Behavior of Rare Earth Metal Oxides during Arcing†

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Abstract

This work was carried out on one standard electrode (W-Tho$_2$) and other electrodes developed by additions of La$_2$O$_3$, CeO$_2$ and Y$_2$O$_3$. Their behavior during arcing was analysed qualitatively after arcing in pure argon at 200 A for several time intervales, also after furnace heated ones for W-La$_2$O$_3$ and W-Tho$_2$ electrodes.

The present results have indicated that the superiority on arc characteristics strongly depends on the behavior of the rare earth metal oxides during arcing.

It was observed that the rare earth metal oxides forming, tungstate or oxy-tungstate during arcing while ThO$_2$ react with tungsten forming pure Th. The differences between the melting points, migration and vaporization rates and feeding rates of these oxides and its reaction products with tungsten have much influences on the stability of these oxides during arcing. Therefore, electrodes activated with La$_2$O$_3$ (2%) showed good arc characteristics related to the stability of La$_2$O$_3$ during arcing comparing with other oxides.

KEY WORDS : (Tungsten) (GTA Welding) (GTA Welding Electrode) (Rare Earth Metal Oxides)

1. Introduction

From the previous study[1], it is obvious that the superiority on the arc characteristics provided by the tungsten electrodes activated by La_2O_3, Y_2O_3 and CeO_2 comparing to ThO_2 tungsten electrodes. Particularly La_2O_3 tungsten electrodes represent the best properties among them.

In order to clarify the differences between all of these oxides and its effects on arc characteristics it is necessary to make a study on the comparable metallurgical characteristics and the behavior of these oxides during arcing.

2. Experimental Procedures

The investigated electrodes in this work were produced by the conventional powder metallurgy process with 3.2 mm. diamater, centerless ground rods. The power system was a conventional constant current type, with a negative direct current in the electrode a copper water cooled anode. A constant arc length of 3 mm. and torch angle of 90 degress to the anode were used throughout the series of tests.

Arcing with constant arc current (200 amp.) at time intervals in pure argon had been done to observe the metallurgical changes and the behavior of oxides.

Specimencs were prepared for metallographic examination by means of hard griding through 1500 emery papers and polishing with fine alumina. Polished specimens were electrolytically etched in a solution consisting of NaOH-10% normal, for SEM observations. During the electrolytic etching, the current voltage was set at 30V for 30 Sec. It helps for delineating the morphological change of the oxide shape after arcing. To observe the microstructure and the recrystallized grains after arcing Murakami's reagent was used. Etching reagent was applied by swabbing for 5-10 Sec.

A comparison had been made between the microstructure after arcing for W-La_2O_3 and W-ThO_2 electrodes in pure argon for one hour and the microstructure after furnace heated ones in pure argon and vacuum for one hour at different temperatures to observe the behavior and the effect of rare earth metal oxides on the electrode microstructure in steady state conditions.

3. Experimental Results

3.1 Tungsten electrode activated with La_2O_3

Figure 1 shows the EDX line analysis of Lanthanum after arcing in pure argon at 200 amp. for different arcing times. It is obvious that the distribution of La_2O_3 changed and concentrated at some places according to the temperature distribution. Moreover, with increasing arcing time the locations of these oxides peacks changed suggesting

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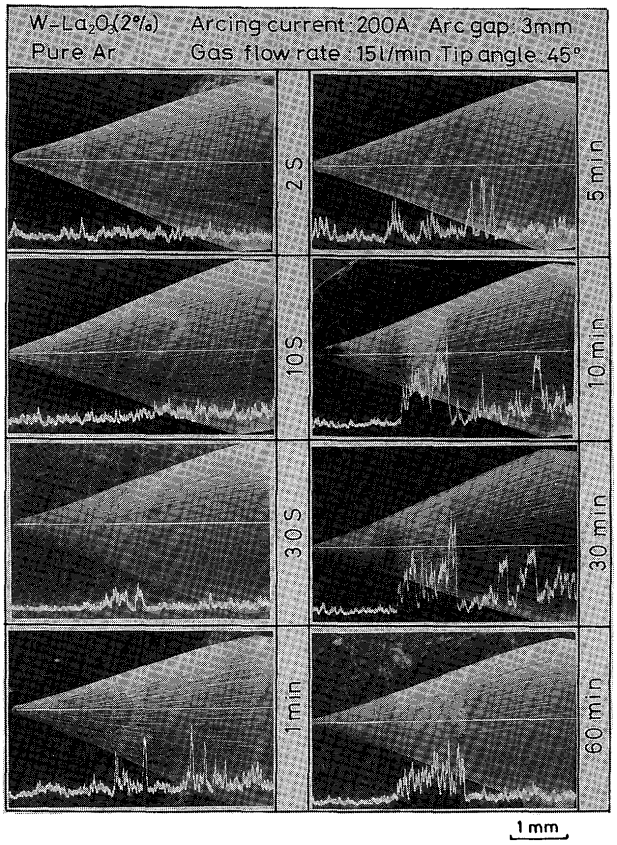

Fig. 1 Apperance of electrode surface with EDX line analysis after arcing for W-La_2O_3 electrodes.

that La_2O_3 may be migrated and accumelated at regions near the tip, while at the tip the vaporization rate of those oxides is much higher than the migration rate.

