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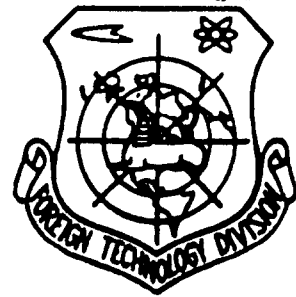
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THERMIONIC CATHODES

by

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ON THE EMISSION MECHANISM OF BARIUM CONTAINING THERMIONIC CATHODES

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Through the analysis and synthesis of data obtained from barium containing thermionic cathodes, especially those by modern surface analysis technique, we have come to a unified theory -- the dynamical surface emission center model. Barium absorbed on the surface of alkaline earth metal oxides in case of oxide cathode or of aluminate, tungstate etc. in case of dispenser cathode may form the emission center. Its size should be large enough to screen off the attractive field produced by the substrate, but small enough to facilitate the transport of electrons from the substrate to the emitting center. The compositions and the dynamical characters of the surface emission center are also discussed.

For a practical thermionic cathode with a barium system, in the past the semiconductor model was used to describe an oxide cathode, and the single atom layer dipole theory was used to describe a dispenser cathode. Along with the increase of thermionic cathode types and the continuous perfecting of measurement methods and instruments, the accumulation of data has speedily grown. But these data make clear: The above two types of theories are not able to make known the fundamental nature of thermionic cathode emissions. In the following we will we discuss simply the status of how the search for a solution is taking place on an international level in the face of this kind of fact.

The best method for examining the semiconductor model is a monocrystalline test. But in monocrystals of BaO, SrO, and CaO the results obtained from the measurement of heat conductivity, photopositive conductivity, photo-electrical emissions, absorption spectrum, etc., are very scattered, and definitely don't allow the drawing of a clear band graph. Furthermore, in numerical values there is also a great contradiction with what is obtained using a practical cathode.^{1,1} In illustrating the viewpoints regarding use of a crystalline internal donor for explaining the fundamental nature of the emissions of the oxide cathode, the repeatedly encountered difficulties are great. Because of this, Zalm offered a surface mixing theory, Nikonov offered a surface donor model, and Surplice also offered a unified model.^{1,2} These viewpoints, to differing extents, have somewhat deepened our understanding of the question, but, because they preserved the semiconductor as a key element, they were unable to solve the problem. For example, using a sudden-rest electron spectrometer it was discovered, in a cathode after a 2000 hour lifetime, the electron emissions do not in fact decline, and furthermore, the atomicity of coated surface oxygen is 40% more than that of alkaline earth metals. This causes the surface donor idea to be difficult to establish.^{1,2} Besides this, despite the coating surface's ability to emit electrons, the question of how the electrons are replenished still needs to be solved.

Examining dispenser cathode surfaces, no matter if they are

BaO-W or Ba-O-W systems, none are able to explain the following fact, that the electron emission parameters of aluminate, tungstate, and scandate dispenser cathodes all show clear differences. The performance of an aluminate cathode rises somewhat after evaporation on osmium, iridium or similar metals, but a tungstate dispenser cathode after evaporation on the same kind of material has no improvement. A person using an electron microscope saw that electrons were emitted from emission material that had been diffused from ventages, and therefore also used the semiconductor model to explain the fundamental nature of dispenser cathode emissions.^[3] But, they did not first explain what the emission material is. Besides this, up to the present time we haven't seen a parameter report on the electrical conduction types, internal work function, maximum band-width dimensions, etc. related to each kind of refractory salt. Therefore, the above ideas are not established. What is interesting is that, using tungstic acid/barium strontium salt applied on a tungsten band, after activation the work function is 1.11 eV, but the emissions at the time of 1100 K are only 2.5×10^{-3} A/cm²^[5]; however, using a cathode formed of sintering a mixture of tungsten powder and tungstate with ZrH₂ also added, the work function is 1.14 eV, basically the same as the former, but the emissions at the time of 1100 K are 1.3 A/cm², over two orders of magnitude higher than the former.^[6] Why is the work function of a simple applied layer not high, while its emissions, on the other hand, are not good? This is a question to cause a person to think deeply.

