

## EFFECTS OF $Y_2O_3$ AND $CeO_2$ ON PROCESSING AND CHARACTERISTICS OF TUNGSTEN ELECTRODES<sup>①</sup>

Chen Ying, Nie Zuoren, Zhou Meiling, Zhang Jiuxing and Zuo Tieyong  
*School of Materials Science and Engineering,  
Beijing Polytechnic University, Beijing 100022, P. R. China*

**ABSTRACT** The effects of  $Y_2O_3$  and  $CeO_2$  in the rare earth tungsten electrodes of W- $Y_2O_3$ , W- $CeO_2$  and W- $Y_2O_3$ - $CeO_2$  on the processing and operating characteristics were discussed. The results suggested that the growth of tungsten powders and sintered crystal granularity is greatly retarded by  $Y_2O_3$ , and hindrance of  $CeO_2$  is comparatively slighter. It was also indicated that tungstates or oxytungstates are the most phases of rare earth elements in the sintered rod, and its stability will affect the forming process. W- $Y_2O_3$ - $CeO_2$  electrode has superior properties of arc starting and consumption resistance. And it is shown that the distribution characteristics of rare earth elements in the surface layer of electrode tip as well as the thermal stability of rare earth compounds are the determinate factors of the characteristics of electrodes' arc starting and consumption resistance.

**Key words**  $Y_2O_3$   $CeO_2$  tungsten electrode arc-starting consumption

### 1 INTRODUCTION

In recent years, tungsten electrode materials containing one kind of rare earth metal oxide as  $La_2O_3$ ,  $CeO_2$  and  $Y_2O_3$ , have been developed in the world<sup>[1-7]</sup>. The effects of rare earth metal oxides on electrodes' operating properties were initially studied, however, the actions of rare earth metal oxides during the electrode preparation have been studied little, and the studies on the effects of combined rare earth metal oxides on the electrode preparation and operation have been hardly carried out yet. In this text, the actions of  $Y_2O_3$  and  $CeO_2$  are analyzed during the preparation of W- $Y_2O_3$ , W- $CeO_2$  and W- $Y_2O_3$ - $CeO_2$  electrodes, and the forms of these rare earth oxides in sintered tungsten rod as well as its effects on the electrode's heat processing are discussed. Moreover, the operating properties of three rare earth tungsten electrodes above and W-Th $O_2$  electrode are measured, and the effects of  $Y_2O_3$  and  $CeO_2$  are also analyzed.

### 2 EXPERIMENTAL

#### 2.1 Materials fabrication

Tungsten powder was produced through two times of reducing by  $H_2$  from  $WO_3$  powder with the average granularity of  $8.4\mu m$ , and the rare earth metal oxides were doped with rare earth metal nitrates. The chemical compositions of tungsten electrode materials produced are listed in Table 1, and the total mass percentages of oxides contained in electrodes are the same.

**Table 1** Chemical composition of electrodes

Sample symbol	Oxide contained
WY	$Y_2O_3$
WC	$CeO_2$
WYC	$Y_2O_3 + CeO_2$
WTh	Th $O_2$

#### 2.2 Rare earth metal oxide effects research methods

The effects of rare earth metal oxides on

① Project 9500810 supported by the National Doctorate Program Fund of Education Ministry of China and Beijing Education Committee Essential Foundation Received Jul. 2, 1998; accepted Nov. 10, 1998

electrode preparation were studied by comparing the granularity of powders with SEM observation as well as X-ray diffraction.

In arc starting characteristics and electrode consumption resistance experiments, electrodes diameter 2.4 mm is used. The minimum open-circuit voltage required for reliable starting and the decrease in the electrode weight after arcing at 240 A for 20 min were measured.

The actions of rare earth metal oxides during the electrode operating was analyzed by means of AES depth profiling and the sputter velocity is 300 Å/min.

### 3 RESULTS AND DISCUSSION

#### 3.1 Materials processing characteristic

##### 3.1.1 Powder

The granularity of  $WO_2$  and W powders are shown in Table 2.

