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Local Thermionic Emission from Bare and Covered Surfaces of Cermet-electrodes[+)]

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Lokale Emission von unbedeckten und bedeckten Oberflächen von Cermetelektroden thermionischer Systeme

Zusammenfassung

Cermetelektroden bestehen aus mindestens einer keramischen und mindestens einer metallischen Phase. Im Vergleich zu Metallelektroden weisen sie einige Vorteile auf, wie

- hohe und gleichmäßige Emissionsstromdichte
- geometrische Stabilität
- Stabilität gegenüber Ionenbeschuß und chemischem Angriff.

Für Röhrenkathoden im Hochfrequenzbereich und für Elektroden in Hall- und in Thermionikgeneratoren sind Cermetemitter von Interesse.

Hinsichtlich des Emissionsstromes lassen sich zwei Typen von Cermetelektroden unterscheiden:

Beim ersten Typ setzt sich der Emissionsstrom aus demjenigen von der metallischen und demjenigen von der keramischen Phase zusammen. Die Stromdichte über der emittierenden Oberfläche ändert sich nicht mit der Temperatur. Lokal gemessene Austrittsarbeiten von Bereichen, die etwa der Kristallitgröße der Metallphase entsprechen, waren konstant.

Beim zweiten Typ von Cermetelektroden sind die Emissionseigenschaften durch einen dünnen Film an der Elektrodenoberfläche bestimmt. Dieser Film entsteht durch laufende Zersetzung und Nachlieferung der keramischen Phase und von ihm aus werden die meisten Elektronen emittiert. Der Bedeckungsgrad der Oberfläche mit diesem Film wird über einen dynamischen Gleichgewichtszustand reguliert, der durch Parameter wie Vorrat, Diffusion und Verdampfung der keramischen Phase bestimmt ist. Durch die Wahl der keramischen Phase ist die optimale Arbeitstemperatur und die Größenordnung der Emissionsstromdichte gegeben. Wie man zu dem gewünschten stereometrischen Elektrodenaufbau kommt, hängt vom technologischen Verfahren ab. Die gemessenen Austrittsarbeiten solcher Elektroden sind temperaturabhängig. Im optimalen Temperaturbereich zeigen auch diese Elektroden gleichmäßige Emissionsstromdichte.

Die in der vorliegenden Arbeit gezeigten Emissionsstromdichten wurden über emissionsmikroskopische Bilder erhalten. Lokale Emissionsstromdichten wurden hinter Lochblenden im Anodenschirm gemessen.

Local Thermionic Emission from Bare and Covered Surfaces of Cermet-electrodes

Summary

Cermetelectrodes consisting of a rigid metal sponge and a ceramic component in the pores offer some better properties in comparison with ordinary metal electrodes:

1. high emission current density and homogeneity
2. geometrical stability
3. stability against ion and chemical attack.

These electrodes are of special interest for cathodes of tubes for very high frequency application and for electrodes in Hall- and Thermionic generators.

The emission current of a first type of a cermetemitter is composed by two contributions : one produced by the metallic phase and another one produced by the ceramic phase.

By varying the electrodetemperature the emission pictures are not changed . The local measured work function is constant similar to the workfunction of a metallic monocrystal in the region of each small patch. Data for intermediate positions cannot be measured.

The emission properties of a second basic type of a cermetemitter are characterized by a dynamic equilibrium at the surface of the electrode. A small amount of the ceramic component continuously decomposes and generates a thin film at the surface. Out of this film most of the electrons are emitted. The degree of coverage

of the surface is governed by a dynamic equilibrium of the parameters supply, diffusion and evaporation, which means that by the choice of the ceramic component the optimal workingtemperature and the magnitude of current density are determined. It is a problem of fabrication (paper Nr.2)to get a good distribution of the components and the desired structure of the electrodes i.e. high emission current and low evaporation. The measured local work function depends on the temperature. In the region of the best operating temperature the emission picture looses its patchy appearance.

The emission properties of electrodes of the first and the second cermettype are shown by a special emission microscope. The local current density for the bare and for the partially Cesium-covered surfaces were determined by the current collected behind a bore-hole in the screen.

1. Introduction

Cermetelectrodes consisting of a rigid metal sponge and a ceramic component in the pores offer some better properties in comparison with ordinary metal electrodes:

1) high emission current density and homogeneity
2) geometrical stability combined with little thermal and electrical resistivity
3) stability against thermal shocks, against ion and chemical attack
4) low evaporation rate.

These electrodes are of special interest for cathodes of tubes for very high frequency applications, for electrodes in Hall and Thermionic Generators. Such electrodes show the

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desired workfunction for themselves and therefore do not need to have a high cesium partial pressure at and above of the surface.