From the facts above one can see that, in elaborating the theories of the above two types of thermionic cathode emissions, each theory draws close to the other. This has a certain truth to it because each theory must reflect the fundamental nature of thermionic cathode emissions; both lack certain things; and these two broad types of thermionic cathode also incorporate basic common ground. But the problem still can't be completely solved this way. An explanation still needs a search for a new model. The objective of this article is, based on the basic principles of electron emissions and the large quantity of data obtained through a long period of domestic and international work, to further clarify the dynamic surface emissions center, this thermionic emissions unified model!⁷

The Surging Barium Concept

Surging Barium is the foundation of the emission of electrons. This is the conclusion derived from the summary of a long period of work. In the past, looking from the oxide cathode semiconductor viewpoint, if you had oxygen omission, this then corresponded to surging barium. But, using a sudden-rest electron spectrometer, it was discovered that, under conditions of more oxygen than alkaline earth metal, there are still considerable electron emissions. This creates a contradiction between the above surging barium concept and experimental facts. Using the dynamical surface emission center model we have proposed, this contradiction can be reconciled, and at the same time the surging

barium concept can be described comparatively clearly.

Theoretically, in barium atom with two high energy 6 s valence electrons, because its atomic number is high, the outer level electrons receive inner level electron shielding, and are easily emitted to a vacuum. But the work function of pure metal barium is 2.5 eV, definitely not low. This is because of the effect of the attraction and holding on the part of the attractive field produced by the nucleus of a barium atom. If it is not barium surrounding barium, but rather is some element with a low atomic number and light mass, for example oxygen, then the attractive field produced is somewhat less, and this facilitates electron effusion. However, this is just one aspect of the question. If the low energy level of a light element can accommodate an electron, then the valence electrons of barium are able to go into the light element and form a bond, and in that case can't be emitted to a vacuum. Barium at this point then changes into ionized barium, and is no longer surging barium. Therefore, surging barium must have not yet completely lost two high energy 6 s electrons, but still be absorbed into some atom grouping. It is called surging barium when there are light elements surrounding it, which based on quantum number can receive electrons, but which based on electronic charge already can't receive more electrons. Under these conditions, the valence electrons of barium have the tendency to enter the low energy levels of a light element, but there is already a negative charge within these low energy levels, and the probability that the

6

electrons in question will be crowded into a vacuum is high. Lampert and others, using an X-ray electron spectrometer and an ion scatterometer to analyze the dispenser cathode, proved that, after activation, the top layer contained barium that was most nearly metal. We believe this is surging barium. [8]

Based on the above definition, surging barium can be present in two forms. One form is to be absorbed in BaO , SrO , CaO , or their mixed crystals. The emission center they form is a partial atomic complex. Therefore, looking at the whole cathode, there can be more oxygen than alkaline earth metal, but, looking at the partial area of the emission center, there is still surging barium. The second form is absorption on to a refractory salt, like Ba_2WO_6 . Its very clear. As when there is a barium molecule absorbed onto a BaWO_4 molecule, then the number of barium molecules is 4, but the number of oxygen molecules is 6. Using a sudden-rest electron spectrometer it can be observed that there is more oxygen than barium, but there is still surging barium. This kind of atom complex can emit electrons. From this it can be seen that, although the emission center components of oxide type and dispenser cathodes are somewhat dissimilar, their basic mechanisms of electron emissions are linked.

The Nature and Function of Oxygen

Oxygen is an element that a low work function cathode can't do without, but at too high a quantity causes the cathode to