To verify this, **Figure 2** shows the microstructure of W-La_2O_3 electrodes after arcing for 30 min. and 1 hr. From this microstructures it may be point out the following: at 30 min. the La_2O_3 concentrated near the tip at about 1mm. while at 2 mm. the concentration of La_2O_3 decreased and lead to increase the tungsten grain size. With increasing arcing time the same area at 2 mm. became rich again while the grain size kept large. Also it can be inferred from these observations that the La_2O_3 migrated throughout the electrode tip.

Using SEM to observe the shape of migrated La_2O_3. The longitudinal shape of La_2O_3 particles were observed to change with leading edge exhibits a sharply angular shape, but the trailing surfaces are rounded as can be seen in **Fig. 3**, both at the edge and at the center of electrode. That morphological changes almost occured in the direction of high temperature. In other words, the migration of La_2O_3 occured from the lower temperature zone to the higher temperature zone.

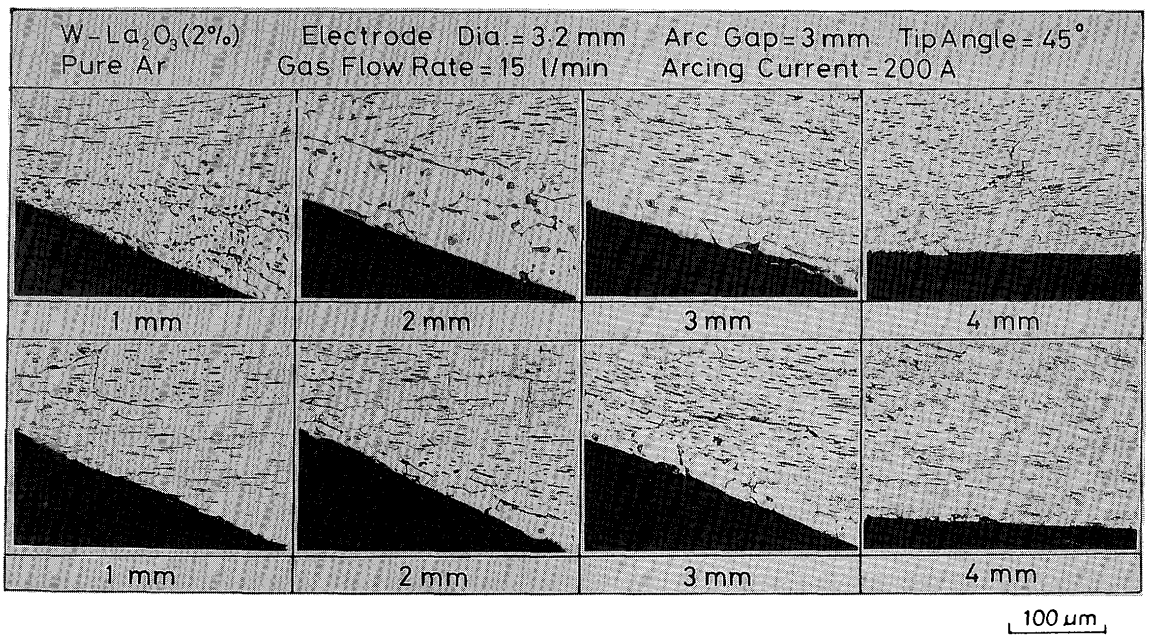

Figure. 2 Typical microstructure of W-La_2O_3 electrode at different distances from the electrode tip. Upper part after 30 min lower part after 60 min.

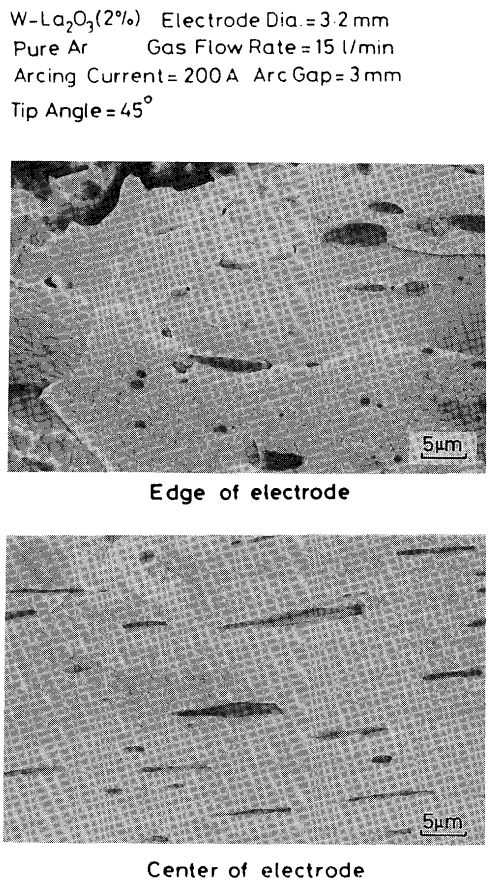

Fig. 3 The shape of migrated La_2O_3 particles observed by SEM.

