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NEW DOPED TUNGSTEN CATHODES. APPLICATIONS TO POWER GRID TUBES.

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ABSTRACT

Thermionic emission behaviour of tungsten/tungsten carbide modified with rare earth (La, Ce, Y) oxides is examined on account of suitability to deliver important current densities in a thermo-emissive set up and for long lifetime.

Work functions of potential cathodes have been determined from Richardson plots for La_2O_3 doped tungsten and for tungsten covered with variable compositions rare earth tungstates. The role of platinum layers covering the cathode was also examined. Given all cathodes containing mainly lanthanum oxides were good emitters, emphasis was put on service lifetime.

Comparisons of lifetime in tungsten doped with rare earth oxides and with rare earth tungstates show that microstructure of the operating cathodes may play the major role in the research of very long lifetime cathodes.

Based on these results, tests still running show lifetime compatible with power grid tubes applications.

KEYWORDS

Thermo-emissive cathodes, rare earth tungstates or oxides, work function, intermetallic compounds $LnPt_5$, cathode lifetime.

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INTRODUCTION

Tungsten covered with rare earth tungstate and directly doped with lanthanide oxides have been widely investigated by Thales Electron Devices in order to reduce temperature emission of the power grid devices and to substitute the thoriated tungsten by a non-radioactive material. Indeed, the risk of the laying down of an European legislation too strict for our suppliers about the handling of the radioactive elements is still present.

Rare earth oxides as La_2O_3, Y_2O_3 and Ce_2O_3 are well known for their interesting electron emission and have already been proposed to replace thoria (1,2). However, high temperature physico-chemical properties show similarities (same conditions of carburization for thoriated tungsten and rare earth oxides) as well as significant differences :

- Chemical equilibrium constants $K= p(CO) / p(MO)$ at T=2000K for the formation of metals

$$W_2C + MO^{(gaz)} = 2\,W + CO + M^{(liq)} \qquad \text{(Eq. 1)}$$

are 10^{-2} for La, Ce and 1 for Y and Th.

- At the same temperature, vapour pressures of liquid La, Ce or Y is 10^{-2} mbar whereas thorium vapour pressure is 10^{-6} mbar.

These simple comparisons show that the replacement of thoria by rare earth oxides in cathodes supposes a deep investigation of the various parameters controlling the efficiency and the lifetime of a power grid tube. In a parent paper (3), we examine the chemistry of rare earth tungstates in contact with tungsten and tungsten carbide at high temperature. The present paper is more focused on the aspects of emission efficiency and cathode lifetime.

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EXPERIMENTAL

SAMPLES AND MATERIALS

Various types of cathodes have been examined :

1 / Tungsten wires of 0.434 mm diameter directly doped with rare earth oxides (in particular lanthanum and yttrium). They are manufactured by PLANSEE firm These wires were directly heated at 2073K for carburisation.
Some surface modifications on cathode can be brought : they consisted of forming a thin platinum layer on its surface by electrolysis of a platinum nitrate solution held at 90°C. Two cases of carburization are possible :

– Pre-carburization : it was performed at 2073K before the platinum deposits.
– Post-carburization : it was performed at 1823K after the platinum deposits.

2 / Pure tungsten wire covered with rare earth tungstates (Ce_2O_3-WO_3, La_2O_3-WO_3, $(La_{0.85}Y_{0.15})_2O_3$ – WO_3). They are prepared from a polyacrylamide gel-assisted citrate process and are then deposited on the tungsten surface by cataphoresis. Two cases of carburization are also possible : the pre-carburization at 2073K and the post-carburization at 1823K were performed respectively before and after the rare earth tungstates deposits.

Two types of wires have been used : some are 0.450mm in diameter and ones of 0.1mm for meshed cathodes.
For cases of post-carburization, cathodes were heated in vacuum until melting of the tungstate was observed and then wire temperature was adjusted at 1823K for post-carburization. Platinum layer could also be deposited with the same way as before.

