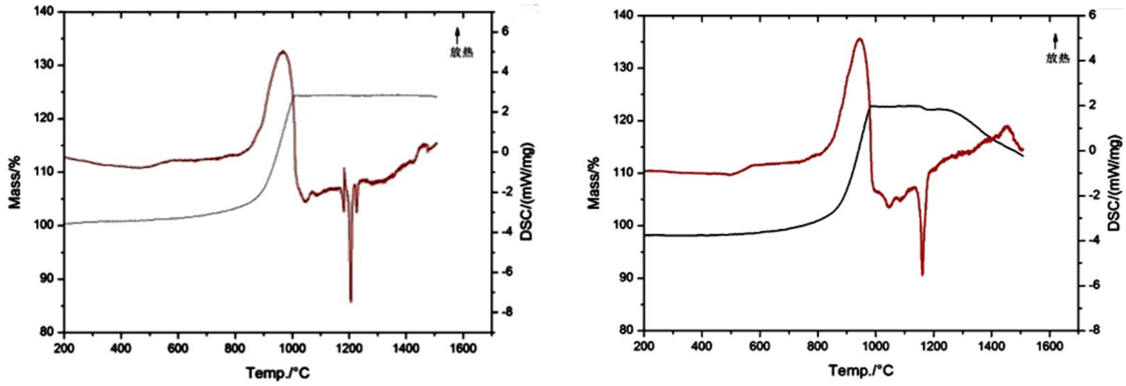

Figure 2. the DSC/TG contrast diagram of couple wires

The oxidation reaction of Tungsten Rhenium alloy in the air is an exothermic as well as height-increasing process, so the DSC/TG testing can be used to judge the oxidation . From the figure2, the Tungsten Rhenium thermocouple wire without doping La emerge a oxidation peak at 940℃,while doping La at 971℃.At the high temperature point, oxide film is easy to crack and peel off, which expose the wire to air and intensify oxidation reaction, thus leading to exothermic peak and weight increase significantly of wires. The DSC and TG curve peaks move to right by adding La element, which illustrate the importance of doping of Rare Earth La between oxide film and matrix enhanced.

3.4 The growth of oxide film

The micrograph morphology of W-Re3 alloy wires doping La or not oxidation at 850°Cwas showed in figure 3 and figure 4, respectively.

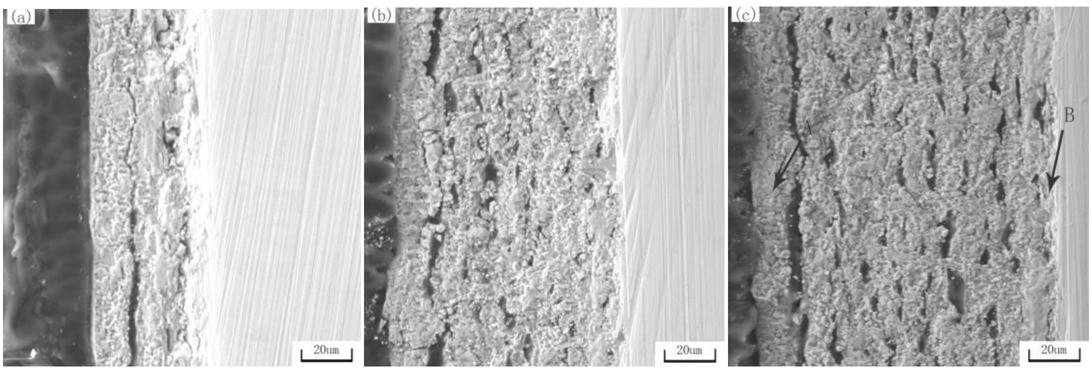

Figure 3. cross-section SEM images of WRe3 wires
（a）0.5h、（b）1h、(c) 1.5h

Figure 3 shows the oxidizing of WRe3 alloy wire without adding La at 850°C from 0.5h to 1h.With the extension of oxidation time , the film become more and more thick and more crack within oxidation film ,which caused large inner stress in the film and intensified the oxidation process. Fig.4 shows the oxidizing of WRe3 wires adding La under the same conditions, the Oxide film was compacted at 0.5h, even at 1.5h. No crack appears especially close to matrix, the permeate of oxygen to matrix/oxide film was hindered because of its compacted film. at the same time ,the film increase in a moderate way with time going on, which reflects that adding La in WRe3 thermocouple wire have more oxidation resistance than normal WRe3 thermocouple wire.