2. Stable Type Cermet Electrodes

To distinguish between two different types of cermet electrodes it is useful to consider their microstructure. This is possible by two ways: optical as well as electron emission microscopy. Commercial microscopes have been used for optical observation. The emission microscopic equipment was home made. Its principle is shown in fig.1 . Two remarkable facts concerning the measuring procedure: Firstly the patch area to be measured is magnified so, that it is bigger than the entrance diameter to the Faraday cage. Secondly it is possible to compensate the field strength at the surface under measurement by variation the potential of the fist electrode of the immersion lense (see fig.2). These points lead to the following advantageous consequences: If the measured area is smaller than the emitting patch no arror arises from adjacent areas. On the other hand a field exists between different area patches on the surface. This field can be compensated leading to comparable results for all patches.

In fig.3 pictures of uraniumdioxid-molybdenum-cermet (UO_2 - Mo) surfaces are given prepared by the optical as well as by the electron emission microscopy. The bulk material has been produced by isostatic hot pressing of molybdenum coated UO_2 spheres [1] . Because of the fact, that UO_2 - Mo forms a monotectic type phase diagramm [2,3] no interaction takes place. This is the reason for telling it a stable type cermet electrode. As a consequence of good wetting behaviour of the phases the matrix structure remains unchanged in operation providing a rather high electrical conductivity of the whole electrode.

The emission current of this first type cermet emitter is composed of two contributions produced by the metallic and ceramic phases separately. No change could be obtained by temperature variation in the emission pictures except the brightness of them. The locally measured work functions remain constant for each patch and no intermediate range between them could be observed [fig.4]. This behaviour is similar to that of the oriented parts of metallic monocristals . Between the

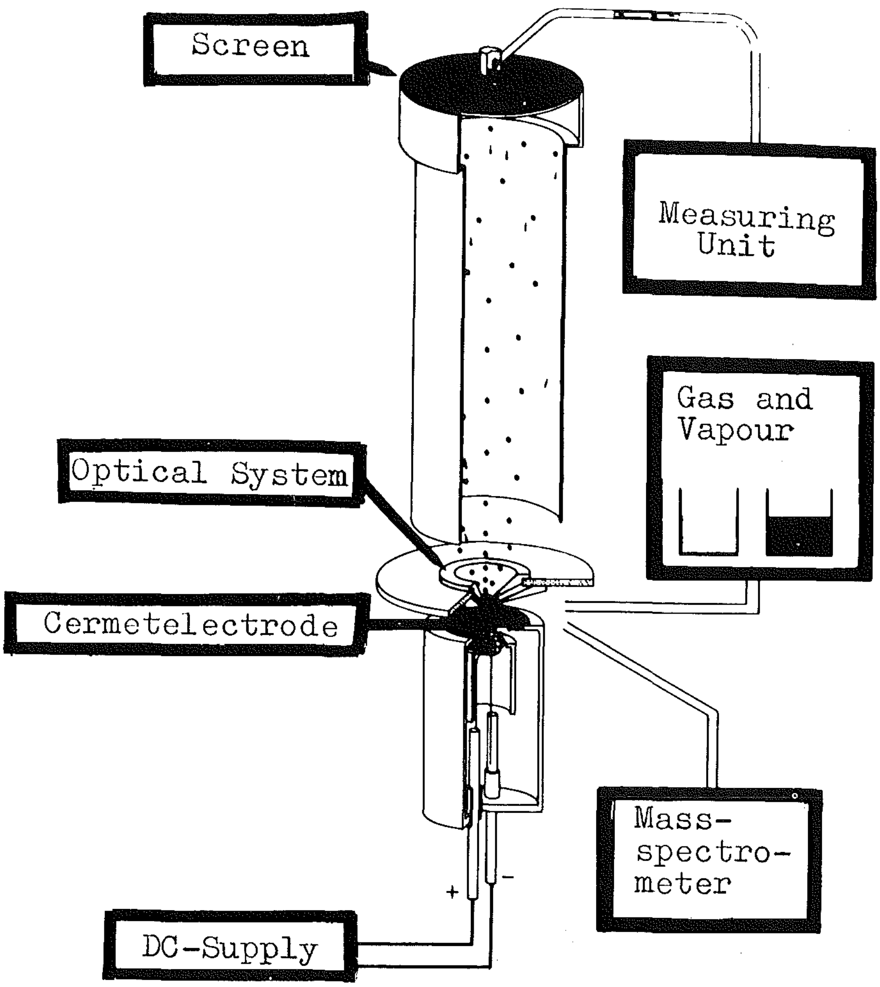

Fig. 1 Principle of the emission microscope.