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Partial carburizations of wires (approximately 10% of diameter) were performed in low pressure C_2H_2 at 1823 or 2073K during times not exceeding 30 minutes.

SET UP

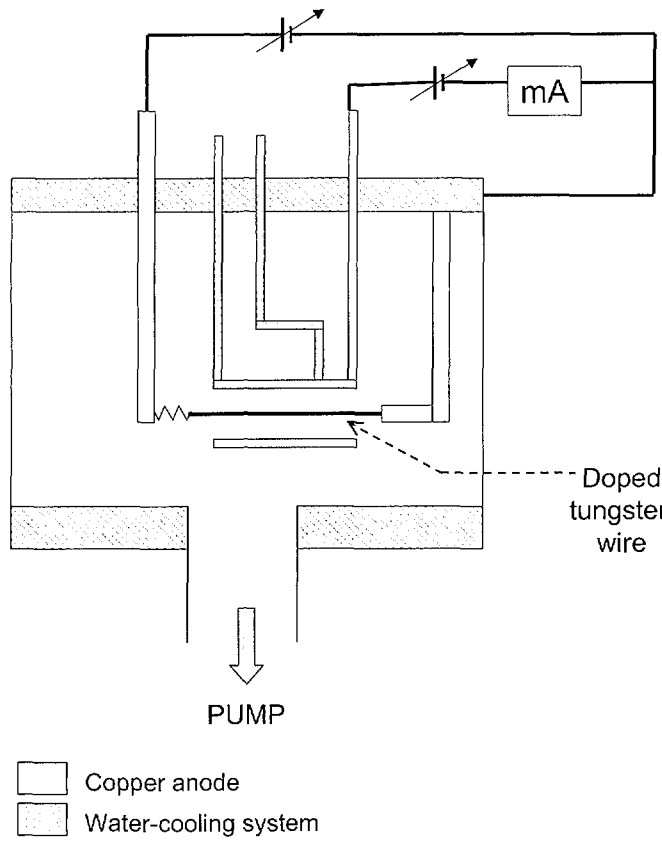

Figure 1 : Experimental set up for electronic emission current densities and work functions measurements.

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The two categories of wires have been tested for emission characteristics in the same type of experimental chamber under vacuum (see figure 1). A diode configuration has been set up inside a glass bell jar. The doped tungsten wire is tightened at the centre of a water-cooled and copper-made anode. A turbo-molecular pump (500 litres / sec speed) is used to reach the limited pressure of $2x10^{-7}$ mbar. The tungsten wire length concerned by the thermo-emission is 2.9 centimetres and that is equivalent to an emissive surface S of 0.395 cm^2. The distance between cathode and anode is 4 mm. The wire temperature is measured with a tungsten filament pyrometer. The thermo-electronic emission of all wire materials have been studied in the temperature range 1200 – 1600°C.

Four other devices were used for various purposes and to test cathode lifetimes :

A diode configuration is made of a stretched cathode wire held at the centre of a 20mm long 5 mm diameter cylindrical molybdenum anode with a slit to perform pyrometry.

1 / The diode can be enclosed in a steel chamber equipped with glass windows. Vacuum is achieved with mechanical + turbo-molecular pump (330 l/s) and liquid nitrogen trap. Residual pressure is $5x10^{-8}$ mbar. This set up is used to measure lifetime of tungsten wires doped with rare earth oxides.

2 / It can also be enclosed in a steel chamber equipped with silica windows. Vacuum is obtained with a molecular pump (400 l/s, residual pressure 10^{-10} mbar). Pressure is measured near diode with a Bayard Alpert vacuum gauge and gases at 10 cm from top of diode are analysed with a quadrupole mass spectrometer (Balzers QMG 311). This set up is used to qualify the nature and the amount of gases evolved during service of cathode.