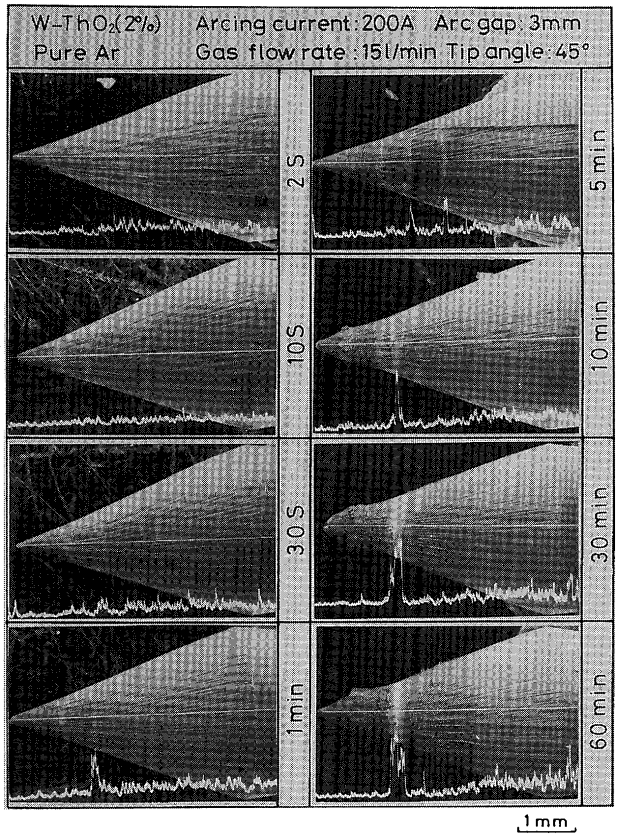

Fig. 4 Appearance of electrode surface with EDX line analysis after arcing for W-ThO_2 electrodes.

3.2 Tungsten electrodes activated with ThO_2

Figure 4 shows the EDX line analysis of thorium after arcing in pure argon at 200 amp. for several arcing times. The same behavior can also be observed as follow, at 5 min. there are two concentrated rings of ThO_2 but after 10 min. arcing these two rings became as one ring and with increasing arcing time the width of this ring became wider as an indication on the migration process, while at the tip there is no ThO_2 can be identified.

Figure 5 shows the microstructure of W-ThO_2 elect rode after arcing in pure argon for 30 min. and 1 hr. at 200 amp. It may be noted that the ThO_2 content which remained after arcing is lower than that in case of W-La_2O_3 electrode.

3.3 Tungsten electrodes activated with CeO_2

Figure 6 shows an example of the EDX line analysis of cerium before and after arcing in pure argon for 30 min. and 1 hr. and in $Ar+O_2(0.2\%)$ for 5 and 15 mins. at 200 amp. It can be noted that, the Ce-oxide has a uniform distribution throughout the electrode tip in both cases without located concentration peaks. Also, from **Fig. 7** which shows the microstructure of W-CeO_2 electrodes after arcing, it is obvious that the Ce-oxide still remain at the edge of the electrode. However, the area which far from the electrode tip (about 4 mm) has lower Ce-oxide content than the area near the tip. These observations suggesting that the migration rate of Ce-oxide is much higher than the other oxides.

3.4 Tungsten electrodes activated with Y_2O_3

In case of W-Y_2O_3 electrodes it is difficult to carry out the EDX line analysis due to the interferance between the tungsten and yttrium peaks. So that, this type of electrodes was studied only microscopically. **Figure 8** shows the microstructures of W-Y_2O_3 electrodes after arcing in pure argon for 30 min. and 1 hr. It is obvious that the Y_2O_3 still remain and stable after arcing while the recrystallization of tungsten occured.

