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The base metal of the oxide-coated cathode

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Abstract

The oxide-coated cathode has been the most widely used electron emitter in vacuum electronic devices. From one manufacturing company to another the emissive oxide is either a double—Ba, Sr—or a triple—Ba, Sr, Ca—oxide, having always the same respective compositions. Conversely, the base metal composition is very often proprietary because of its importance in the cathode emission performances.

The present paper aims at explaining the operation of the base metal through a review. After a brief introduction, the notion of activator is detailed along with their diffusivities and their associated interfacial compounds. Then, the different cathode life models are described prior to few comments on the composition choice of a base metal. Finally, the specificities of the RCA/Thomson "bimetal" base metal are presented with a discussion on the optimized composition choice illustrated by a long-term life-test of five different melts.

Keywords: Oxide-coated cathode; Base metal; Nickel alloys; Thermochemistry; Diffusion; Interface compounds

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1. Introduction

Since the discovery of its excellent thermionic emission performances, 100 years ago by Wehnelt [1,2], the oxide-coated cathode has been the most widely used electron emitter in vacuum electronic devices: in vacuum valves up to the late 1960s, and afterwards in CPTs and CDTs. Schematically, this cathode is composed of a 60–150 μm thick nickel alloy substrate called the base metal, covered with a 50–100 μm thick porous layer of alkaline-earth oxide. The exact definition of its "emitting system", i.e. base metal and emissive oxide, varies from one company to another. It is noteworthy that the emissive oxide is either a mixture of BaO, SrO or BaO, SrO and CaO, respectively called double or triple oxide having always sensitively the same respective composition. The base metal composition is of primary importance for the cathode emitting properties and is very often proprietary of the cathode manufacturing companies.

2. The base metal physical chemistry

Four years after the Wehnelt discovery, Deinninger made the clear first mention of the influence of the

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base metal on the emission of the oxide-coated cathode [3]. As far as the authors are aware, Smithells from General Electrics Ltd. (UK) is the first to hold a patent concerning the influence of the alloying elements of the base metal in 1924 [4]; and the first methodical experimental study of the influence of the base metal composition on the cathode emission performance was issued in 1935 by Benjamin [5].

According to a schematic mechanism of the oxide cathode thermionic emission, commonly assumed in the works on the influence of the base metal composition on the electron emission, the activated oxide coating is an intrinsic n-type semiconductor having barium atoms in excess called "free barium". This free barium tends to evaporate from the cathode due to its relatively high vapor pressure at the cathode operating temperature. In order to maintain the cathode activity, free barium must be produced at a rate at least as large as the evaporation one—the optimal production rate is of the order of 10^{10}–10^{11} atoms/(cm^2 s) [6]. Therefore, the nickel base metal is not only the substrate of the emissive oxide coating, but also the reservoir for the doping elements that sustain the cathode activity. Three factors characterize the action of these activators:

- their ability to reduce BaO;
- their diffusivity;
- the compounds created at the base metal/oxide coating interface.

2.1. Element reducing power: strong activators, mild activators and inert elements

The reducing power of an element is evaluated by calculating the vapor pressure of gaseous barium generated by its reducing action on BaO, at the cathode operating temperature [7–9]. Table 1 shows different examples of BaO reducing reactions by various elements, with for each of the reactions:

- its equilibrium constant, noted K_{eq};
- the generated barium equilibrium pressure, noted P_{Ba}.

Table 1
Equilibrium constants and Ba equilibrium pressures for various BaO reduction reactions at 1070 K