3 / The third device consists of enclosing the diode in a steel chamber equipped with silica windows. Vacuum is obtained with a molecular pump (80 l/s, residual pressure 10^{-10} mbar). Pressure is measured near diode with a Bayard Alpert vacuum gauge. This set up

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has been used to measure lifetime of tungsten wires covered with tungstates.

Another diode configuration is made of a meshed cathode held inside a water cooled copper anode. Distance between anode and cathode is 3 mm and it is not possible to measure temperature. Vacuum is obtained with mechanical + turbo-molecular pumps (250 l/s, residual pressure, 10^{-7} mbar). This set up has been used to measure lifetime of meshed cathodes made of tungsten wires covered with rare earth tungstates.

EMISSIVE PROPERTIES OF CATHODES

In the following, work function calculations are based on the thermo-emission principle described by the Richardson-Dushmann equation (4) :

$$J_S = A_0.T^2.\exp(-\Phi_S / kT) \qquad \text{equation 2}$$

where J_S is the emission current density (A/cm^2), A_0 is the Richardson constant ($A/cm^2/K^2$) and Φ_S is the electron work function (Joules). Temperature T is in Kelvin.

The experimental protocol for measurements is the following : electronic emission current I is measured when inter-electrode pulsed voltages U_A in a range 20-800 volts is applied. The emission curves Ln I versus $(U_A)^{1/2}$ are drawn and value of the zero field saturation current I_S at some cathode temperature T is determined. Schottky straight lines Ln (I_S/T^2) = f (1/T) are then drawn and the electronic work function is deduced from slope. Extrapolation at 1/T approaching zero gives Richardson constant A_0.

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The results appear in table I. Important variations of the work function are observed between doped and covered tungsten wires with the exception of the $3La_2O_3 - 2WO_3$ tungstate (3:2) cathode. There is no clear explanation for these variations although chemistry (3) suggests that 3:2 behaviour is different from other compositions. We may suggest that one possible explanation would be that low work functions are obtained on tungsten covered with tungstate grains which were observed by SEM after emission tests, except for the composition 3:2 where the surface does not show any trace of lanthanum.

The last column of table I reveals that all the compositions of cathodes allow to obtain good emission at high temperature (a typical good value is $1A/cm^2$). This suggests that emission efficiency is not a critical parameter and that we may concentrate more attention on service lifetime which is at least as important as emissive property.

	Doping nature	Φ_S(eV)	A_0 ($A/cm^2/K^2$)	J_S (calc) at 2000K (A/cm^2)
Tungsten wires doped with rare earth oxides	La_2O_3 (1%)	3.30 ± 0.44	990	23
	La_2O_3 (1%) + Y_2O_3 (0.1%)	3.71 ± 0.13	6900	15
Tungsten wires covered with a thin layer of rare earth tungstate	$2(Ce_2O_3) - 9(WO_3)$	2.58 ± 0.14	2	3
	$2(La_2O_3) - 9(WO_3)$	2.01 ± 0.22	0.17	6.5
	$2(La_{0.85}Y_{0.15})_2O_3 - 9(WO_3)$	2.06 ± 0.04	0.23	6.5
	$1(La_2O_3) - 2(WO_3)$	2.34 ± 0.05	1.34	8
	$7(La_2O_3) - 8(WO_3)$	2.27 ± 0.07	0.38	3
	$3(La_2O_3) - 2(WO_3)$	3.37 ± 0.17	68.1	1
	$3(La_2O_3) - 1(WO_3)$	2.43 ± 0.30	0.45	1.5

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Tungsten wires doped with rare earth oxides and Pt covered	La_2O_3 (1%) + 15µm Pt	2.39 ± 0.16	6.6	28
	La_2O_3 (1%) + Y_2O_3 (0.1%) + 15µm Pt	2.66 ± 0.15	91	83
Tungsten wires covered with a thin layer of rare earth tungstates and Pt covered	$2(Ce_2O_3)$ - $9(WO_3)$ + 15µm Pt	2.64 ± 0.08	6.4	6
Tungsten wires doped with thoria (5)	ThO_2 (1%)	2.63	3	3

Table I : Electronic work functions Φ_S and Richardson constants A_0 values for doped tungsten wires.