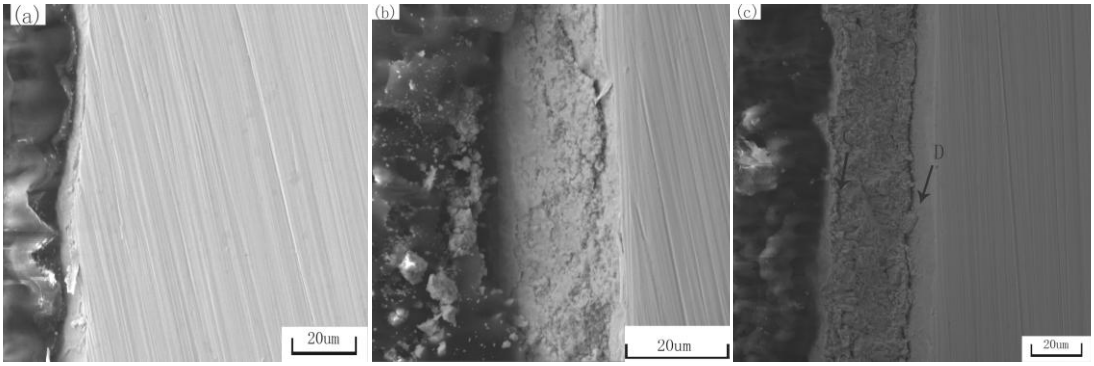

Figure 4. cross-section SEM images of WRe3 adding La
（a）0.5h、（b）1h、(c) 1.5h

3.5. Analysis of oxide film composition

The scanning results of W are shown in Figure. 5 through XPS (X-ray Photoelectron Spectroscopy), there are two types of Tungsten oxides. First, Fig.5 (a) the main peak position 35.7eV, shoulder position 37.85eV, Genus WOx compound W6+ ion peaks characteristic. Corresponding to the 4f7 and 4f5 peaks of W6+, While the 41.5 eV peak belongs to the peak of W6+, corresponding to the 5p3 peak of W6+. The oxide type is believed to be WO3. Another category, The main peak position 35.9eV, shoulder position 38.05eV, The W5+ ion peaks of WOx ion compounds correspond to the 4f7 and 4f5 peaks of W5+. Fig.5 (b) are also two types of products, The main difference between the two membrane components is the W5+ content. Calculation shows that the content of W5+ in Lanthanum oxide film accounts for 19.33% of W element content, otherwise，W5+ element content accounts for 14.39% of W element content。The results showed that the oxidation resistance of Tungsten-Rhenium wire was improved to a certain extent.

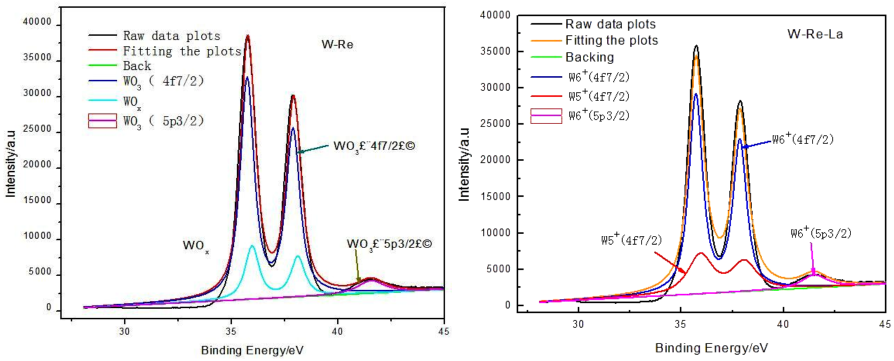

Figure 5. The XPS patterns of W element

4. Conclusion

(1)The EMF (Electromotive Force) is relatively stable within a period of time , before its significant mutations. Adding the Rare earth element in the wires, can prolong the stable state by 10% at 800 °C.

(2) By addition Rare earth ,The oxide film closing to the substrate is still relatively dense ,even oxidating at 850℃for 1.5 hours.
(3) Tungsten rhenium alloy wire can improve the anti-oxidation by droping rare earth element. which may be significant to enlarge the range of application and improve storage method of tungsten rhenium alloy wire, especially at low temperature oxidation atmosphere.

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