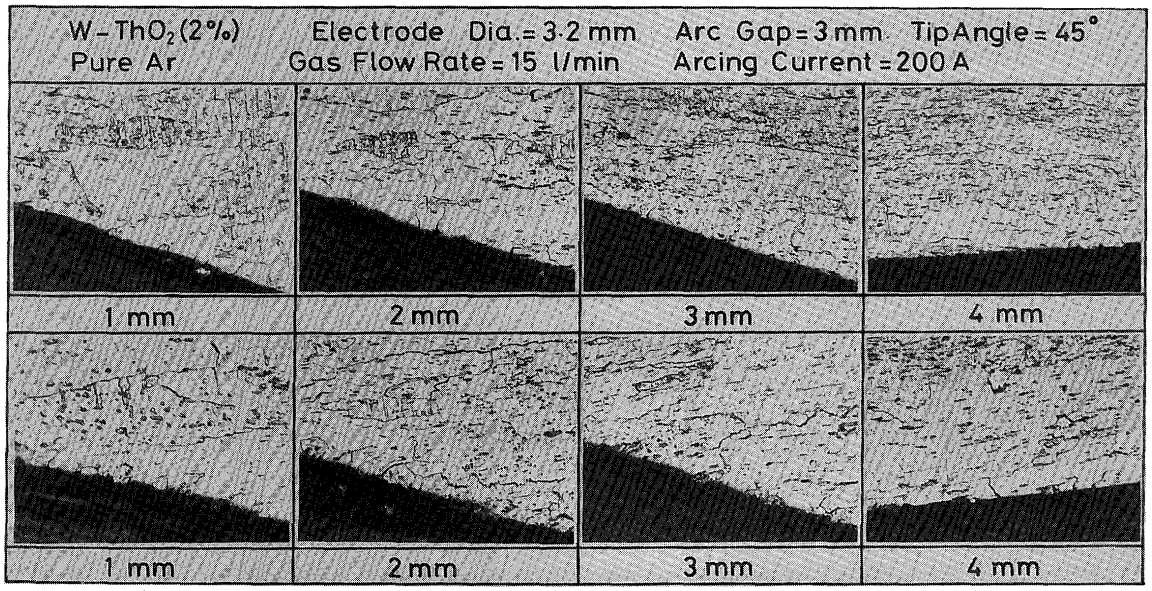

Fig. 5 Typical microstructure of W-ThO_2 electrode at different distances from electrode tip. Upper part after 30 min lower part after 60 min.

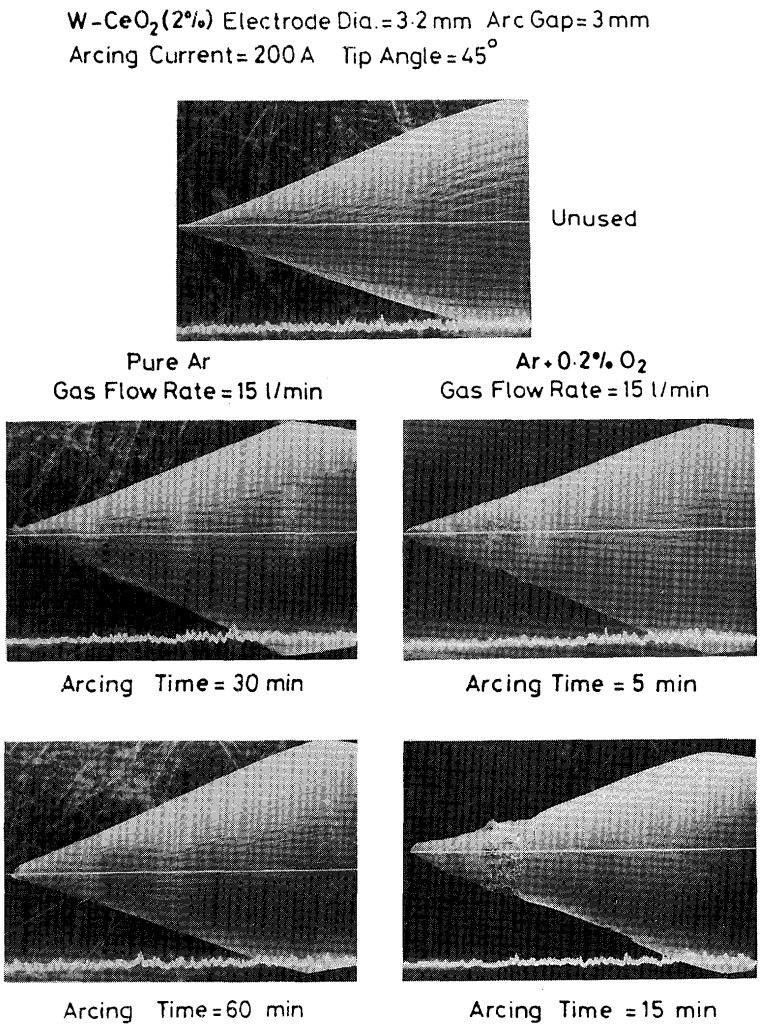

Fig. 6 Appearance of electrode surface with EDX line analysis before and after arcing for W-CeO_2 electrodes.