LIFETIME OF CATHODES

PLANSEE WIRES STUDY :

Results of emission lifetimes obtained on tungsten wires directly doped with rare oxides and manufactured by PLANSEE are shown in table II. As we hope it in regards to the low work function values for platinum covered wires, the figures of table II show the fact that, for composition W + 1% La_2O_3, platinum allows electronic emission. This is less obvious for the composition with yttrium.

These data also indicate that thicker the platinum layer is, longer the cathode lifetimes appear. We do not reach lifetime as long as the one that Buxbaum (2) in 1979 had said to get on similar molybdenum cathodes (a factor 10 in difference).

However we can say that the platinum layer addition on lanthanum oxides doped tungsten improves not only the work function but also in the same time the running cathode lifetime.

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Doping nature	carburization	Pt	Cathodes death after (hours) *	Cathodes still alive after (hours)	Working cathode T maxi (Kelvin)
1% La_2O_3	Pre	NO	4 (L.E.)		2223
	Post	YES 5 µm	100 (L.E.)		1823
	Post	YES 10 µm	180 (L.E.)		1823
	Post	YES 15 µm	1050 (L.E.)		1773
	Pre	YES 15 µm	1750 (L.E.)		1773
	Post	YES 40 µm		> 2000 **	1703
1% La_2O_3 + 0.1%Y_2O_3	Pre	NO	980 (W.M.)		> 2073
	Post	YES 5 µm	315 (L.E.)		1823
	Post	YES 10 µm	675 (L.E.)		1823
	Post	YES 15 µm	865 (L.E.)		1823
	Pre	YES 15 µm	1050 (L.E.)		1823
	Pre	YES 40 µm		> 550 **	1533

* : L.E. = Low Emission and W.M. = Wire Melting are the death cathode reasons.

** : The running of these two cathodes was stopped because of a power cut in the devices.

Table II : Running lifetime of Plansee tungsten wires doped with rare earth oxides.

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TUNGSTATES COVERED CATHODES :

The lifetime results are shown in table III and IV. Some very scarce data showing lifetime equal to or less than one day were excluded because we considered them due to some accidents in cathode preparation.

Rare earth tungstate composition	Carburization	15µm Pt covered	Lifetime (hours) (dead cathodes)	Cathodes still alive after (hours)
$2Ce_2O_3 - 9WO_3$	Post-carburized	NO	2680 2450	
		YES	1660	
	Pre-carburized	NO	1550 1180 1200	
		YES	525 2600	
$2La_2O_3 - 9WO_3$	Post-carburized	NO	170	
$2(Ce_xGd_y)_2O_3 - 9WO_3$ (x+y=1)	Post-carburized	NO	2750 120	
		YES	270	
	Pre-carburized	NO	527 140 530	
		YES	500	
$2(La_xGd_y)_2O_3 - 9WO_3$ (x+y=1)	Pre-carburized	NO	250	
$2(Ce_xY_y)_2O_3 - 9WO_3$ (x+y=1)	Post-carburized	NO	350	
	Pre-carburized	NO	400	
$2(La_{0.85}Y_{0.15})_2O_3 - 9WO_3$	Post-carburized	NO		>6900
		YES	4400	
	Pre-carburized	NO	1210 1200	
		YES	1250	

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Table III : Lifetime of various 2:9 tungstates doped cathodes.