become toxified, and is detrimental to emissions. This has already been discussed in the literature^[7]. Recently, Shih et al.^[9] discovered in an experiment oxidizing barium film by applying oxygen that, when the oxygen was applied the work function of the film first dropped, then rose again after falling to a certain numerical value, and a minimum value emerged (1.4 eV). They began with a semiconductor model of emissions and believed that the oxygen produced two kinds of function on the film when it was applied: one is that it caused the oxygen vacancy donors in the film to be reduced, even though the internal work function was amplified; the other is that it caused the affinity of the surface electrons of the film to fall, even though the external work function was reduced. The effect of these two kinds of cathode function is to cause the overall work function to produce a smallest value. This is to say, in practice there exists an appropriate amount of oxygen, which causes the smallest work function in the film. Also, when Maloney et al.^[10] used an emissions pattern electron microscope to observe the non-uniformity of the change in emissions during the process of applied oxygen toxification in a dispenser cathode, they discovered that some previously dark (lacking emissions) areas became lighter after application of oxygen, but that some previously light areas, however, became darkened after the process of oxygen toxification, as shown in figure 1. From this experiment it can be seen that oxygen displays a completely opposite effect on different areas of the surface components. This is because there is an excess of barium atoms in some places and oxygen combines

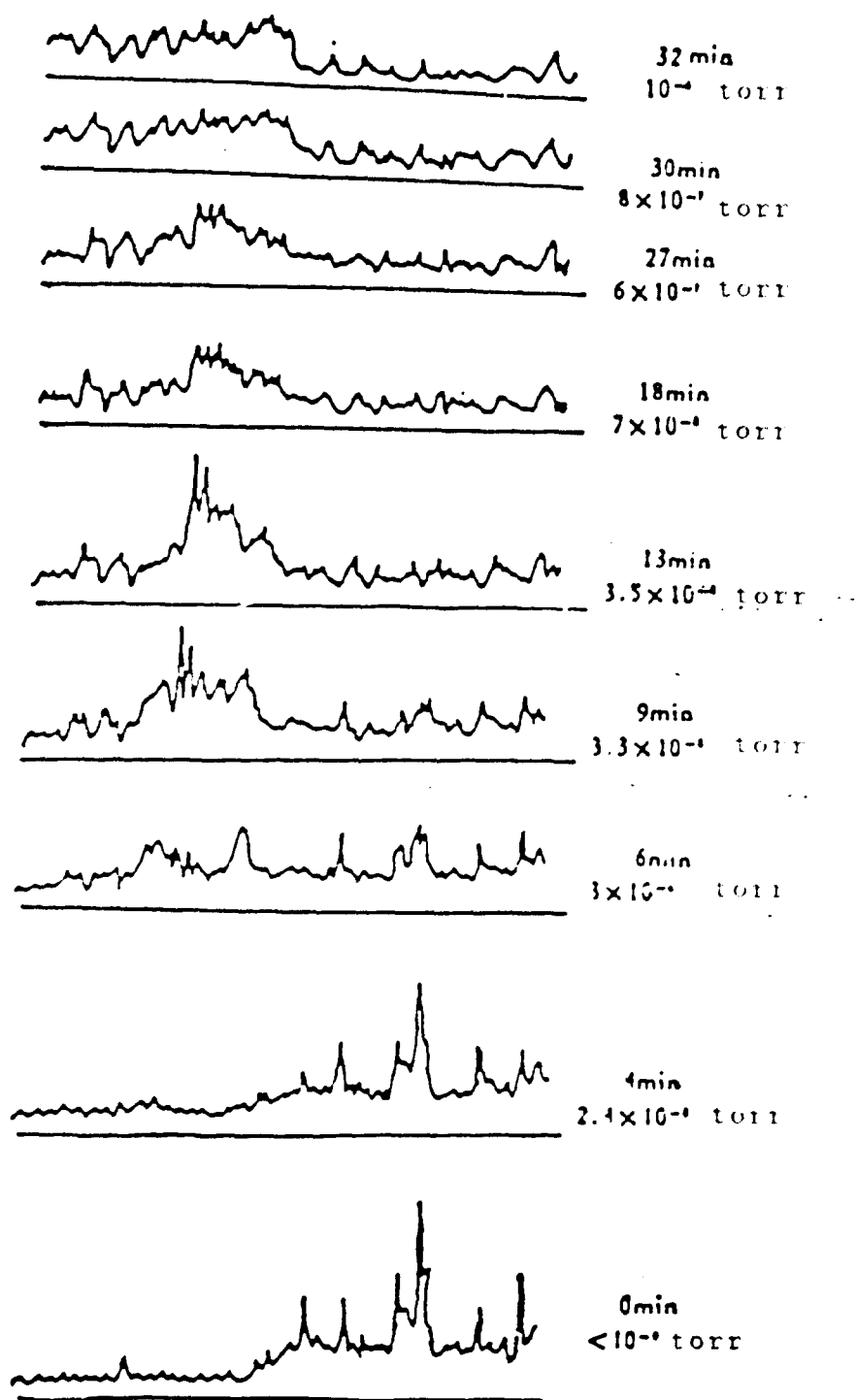


Fig. 1 Change of emission of impregnated aluminate dispenser cathode, when gas pressure is increased

with a part of them, but there still remains a certain amount of surging barium, and a good emission center is then formed. But, if the period of oxygen application is increased or the oxygen gas pressure increased, then the combining of oxygen and barium causes the amount surging barium to fall; at the time when the barium replenishment rate is smaller than the attachment rate of oxygen, the previously good emission center can be damaged, and oxygen toxification created. The results of the experiment make clear that the oxygen toxification is not comprehensive, but progresses based on the specific conditions of each different area. On the surface of the same cathode each separate emission center complex has a relatively independent character.