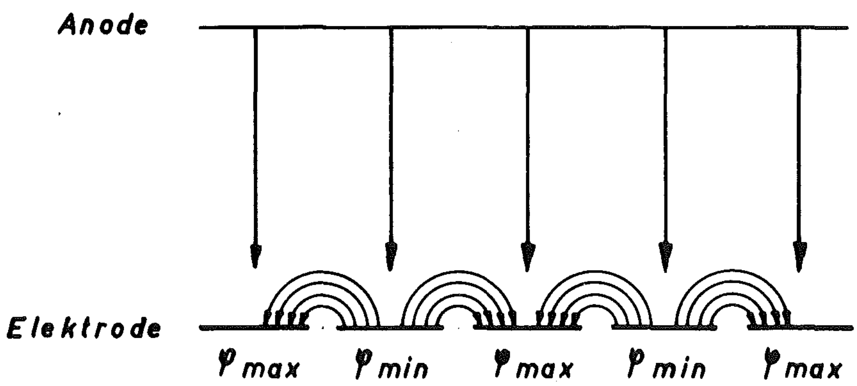

Fig. 2 Patch field in front of the electrode.

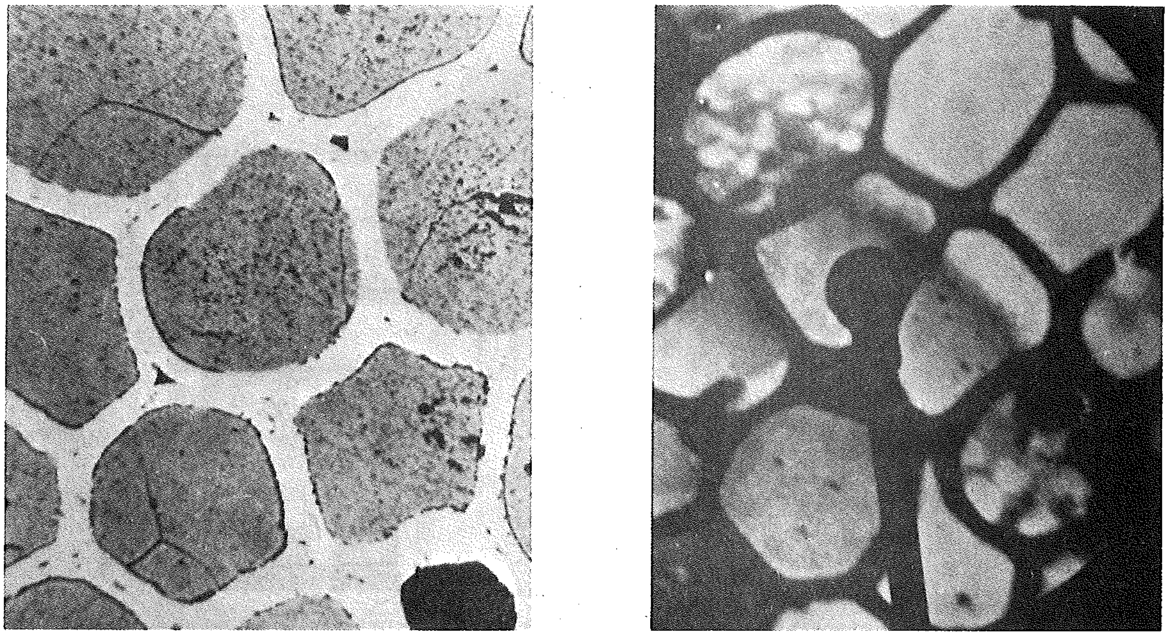

Fig. 3 Pictures of an uraniumdioxid-molybdenum cermet-electrode
left side by an optical microscope
right side by an electron emission microscope.