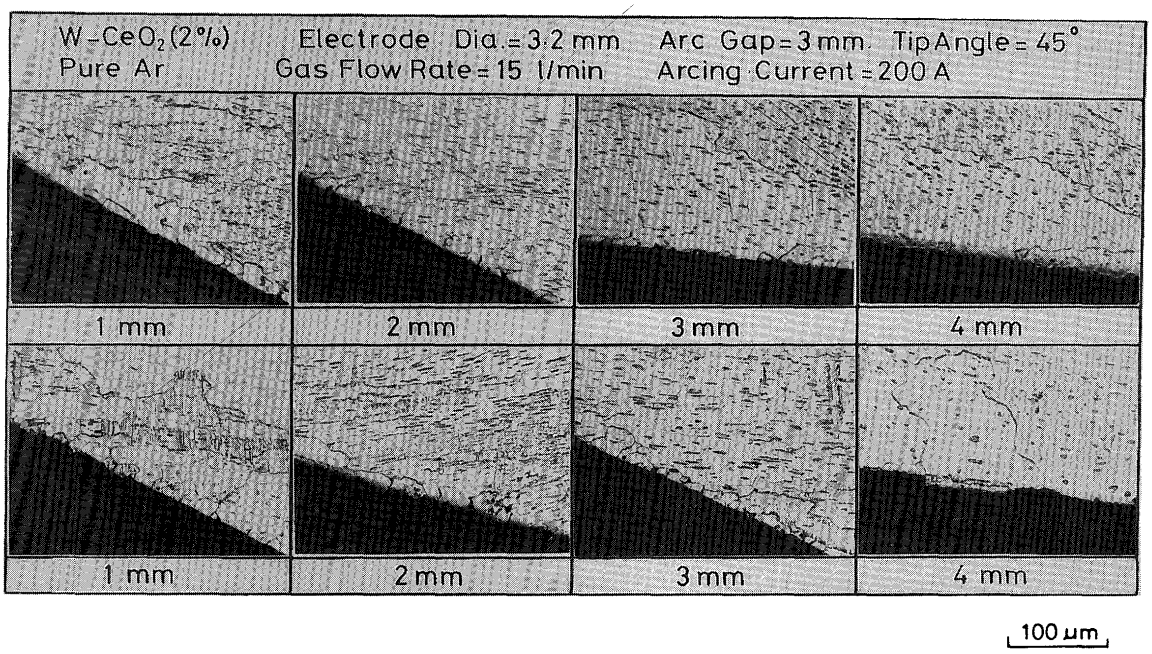

Fig. 7 Typical microstructure of W-CeO_2 electrode at different distances from electrode tip. Upper part after 30 min lower part after 60 min.

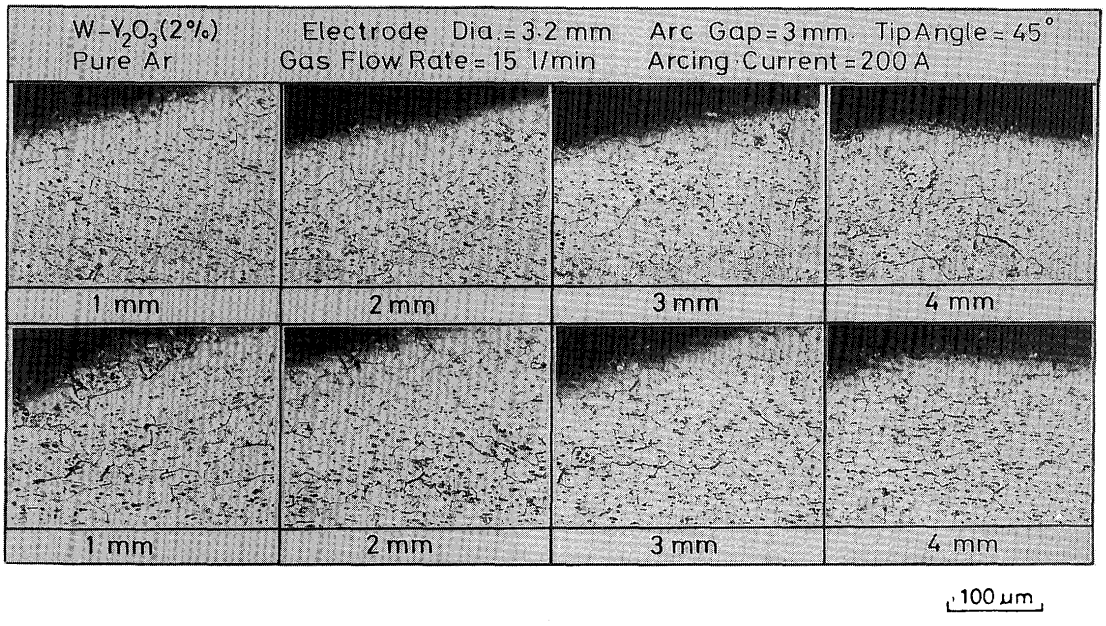

Fig. 8 Typical microstructure of W-Y_2O_3 electrode at different distances from electrode tip. Upper part after 30 min lower part after 60 min.

3.5 Heat treated electrodes

To study the migration and vaporization behaviors of these oxides precisely a comparison had been made between the microstructure after arcing for W-La_2O_3 and W-ThO_2 electrodes in pure argon for 1 hour and the microstructure after furnace heated in pure argon and vacuum for the same time at different temperatures.

Figures 9 & 10 show the microstructures of W-La_2O_3 and W-ThO_2 electrodes respectively, at the edge and bulk of electrodes after furnace heating at 1800^{0}C, 2000^{0}C and 2200^{0}C. It can be seen that;

(1) The La_2O_3 started to leave the electrode surface at 1800^{0}C in case of pure argon.

(2) With increasing the temperature the concentration of both oxides decreases at the edge and bulk of the electrode. That can be considered as an indication about the migration of those oxides from the bulk to the electrode edge at which vaporization of these oxides takes place.

(3) The concentration of both oxides in case of vacuum is lower than that in case of pure argon. That can be logically understood due to the highest vaporization rate in that case.

(4) The concentration of La_2O_3 which remained in the electrodes after heating is much higher than the concentration of ThO_2. That's can be clearly observed from **Table 1** , which shows the relative volume fraction of both oxides. Also, from Table 1, it can be inferred that the concentration of both oxides decreases with increasing temperatures at the edge and bulk of electrodes as mentioned before.

4. Discussions

The collected data for physical and thermodynamics properties and the experimental observations for oxides behaviors are given in **Table 2**. Also, typical microstructures for the investigated electrodes tip after arcing are shown in **Fig. 11**. Based on such data, the following statments become obvious.