$2Ln_2O_3$ - $9WO_3$ modified tungsten cathodes have been particularly studied because of their very promising electronic work functions (see table I). Six different compositions containing Ce, La, Y and Gd were examined The choice of rare earth was based on previous results not described here and on similarities of physico-chemical and thermodynamical properties of La and Ce on the one hand and Y and Gd on the other. Table III reveals interesting features which are :

1) Various cathodes of same composition have approximately same lifetime (this is not always true).
2) Post-carburization is slightly more favourable for lifetime than pre-carburization.
3) Platinum coverage of cathode has no clear influence on lifetime.
4) There are huge and unclear differences of lifetime with chemical composition of tungstates.

Rare earth tungstate composition	carburization	15µm Pt covered	Lifetime (hours) (dead cathodes)	Cathodes still alive after (hours)
$7La_2O_3 - 8WO_3$	Post-carburized	NO		>3900
			1450	
$7La_2O_3 - 8WO_3$	Post-carburized	YES	1450 1250	
$3La_2O_3 - 2WO_3$	Post-carburized	NO		>2600

Table IV : Service lifetime of various cathodes modified with refractory tungstates

Examination of lifetime of tungsten modified by refractory tungstates is shown in table IV. Except the fact that all cathodes covered with platinum were dead after a thousand of hours, showing that for this kind of cathodes platinum has not got a real improving effect on lifetime, other comments on

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uncovered cathodes are difficult to be made : two cathodes (7:8 and 3:2) are living with relatively important times and one (7:8) is dead. So it is difficult to conclude.

DISCUSSION

All these results were obtained on tungsten wires modified by rare earth oxides or rare earth tungstates and also by platinum.

We have already mentioned that all of them are good electronic emitters. We will then focus discussion on lifetime where we observe large variations in the results.

Lifetime is difficult to measure because cathode death can be natural or accidental (poisoning, melting, deformation, power supply cut off, etc...). To clarify tables, we have not reported these parameters. If we consider that most of cathodes have a natural death (Low Emission), the cause may depend on the ratio of the time needed to diffuse rare earth metal and CO from their formation site inside tungsten (by reacting W_2C with Ln_2O_3) to the time of evaporation of the first layer of rare earth adsorbed on tungsten. If this ratio becomes too high death will happen before we have exhausted the reactive products (W_2C and Ln_2O_3). In the opposite case, death will happen when one of the two reactive products will have been exhausted. In these two extreme cases we expect lifetime to be relatively short. Long lifetime will happen when the ratio of these two times is neither long neither short allowing to produce just the right quantity of rare earth to keep the first adsorbed layer. An example of such a behaviour is shown on figure 2.

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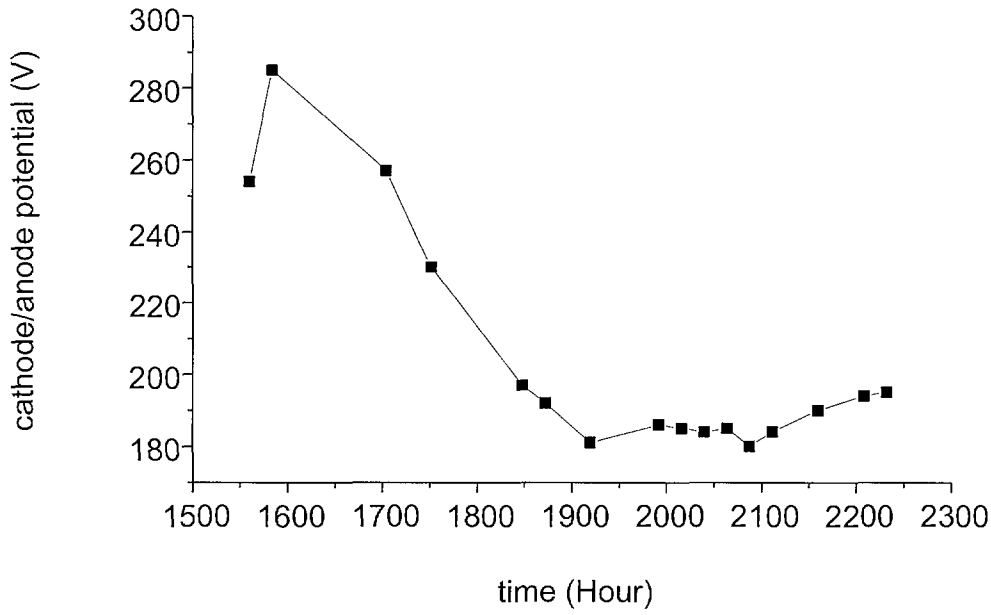