**Table 2** Average granularity of powders ( $\mu m$ )

Sample symbol	$WO_2$	W
WY	4.04	1.26
WC	3.53	1.90
WYC	4.40	1.30

The enlargement of powder particle during the  $WO_3$  reducing is mostly due to the volatilization and sedimentation of oxides<sup>[8]</sup>. In the reduction process,  $WO_x$  ( $x < 3$ ) may react with  $H_2O$ , and as a result,  $WO_x \cdot nH_2O$  is obtained, which is easy to volatilize. These substances settle onto the surface of tungsten oxides or tungsten powder, and the tungsten powder particles enlarging is resulted from followed reduction of  $WO_x \cdot nH_2O$ .

Rare earth nitrates are decomposed to rare earth oxides ( $ReO$ ) during the powders reducing. As described above,  $WO_x$  ( $x < 3$ ) reacts with rare earth oxides and the compounds of  $WO_x \cdot nReO$  are produced. As well known, rare earth oxides are all stable substances, and they are not only uneasy to volatilize, but also unable to be reduced by  $H_2$ . So the compounds of  $WO_x \cdot nReO$  covered over the powder surface forestall the powder particle enlargement.

The decomposition temperature of different rare earth nitrates differ from each other (Table 3)<sup>[9]</sup>. The higher the temperature is, the longer the time needed to form  $WO_x \cdot nReO$  compound, then the slighter the retarding action is. The decomposition temperature of  $Y(NO_3)_3$  is higher than that of  $Ce(NO_3)_3$ , so the granularity of  $WO_2$  powders in WY sample is larger than that of WC sample. However, the amount of rare earth oxide particles decomposed from rare earth nitrate, may be another important factor to affect the powders' granularity, and it just may be the above two factors that the granularity of  $WO_2$  powders in WYC is larger than that in WY and WC.

**Table 3** Decomposition temperature of rare earth nitrate

Rare earth nitrate	Decomposition temperature/ K
$Y(NO_3)_3$	753
$Ce(NO_3)_3$	723

The granularity of tungsten powder after the second reducing depends on the granularity of  $WO_2$  powder and the amount of rare earth oxide particles. As mentioned above, the more the rare earth oxide particles on the powder surface, the greater the retarding action is. The mass ratio in all electrodes are the same, so it can be worked out from the density of rare earth oxide (Table 4)<sup>[9]</sup> that the rare earth oxide's volume ratio of WY are the largest in the three specimens of WY, WYC as well as WC, and that of WC is the least. As a result, the tungsten powder's granularity of WY sample after reducing is the smallest, and that of WC is the largest.

**Table 4** Physical parameters of rare earth oxides

Oxide	Density / ( $g \cdot cm^{-3}$ )	Melting point/ K	Boiling point/ K
$Y_2O_3$	5.01	2708	4573
$CeO_2$	7.312	2873	-

The SEM morphologies of  $WO_2$  and W powders are shown in Fig.1.  $WO_2$  powders are mostly diploid particles consisting of single ones,

however, the W powders are single having regular shape.

### 3.1.2 Sintered rod

In the SEM morphologies of sintered rods' fracture of WC and WYC specimens (Fig. 2), it is shown that the fracture is of brittleness along the crystalline interfaces, on which some particles of the second phases are distributed, and the crystal particles' size of WYC is smaller than that of WC. Therefore, it can be concluded that the obstacle of  $\text{CeO}_2$  to the crystal enlargement of the sintered rod is slighter than that of  $\text{Y}_2\text{O}_3$ .

X-ray diffraction result of WYC specimen

(Fig. 3) elucidates that tungstates or oxytungstates are the most phases of rare earth elements in the sintered rod. The melting point and heat stability of these tungstates or oxytungstates formed from different rare earth metal oxides and tungsten, are different from each other with the type of rare earth oxide (Table 5)<sup>[10]</sup>, and these salts will hamper the distortion of crystal particles. The better the stability of these salts is, the greater the hamper action will be. Therefore, different processing technology should be adopted with different rare earth oxide doped in tungsten materials.