	Reactions	K_{eq} at 1070 K	P_{Ba} at 1070 K (atm)
1	$BaO_{(s)} + Ni_{(s)} \Leftrightarrow Ba_{(g)} + NiO_{(s)}$	3.71×10^{-19}	3.71×10^{-19}
2	$BaO_{(s)} + Co_{(s)} \Leftrightarrow Ba_{(g)} + CoO_{(s)}$	1.97×10^{-18}	1.97×10^{-18}
3	$3BaO_{(s)} + Mo_{(s)} \Leftrightarrow 3Ba_{(g)} + MoO_{3(s)}$	9.41×10^{-54}	2.11×10^{-18}
4	$BaO_{(s)} \Leftrightarrow Ba_{(g)} + 1/2O_{2(g)}$	3.62×10^{-26}	1.38×10^{-17}
5	$3BaO_{(s)} + W_{(s)} \Leftrightarrow 3Ba_{(g)} + WO_{3(s)}$	2.68×10^{-49}	6.45×10^{-17}
6	$BaO_{(s)} + Fe_{(s)} \Leftrightarrow Ba_{(g)} + FeO_{(s)}$	1.24×10^{-16}	1.24×10^{-16}
7	$4BaO_{(s)} + Mo_{(s)} \Leftrightarrow 3Ba_{(g)} + BaMoO_{4(s)}$	1.11×10^{-43}	4.80×10^{-15}
8	$4BaO_{(s)} + W_{(s)} \Leftrightarrow 3Ba_{(g)} + BaWO_{4(s)}$	2.31×10^{-37}	6.13×10^{-13}
9	$3BaO_{(s)} + 2Cr_{(s)} \Leftrightarrow 3Ba_{(g)} + Cr_2O_{3(s)}$	1.24×10^{-35}	2.31×10^{-12}
10	$BaO_{(s)} + Mn_{(s)} \Leftrightarrow Ba_{(g)} + MnO_{(s)}$	3.32×10^{-11}	3.32×10^{-11}
11	$2BaO_{(s)} + Si_{(s)} \Leftrightarrow 2Ba_{(g)} + SiO_{2(s)}$	1.43×10^{-16}	1.19×10^{-8}
12	$BaO_{(s)} + C_{(graphite)} \Leftrightarrow Ba_{(g)} + CO_{(g)}$	4.33×10^{-16}	2.08×10^{-8}
13	$2BaO_{(s)} + Ti_{(s)} \Leftrightarrow 2Ba_{(g)} + TiO_{2(s)}$	5.64×10^{-15}	7.51×10^{-8}
14	$3BaO_{(s)} + 2Al_{(g)}{}^{a} \Leftrightarrow 3Ba_{(g)} + Al_2O_{3(s)}$	$2.73 \times 10^{+7}$	2.14×10^{-4}
15	$2BaO_{(s)} + Zr_{(s)} \Leftrightarrow 2Ba_{(g)} + ZrO_{2(s)}$	6.50×10^{-8}	2.55×10^{-4}
16	$Ba_{(s)} \Leftrightarrow Ba_{(g)}$	2.67×10^{-4}	2.67×10^{-4}
17	$4BaO_{(s)} + Ti_{(s)} \Leftrightarrow 2Ba_{(g)} + Ba_2TiO_{4(s)}$	5.41×10^{-5}	7.36×10^{-3}
18	$BaO_{(s)} + Mg_{(g)}{}^{a} \Leftrightarrow Ba_{(g)} + MgO_{(s)}$	4.13×10^{-1}	1.74×10^{-2}
19	$4BaO_{(s)} + 2Al_{(g)}{}^{a} \Leftrightarrow 3Ba_{(g)} + BaAl_2O_{4(s)}$	$6.29 \times 10^{+13}$	2.83×10^{-2}
20	$4BaO_{(s)} + Si_{(s)} \Leftrightarrow 2Ba_{(g)} + Ba_2SiO_{4(s)}$	3.44×10^{-3}	5.86×10^{-2}
21	$3BaO_{(s)} + Zr_{(s)} \Leftrightarrow 2Ba_{(g)} + BaZrO_{3(s)}$	1.87×10^{-2}	1.37×10^{-1}

N.B.: The equilibrium constants, K_{eq}, have been evaluated with the software FACT 2.1. (Facility for the Analysis of Chemical Thermodynamics) edited by the Center for Research in Computational Thermochemistry of the Ecole Polytechnique de Montréal (Canada).

[a] Respective vapor pressures at 1070 K: $P_{vap.sat.}(Mg) = 4.2 \times 10^{-2}$ atm; $P_{vap.sat.}(Al) = 6.0 \times 10^{-10}$ atm.