Figure 2 : variations of emissive properties of 3:2 tungstate cathode after a sudden rise of temperature.

In this experiment, temperature of the cathode was abruptly changed from 1600 to 1700°C. The potential dropped from 400 to 255V (starting point of the graph of figure 2) after what we can make the difference between the relaxation times of evaporation and diffusion of reactive products. We observe an initial rise corresponding to a partial evaporation of the lanthanum monolayer followed by a slow decrease towards a new working potential. Although badly defined these characteristic times of evaporation and of diffusion are of the same order of magnitude, approximately 100 hours.

Tentative calculations of lifetime may be done for distinct hypothesis. We will do it for a 3:2 cathode at 2000K because this cathode lifetime experiment was particularly well studied:

We observed its behaviour during a long time (as shown on figure 2). We could also show from mass spectrometry that the majority of gases evolved from cathode was CO and the total pressure measured in the chamber was between 1 and 2×10^{-9} mbar during operations. Pumping speed is also calculated as 42 l/s.

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- A first rough calculation consists of lifetime prediction considering surface covered with a thick layer of lanthanum metal. Vapour pressure of La being $1.3x10^{-2}$mbar (6) we obtain 7 seconds. This instructive calculation illustrates the Langmuir idea of the monolayer of active material.

- We can calculate lifetime of 3:2 cathode using total pressure (CO) equal to $1x10^{-9}$ mbar. We deduce a lifetime of 826 days from pumping speed and hypothesis that we transform completely W_2C to W.

These considerations show that cathode lifetime depends on low vapour pressures of chemically adsorbed monolayers of rare earth and that rare earth and CO diffusions in W are time limiting processes in the cathodes service. These two points emphasize a critical parameter for long life which is the microstructure of the tungsten host. It may condition to a large extent the diffusion controlled character of the service of cathodes.

If we try to apply the above ideas to lifetime results shown in tables II-III-IV, we should first note that Plansee cathodes have a well-defined and reproducible microstructure. It is then possible to use them to compare the different modifiers. On account of this we observe in table II that lifetime is not basically changed with the doping nature or covering element. In terms of physical explanation, this means that yttrium and lanthanum behave similarly for diffusion and evaporation. But it also shows the very useful role of platinum on a La_2O_3 doped tungsten wire, without which emission does not occur : a running temperature of 2223 K is too high and so not realistic.

Contrary to Plansee tungsten modified wires, tungstate covered wires have an essentially unknown microstructure during operation. We have reported in the parent paper (3) on chemistry of tungstates observations of the lanthanum distribution after the melting of tungstate for different compositions. It reveals important differences of rare earth repartition in and on the solid. In particular we have observed infiltration behaviour of 3:2 through tungsten channels (3). These channels may offer the good microstructure for low speed lanthanum diffusion during cathode service. Obviously more work is needed to describe this unknown infiltration phenomenon and to confirm these new ideas.

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CONCLUSION

New doped cathodes – W / W_2C covered with various composition of rare earth tungstate (La, Ce, Y, Gd) and sometimes with platinum – have been examined for their ability to produce large emission currents during long times. They have been compared with all solid Plansee cathodes of same chemical composition. Results show that all cathodes are good electronic emitters. Cathode lifetimes are very different from one system to another. Comparison between them reveals that microstructure is the key point of long life cathodes.

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