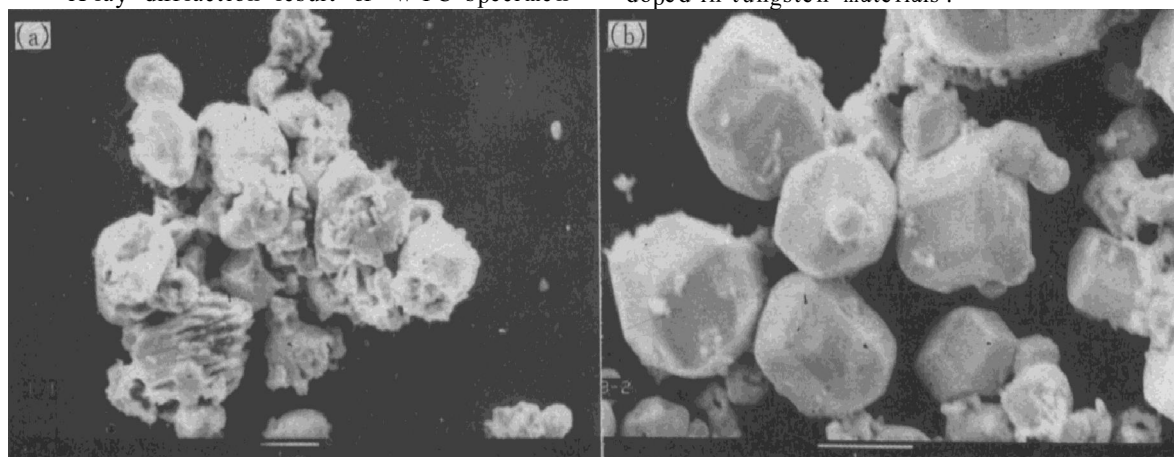


Fig.1 SEM morphology of powders  
(a) —  $\text{WO}_2$ ; (b) — W

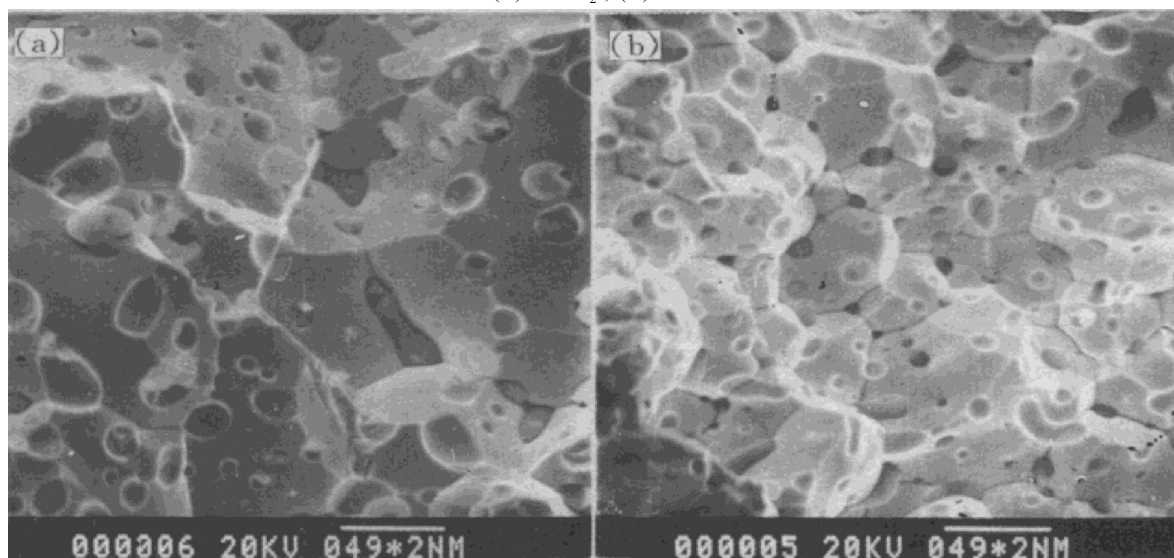
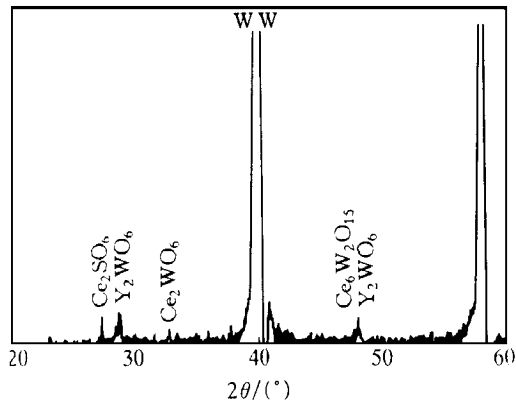