4.1 Effect of oxides on tip shape

The stability of tip shape of tungsten electrode activated by rare earth metal oxides is significantly higher than that of tungsten electrode activated by ThO_2. The most stable oxide is Y_2O_3 followed by La_2O_3 and CeO_2. However, the previous studies[1,2] about the arc characteristics of these electrodes showed the superior characteristics of La_2O_3 while in case of Y_2O_3 and CeO_2 showed acceptable and good characteristics comparing to ThO_2. In that order it can be said that the best electrode among those electrodes is W-La_2O_3.

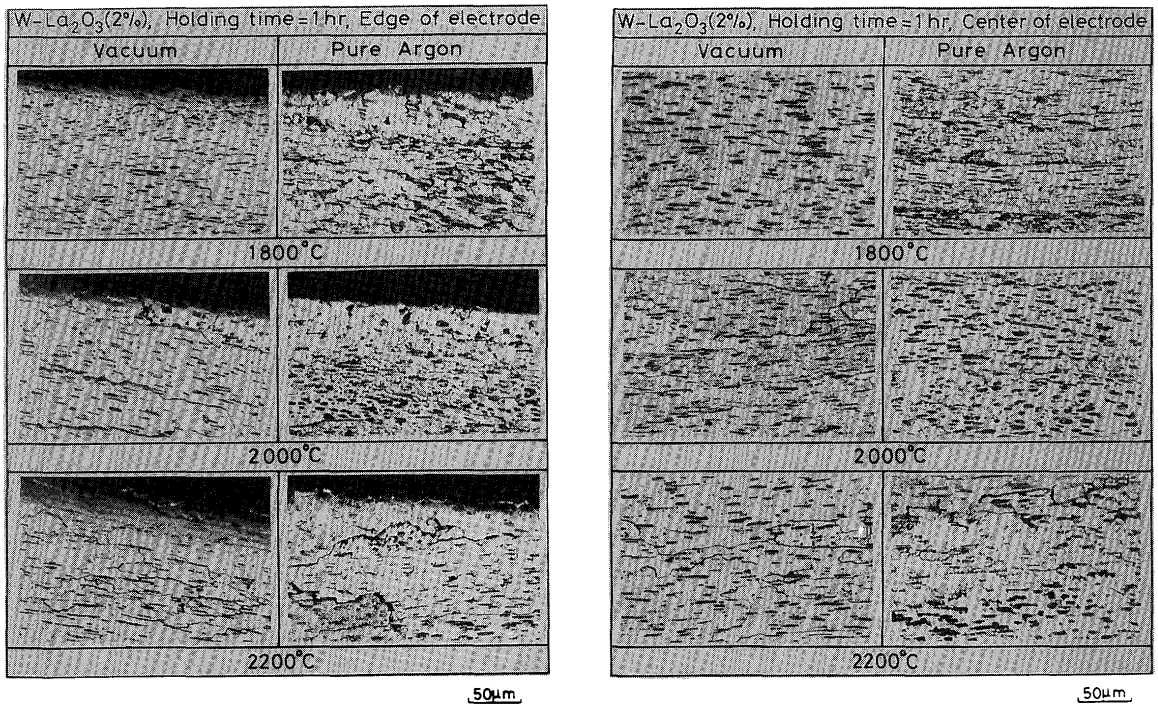

Fig. 9 Microstructure changes after furnace heating in pure argon and vacuum for W-La_2O_3 electrodes.