Since oxygen has a positive effect on emissions, why must we eliminate oxygen by every possible means in cathode technology? For example, why must tungsten powder only be used after going through thorough reduction? This is because there is a lot of oxygen in the natural world and oxygen has a very active chemical nature, extremely easily combining with metals or being absorbed on the surface of metals. In metal powder with a large surface area there is a lot of absorbed oxygen, which far exceeds an amount that would create a beneficial effect in an emission center. So, how much oxygen is appropriate? Because the composition of emission centers is fairly complex, at present a precise quantitative determination has not been able to be made, and there is a need for researchers in their own work to take the matter in hand based on experimentation.

Regarding the Emission Center

The non-uniformity of electron emissions, the fragmented scaled effect, had already earlier been observed in the international sphere. Using an emissions pattern electron microscope, one can see the distribution of light points and dark points directly on the fluorescent screen, thereby giving rise to the term "emission center". But it is regrettable that, because the semiconductor model and the single atom dipole theory were in vogue at the time, it blocked deeper research of emission centers, and it was believed that the work function was brought about by dissimilar crystal surfaces, and was fixed and unchanging. But work functions measured using a scanning low energy electron probe are distributed, as shown in figure 2. Figure 2(a) is that of an oxide coated cathode, and figure 2(b) is that of a dispenser cathode. From the figures it can be seen that after activation the numerical value of the work function not only got lower, but that the shape distribution curve also got narrower. For this, the cause of the work function distribution can't be explained simply by the difference of crystal surfaces, because after cathode activation its crystal surface distribution won't change. Besides this, the two types of cathodes both have a work function distribution, and their numerical values and the shape of their distribution curves are similar, showing that the non-uniformity of emissions is a fundamental characteristic of the thermionic cathode, and a

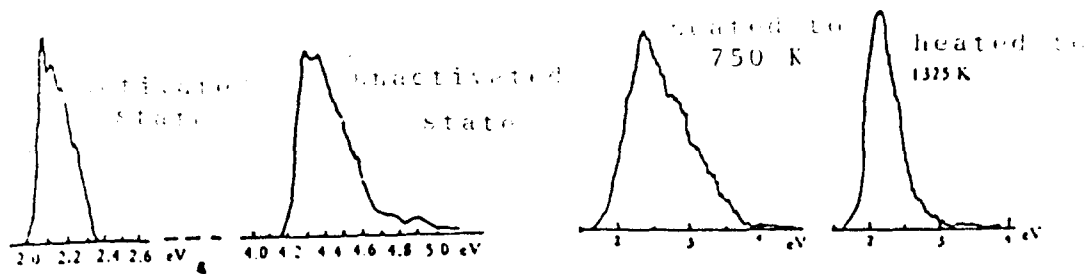


Fig. 2 Variation of work function distribution
(a) Oxide coated cathode (300K) (b) Dispenser cathode



Fig. 3 Emission photograph of dispenser cathode
(a) Scandate dispenser cathode (b) Tungstate dispenser cathode 600X

unified theory can be used to describe it.