Fig.2 SEM morphology of sintered rod's fracture  
(a) — WC; (b) — WYC



**Fig.3** X ray diffraction pattern of sintered WYC rod

**Table 5** Reaction between rare earth oxide and tungsten

Rare earth oxide	Substance obtained (MP: Melting point)
$Y_2O_3$	Tungstates (MP: 1 743 K) or oxytungstates (MP > 2 073 K)
$CeO_2$	Tungstates (MP: 1 363 K)

### 3.2 Operating properties

#### 3.2.1 Arc starting

It can be seen distinctly from the results of arc starting experiments (Table 6) that WYC electrode has the lowest critical arc starting voltage, and comparatively, WTh electrode has the highest critical voltage, the arc starting property of WYC electrode are the best in all, and that of WTh electrode is the worst. In addition, in the experiments, arc breaking was easy to be detected when WC was used.

**Table 6** Critical arc starting voltage

Sample symbol	Critical arc starting voltage/ V
WY	32
WC	35
WYC	29
WTh	36

#### 3.2.2 Consumption

It is indicated from Table 7 that WY and WYC electrodes were consumed slightly, yet

WC and WTh electrodes were spoiled seriously.

**Table 7** Electrode's consumption after arcing

Sample symbol	Mass/ g		Decrement/ mg
	Before arcing	After arcing	
WY	6.867 6	6.864 6	3.0
WC	7.192 8	7.188 6	4.2
WYC	7.274 6	7.271 5	3.1
WTh	7.237 7	7.233 2	4.5

### 3.3 Action analysis of $Y_2O_3$ and $CeO_2$

The distribution change of rare earth metal elements is illustrated in Fig.4. it can be seen from Fig.4(a) that cerium had moved from the center part to the sub-surface layer during the electrode preparation. The distribution of yttrium and cerium as Fig.4(a) is beneficial to the arc starting of electrode. Firstly, rare earth metal elements can be assured from the amount rising of cerium in the sub-surface layer of electrode's tip. Secondly, the existence of yttrium compounds, which are more stable than cerium compounds<sup>[10]</sup>, may need to avoid consuming of rare earth elements on the surface of electrode tip so fast as not to be compensated in time and arc breaks with easy. After arcing for some time, the consistence of cerium in the sub-surface layer of electrode tip was decreased, meanwhile, that of yttrium was increased, it is to say that the migration of yttrium from the electrode matrix to the surface can compensate the consumption of rare earth elements on the surface, as a result, it is assured that the electrode can work with enhanced stability and duration for longer time.

Based on the discussion above, we consider that in the sub-surface layer of WC electrode tip there are lots of cerium compounds before arcing, which has low melting point<sup>[10]</sup> and is so easy to be consumed heavy during arc starting that arc starting failure and arc breaking are resulted; after arcing with a heavy load and for a long time, cerium in the sub-surface of electrode tip was consumed terribly and electrode worked as a pure tungsten electrode, therefore, was destroyed seriously. However, the increasing of