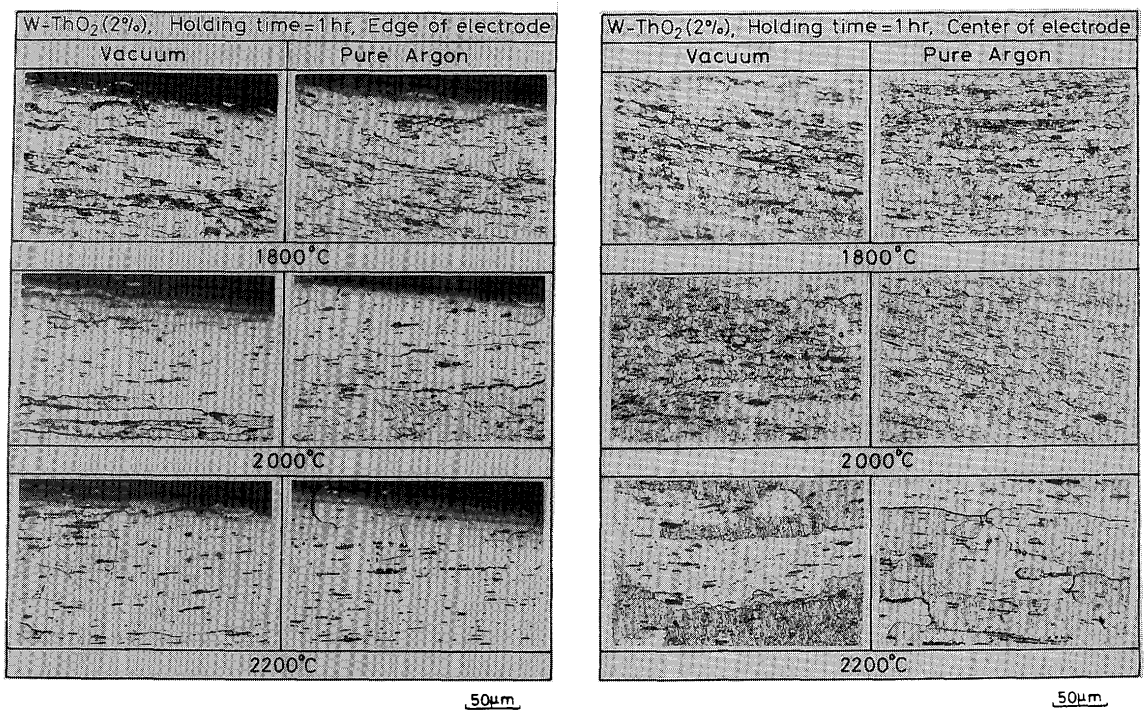

Fig. 10 Microstructure changes after furnace heating in pure argon and vacuum for W-ThO_2 electrodes.

Table 1 Relative volume fraction of oxides after furnace heating(%).

Temperature °C	W-ThO_2				W-La_2O_3			
	Vacuum		Pure Ar		Vacuum		Pure Ar	
	Edge	Bulk	Edge	Bulk	Edge	Bulk	Edge	Bulk
1800	35	45	32	47	35	49	69	99
2000	28	39	23	34	31	44	64	82
2200	17	23	20	33	22	40	23	56

$$\text{These values} = \frac{\text{oxide volume fraction after heating}}{\text{oxide volume fraction before heating}} \times 100(\%)$$

4.2 Migration mechanism

The most favorable mechanism for oxides migration was thought as follows; the rare earth oxides react with tungsten forming tungstate and oxy-tungstates except Ce-oxide which form only tungstate as indicated by the X-ray diffraction analysis and showed in **Fig. 12**. The melting points of those tungstate and oxy-tungstate are lower than the melting points of oxides or tungsten as can be seen from **Table 2**.

According to the temperature gradient throughout the electrode during arcing the rare earth metal oxides reacts with tungsten forming tungstate or oxy-tungstate at lower temperature zone then, it melt and migrate from the lower temperature zone to the higher temperature zone. This mechanism can be explained theoritically if we consider an ensemble consistes of upper portion of solid solvent

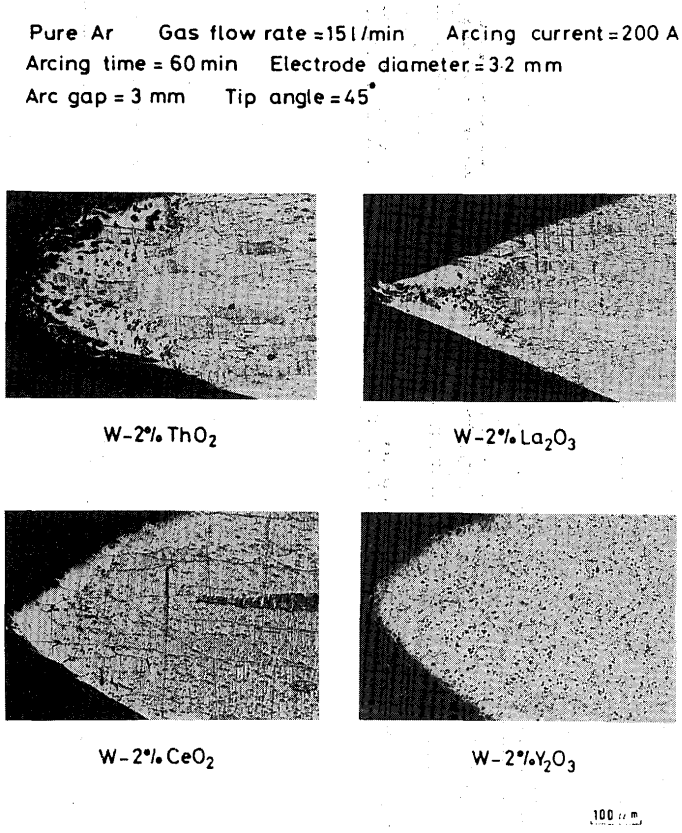

Fig. 11 Typical microstructure of several electrode tips after arcing.

(pure tungsten) and may be some rare earth metal oxides and the middle region consists of substantial alloy solte and solvent (tungstate or oxy-tungstate). The lower portion also consists of solid solvent (pure tungsten). when this ensemble is placed in a temperature gradient such that the temperature of the middle zone (tungstate or oxy-tungstenate) is above its melting point and such that the highest temperature in the system is below the melting point of the upper or lower portion. Under these conditions, the middle region melts and reactions occur at the two solid-liquid interfaces to produce the equilibrium concentrations corresponding to the temperatures under consideration. A solvent concentration gradient is set up in the middle region and the combination of solution reaction at the upper temperature, diffusion in the region and freezing at lower temperature causes the molten region-(tungstate or oxy-tungstate) to migrate through the ensemble.

The migration rate is considerably increase with increasing the temperature gradient and depend on the melting point of the tungstate or oxy-tungstate. Also, as the migrated particles traveled up the temperature gradient, they accelerated and increased in size.