Figure 3 gives our lab photographs of scandate (a) and tungstate (b) dispenser cathodes from an emission pattern electron microscope. From the figure it can be seen that, under conditions of the same magnification, the light spots of scandate are comparatively large, and their emission power is also comparatively strong. This clearly relates to the characteristics of salts, but it can't be explained by saying that the different tungsten crystal surfaces have a different work function, because the grain size distribution of the tungsten powder we used was the same, and it was not possible for there to be monocrystalline surfaces reaching into the tens of microns in size. Therefore, the ideas of BaO-W or Ba-O-W single layer absorption both do not fit the dispenser type cathode.

As the term suggests, monocrystalline surfaces that frequently contain more than a million atoms can't be called emission centers. Based upon the surging barium concept we discussed above and oxygen's divisible character, the emission center is a complex formed in the coordination of each kind of atom and beneficial effects on electron emissions. It must have a certain size in order to screen off the nucleus attractive field produced by the substrate, but also must not be too big, so the free electrons of the substrate can then more easily be transported to the emissions center. From the deposited activated material to the minimum work function, we estimate the size of

the emission center to be about ten molecules thick^[13]. Take, for example, Ba_3WO_6 . Its crystal lattice constant is $8.6 \text{ \AA}$, and thus the linear dimension of the emission center is about $100 \text{ \AA}$. If it was any bigger the transport of electrons might be inhibited. If our analysis is correct, then the light points seen from an emission pattern electron microscope are not single emission centers, but emission center complexes. Using a detector with an electron beam spot on the micron order of magnitude (scanning sudden-rest, scanning electron probe, etc.), one still covers a great number of emission centers. To see an emission center, the resolution of instruments needs to be improved.

The Composition of the Emission Center

We started from the fact of emissions not being uniform, and combined the results of other work on thermionic cathodes in order to explore the composition of the emission center. In order to do this we first had to research absorption, because emissions and absorption have a very close connection^[14]. In general, chemical absorption is firmer than physical absorption, because the amount of energy needed for electron exchange is somewhat larger than that needed for deformation of the spatial electron charge cloud. Let's take tungsten as an example. In the conduction band of tungsten there are free electrons. If that which is absorbed is oxygen, which can capture electrons in its outer most orbit, this then creates chemical absorption produced through electron exchange, and this way is comparatively firm; if that which is absorbed is barium, an atom that has two 6 s valence electrons, then only the electron cloud of barium

produces a deformation, and its absorption is not at all firm and it is easily evaporated away. Because of this, the idea that the dispenser cathode is a Ba-W system (that is, a single atom layer) has been done away with on the international level. An emission center must have comparatively firm absorption in order to not have it evaporate easily in high temperature use.

After electron emission, there is a need for very quick replenishment through electrons transported from the substrate. Otherwise, because the surface charge is not balanced, it will be hard to emit more electrons. With a good emission center, if the electrons aren't easily replenished, then it can't emit many electrons in a given unit of time. The energy of electrons in a bond is usually fairly low, and they are in a bound state, and can't easily serve as conduction electrons. Therefore, in order to cause the free electrons in the substrate to efficiently transport to the emission center, the absorbed atom groups must have a fairly large number of unsaturated bonds, and furthermore, the difference between the Fermi energy level and the energy of the conduction electrons must be small, in order to make it easier for the electrons to reach the emission center from the substrate.

In the semiconductor model and single atom dipole theory of the past, electron transport was not a problem, and therefore, there was no research at all at the international level on the problem of transport. But the above theories were not able to

explain the electrosark phenomenon. Experiments show that electrosarks are spurts carrying positively charged atoms^[15]. A cathode with good conductivity shouldn't let out electrosarks, because there is no reason for them to be able to spurt out positively charged atom groups. But, the fact is, even a cathode with strong metallic characteristics like a dispenser cathode still has electrosarks. However, the probability of it occurring is comparatively less than in an oxide cathode and the process is gentler than in an oxide cathode. When a tungsten metal surface has absorbed some atom groups, if the electron transport doesn't keep up with emissions, then the surface has positive charge accumulation, giving rise to bombardment by nearby electrons, thus reaching a level of breakdown and spurting. This is the cause of electrosarks. The dynamical surface emission center model itself requires good electron transport, and at the same time can also explain the electrosark phenomenon.