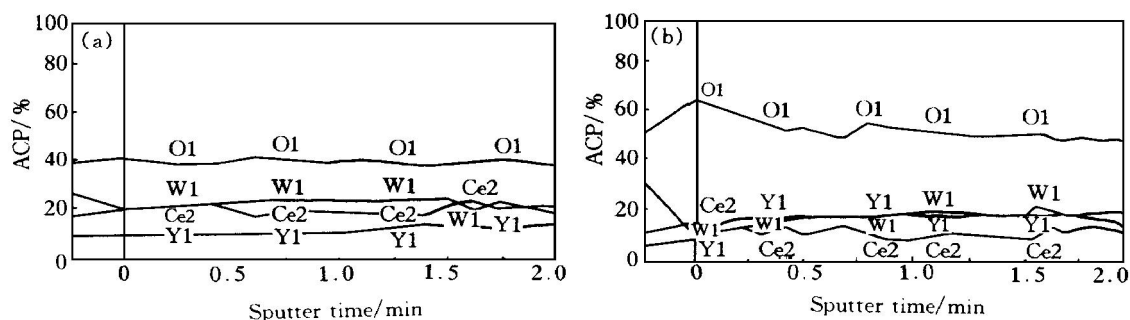


Fig.4 AES pattern of rare earth elements on the sub-surface layer of WYC electrode's tip  
(a) —Before arcing; (b) —After arcing

rare earth elements in the sub-surface layer, which happened in WYC electrode, didn't take place in WY electrode, and this may be the reason why the critical arc starting voltage of WY electrode is higher than that of WYC electrode. On the other hand, yttrium compounds have high melting point and good thermal stability, once electrode starts to arcing, it can arc steadily, so the property of arc starting of WY electrode is better than that of WC electrode. Moreover, because of the same reason as above, the yttrium compounds is decreased slightly in the sub-surface layer of WY electrode tip as in WYC electrode, and WY electrode has almost the same consumption resistance as WYC electrode.

#### 4 CONCLUSIONS

(1) The actions of rare earth metal oxides are different during electrode preparation.  $Y_2O_3$  retards the enlargement of tungsten powder and the crystal particles of sintered rods more greatly than  $CeO_2$ .

(2) In sintered rods, tungstates or oxytungstates are the most phases of rare earth elements, the heat stability of which will affects the processing properties.

(3) WYC electrode has not only the best properties of arc starting in all electrode studied, but also good consumption resistance; WY electrode has almost the same consumption resistance as WYC electrode, while its arc starting property is not so good as WYC electrode; WC and

WTh electrodes are the worst in contrast with WY and WYC electrodes not only in arc starting property but in consumption resistance.

(4) The heat stability of rare earth metal compounds influences decidedly the distribution of rare earth elements in the sub-surface layer before arcing and its actions during arcing forward the operating properties.

#### REFERENCES

- 1 Matsuda F, Ushio M, Sadek A A. Trans Japan Weld Soc, 1990, 21(2): 3.
- 2 Ushio Masao, Sadek Albert A, Matsuda Fukuhisa. Plasma Chemistry and Plasma Processing, 1991, 11(1): 81.
- 3 Matsuda Fukuhisa, Ushio Masao, Hasegawa K. 1993, EP0651065.
- 4 Matsuda Fukuhisa, Ushio Masao, Hasegawa K. 1993, EP0651066.
- 5 Yang Yang, Zhou Meiling, Li Hanguan. J of Central South Institute of Mining and Metallurgy, (in Chinese), 1993, 24(1): 69.
- 6 Nie Zuoren, Zhou Meiling, Zhang Jiuxing *et al.* Materials Review, (in Chinese), 1997, 11(5): 19.
- 7 Nie Zuoren, Zhou Meiling, Zhang Jiuxing *et al.* Rare Metal Materials and Engineering, (in Chinese), 1997, 26(5): 1.
- 8 Huang Peiyun. Principle of Powder Metallurgy, (in Chinese). Beijing: Metallurgical Industry Press, 1982: 11.
- 9 Xu Guangxian. Rare Earth, (in Chinese). Beijing: Metallurgical Industry Press, 1995: 8.
- 10 Sadek A A, Ushio M, Matsuda F. Metallurgical Trans A, 1990, 21(A): 3221.

(Edited by Zhu Zhongguo)