In case of the tungsten electrode activated with ThO_2 there is no tungstate or oxy-tungstate were detected by X-ray analysis. Then, the ThO_2 was believed to react with tungsten at about 2000-2300^{0}C forming pure thorium, which has lower melting point than ThO_2 as shown in

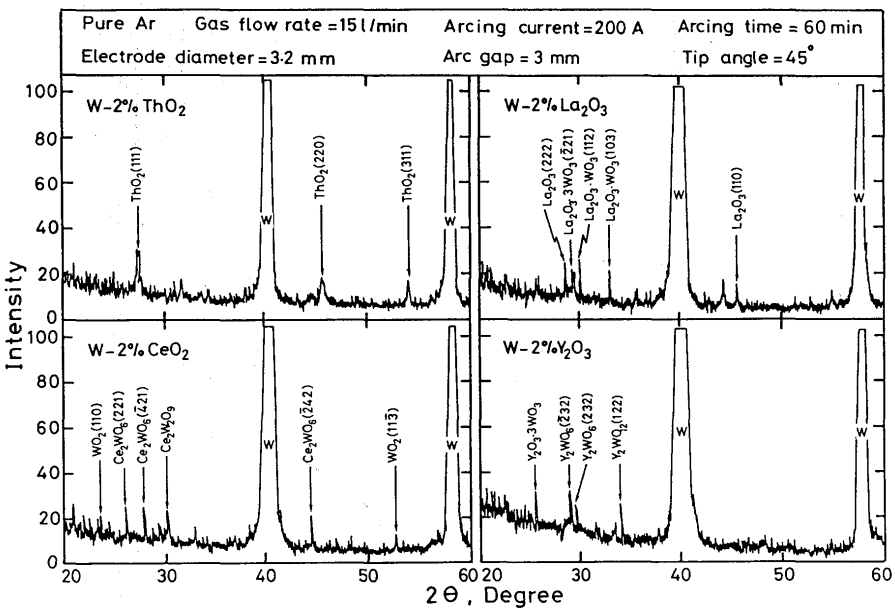

Fig. 12 X-ray analysis of different electrode tips after arcing.

Table 2 Summary of oxides behavior.

Summary of oxides behavior

Type of oxides	ThO_2	La_2O_3	CeO_2	Y_2O_3
Melting point °C	3050 (Th: 1755)	2217 (La: 920)	2600 (Ce: 798)	2435 (Y: 1526)
Heat of decomposition, Kj	1227.6	1244.7	(523.4)	1271.1
Type of oxides after sintering	ThO_2	La_2O_3	Ce_2O_3 (1690°C)	Y_2O_3
Reaction with tungsten	Reduction of ThO_2 by W occurs, forming pure Th.	Forming tungstate (M.P: 1080°C) and oxytungstate (M.P: >1500°C).	Forming tungstate (M.P: 1090°C).	Forming tungstate (M.P: 1470°C) and oxytungstate (M.P: >2200°C).
Oxide behavior	1-Diffusion of Th atoms to the electrode surface. 2-Vaporization of Th from the electrode surface.	1-Migration of La_2O_3 occurs, a-throughout the electrode edge. b-from the center to the electrode edge. 2-Vaporization of La_2O_3 from the electrode surface.	1-Migration rate throughout the electrode edge is higher than from the center to the electrode edge. 2-Vaporization of Ce-oxides from the electrode surface.	Very low migration and vaporization rates
Stability of oxides	Lower stability	Higher stability	Reasonable stability at the electrode edge but lower stability at the electrode tip	High stability

Table 2. These pure Th atoms diffuse easly from the bulk to the edge of electrode at which it is easy to evaporate.

From this point of view it may be possible to explain the differences in the migration rates of those oxides which were observed previously as follows; The most higher migration rate among those oxides is Ce-oxide which has lower melting point (even for the oxide it self or for the tungstate). Then, it is easy to migrate and making a continouse feeding of oxides to the electrode tip. But, in that case the consumption rate of oxide is much higher.

The stability of Y_2O_3 and La_2O_3 were related to the higher melting point of these oxides as well as for there tungstate or oxy-tungstate.

According to the higher melting point of ThO_2 and the temperature range at which ThO_2 reduced by tungsten, the feeding and diffusion rates in case of W-ThO_2 electrodes are much lower than the other oxides. Then the electrode tip will loss the ThO_2 and work as pure tungsten. This can explain the superiority of rare earth metal oxide than ThO_2.

5. Conclusions

This study has been carried out to investigate the behavior of rare earth metal oxides during arcing comparing with Th-oxide.

The main conclusions drawn from the experimental data are:

(1) The ThO_2 react with tungsten forming pure Th. The pure Th diffuse easly from the bulk to the edge of electrode and then evaporate from the electrode surface.

(2) Rare earth metal oxides reacts with tungsten forming tungstate and oxy-tungstate. These tungstate or oxy-tungstate melt and migrate from the lower temperature zone to the higher temperature zone. The differences in their migration may be atributed to their melting points.

(3) The tungsten electrodes activated with La_2O_3 showed the best compromisation between stability behavior and arc characteristics among the investigated electrodes.

Acknowlegement

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