Metals such as rhenium, osmium, and iridium deposited on an aluminate dispenser cathode can raise the emission capacity^[16]. But these three transition elements themselves also have a high work function, and won't make a direct contribution to emissions. The actual pattern through which the function of rhenium, osmium, and iridium is created is a subject for future research. Aluminate, tungstate and scandate dispenser cathodes all have barium and oxygen, but their emission and evaporation performance are somewhat dissimilar. How does the structure of these salts actually produce their function? Why does a tungstate dispenser

cathode not produce a function anymore after metallization?

Clearing up these questions can point out the road to improving cathode performance.

Dynamical Characteristics of the Emission Center

Even if there is a pure monocrystalline surface, it still can't be held that its surface barrier is fixed, or said that it is stable. Given a vacuum level up to 10^{-10} torr, at room temperature there are still $10^{10}/\text{cm}^2$ gaseous molecules per second hitting the surface, causing the solid surface to often be in an excited state. From the point of view of an electron in the surface, the things that effect it are the nucleus attractive field of the surface atom front, the screening field of other electron clouds, vacuum side particles, and hertzian waves. This way, in order to find the wave function which describes the state of movement of the given surface electrons, one must compute the Schrodinger equation of time. Therefore, from the point of view of electrons, electron emissions are completely dynamic and random.

Now, let's look again at the dynamic characteristics of a practical thermionic cathode from the point of view of the electron. Substrates are all polycrystalline surfaces, they have defects, and they have narrow chinks. Therefore, their absorbtion power is then not identical for atoms with different characteristics; this is the objective basis for the formation of

the emission center. At high temperatures the cathode has lattice vibration, and the surface elements can diffuse and undergo movement of place. Generally speaking, the response is to cause the surface energy to be at its lowest and stability to be reached, but concretely speaking, surface energy is often changing. Besides the above mentioned vacuum side energy exchange, emitted electrons also carry away a certain amount of energy. This then causes the surface atoms to not be able to be in a completely stable state. Processes like evaporation, toxification, and spatter scattering are processes that change the structure of surface atom groups. They can destroy an emission center, and can also produce new emission centers. This is the reason that the emission performance of some poorly activated cathodes improves after a one time low vacuum electron exposure. The conditions of surface atom movement are very complex. Some only showing on a millisecond order of magnitude, like change in the electrical current in an ongoing pulse, in a flickering hum; others appear very slowly, needing ten minutes, like activation (see fig. 2), toxification (see fig. 1), and the renewal of emissions after toxification; the final exhaustion of the active material, however, is shown in the life of the cathode.

One can realize from the above analysis that, because of the great many requirements, including that the emission center absorption be firm, that it easily emit electrons, and that the electrons also have ease of transport to the center from the

substrate, if each kind of element is poorly coordinated, the desired conditions will be hard to achieve. Besides this, because the surface atoms are in a dynamic barrier and also receive the influence of the vacuum side atmosphere, the center's emission potential can change. Therefore, there is a certain randomness in both the formation and destruction of an emission center. This kind of randomness is shown in the work function distribution curves in figure 2, because the shape of these curves are all very like a Gauss type distribution.

Prospects

The dynamical surface emission center model is able to coincide with the many phenomenon observed in a practical thermionic cathode. It points to good prospects for the development of thermionic cathodes: (1) if the amount of emission centers can be increased, then density of emission electrical conductivity can be raised, (2) by clearing up the problem of electron transport through research, a cathode with good performance can be prepared, (3) it has benefits to standards for correctly mastered cathode activation in specific environments, and, (4) for choosing an appropriate cathode type under the requirements of fixed parameters, such as evaporation rate, electrical conductivity density, work temperature, etc.

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