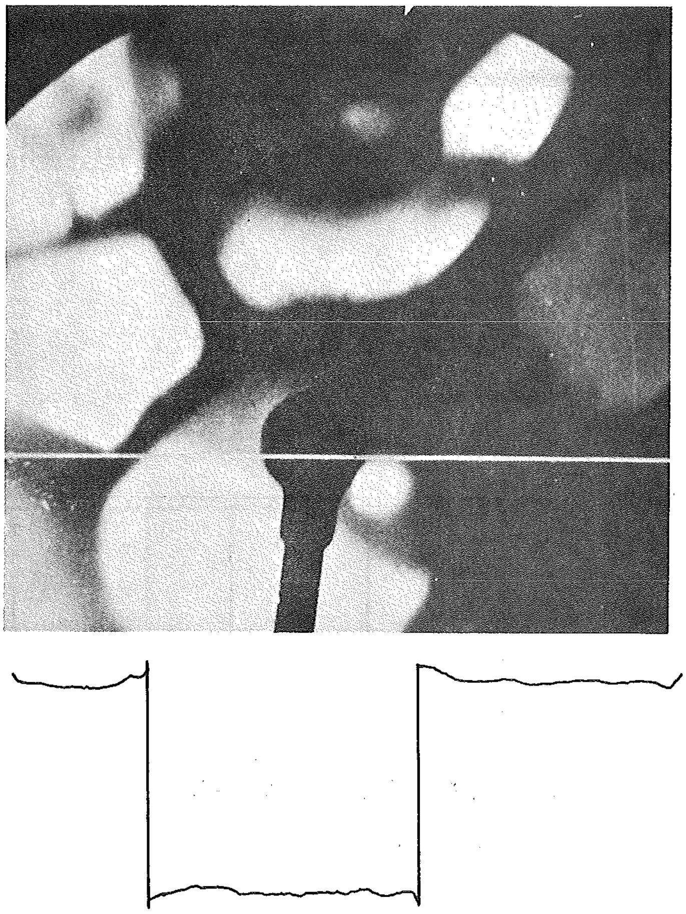

Fig. 4 Local workfunction of an uraniumdioxid-molybdenum cermetelectrode.

different emitting material parts the electric field power is extremely strong.

On the basis of the measured current density of the bright patches the maximum current density of the electrode has been calculated. Special features of the samples microstructure such as form and size of the individual grains as well as the amount of the pores do not have a strong influence to the current density. Due to the fact, that the UO_2 ceramic phase has a work function the values of which are below the values of the molybdenum, most of the emitted current comes from the ceramic phase (see fig.5). This is, why a low concentration of the metallic phase is desirable achieved in the present case by coating the UO_2 by 1 vol % Mo.

3. Unstable Type Cermet Electrodes

Unstable electrodes - in the contrary to stable electrodes - do not show similar surface pictures made by optical and by thermal electron emission microscopy. The material for this type of electrodes used here is barium-calcium-tungstate-tungsten (Ba_2 Ca WO_6 - W). In fig.6 it can be seen, that a nearly uniform film appears in the emission type microscope whilst a different impression is given by light microscopical pictures. The metallic phase is covered by a ceramic phase film formed by up to several monomolecule layers. The bright patches representing hight current density are caused here by the ceramic phase covered metal. No defined boundaries can be observed between patches with different brightness. In the average both the work function difference as well as the electric field strength are lower compared to stable type electrodes. Independantly of the diameter of the measured area spots the work function never was that of neither pure tungsten nor that of barium-calcium-tungstate. The emission properties of this second type of cermet electrodes are characterized by a dynamic equilibrium on the electrode surface. The mechanical properties as well as the electrical conductivity are controlled by the metal sponges. The operating mechanism, which takes place in such electrodes, is characterized by the dissociation of small amounts of the ceramic phase in the pores forming a continuous film allover the surface. This film is - in a steady state manner -

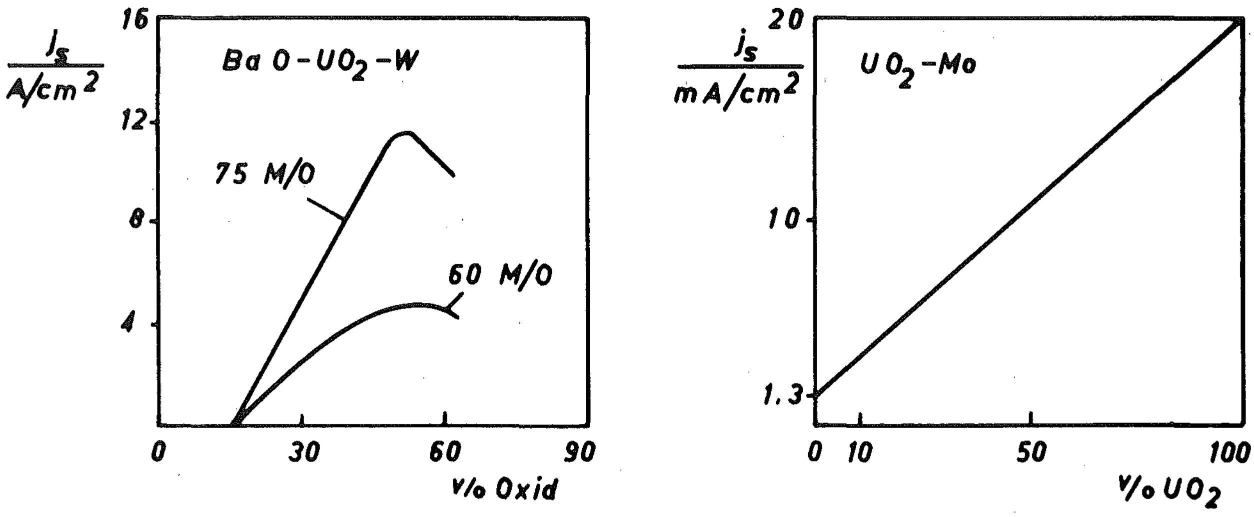

Fig. 5 Emission current of cermetelectrodes as function of the content of the ceramic phase
left side unstable type cermetelectrode
right side stable type cermetelectrode.

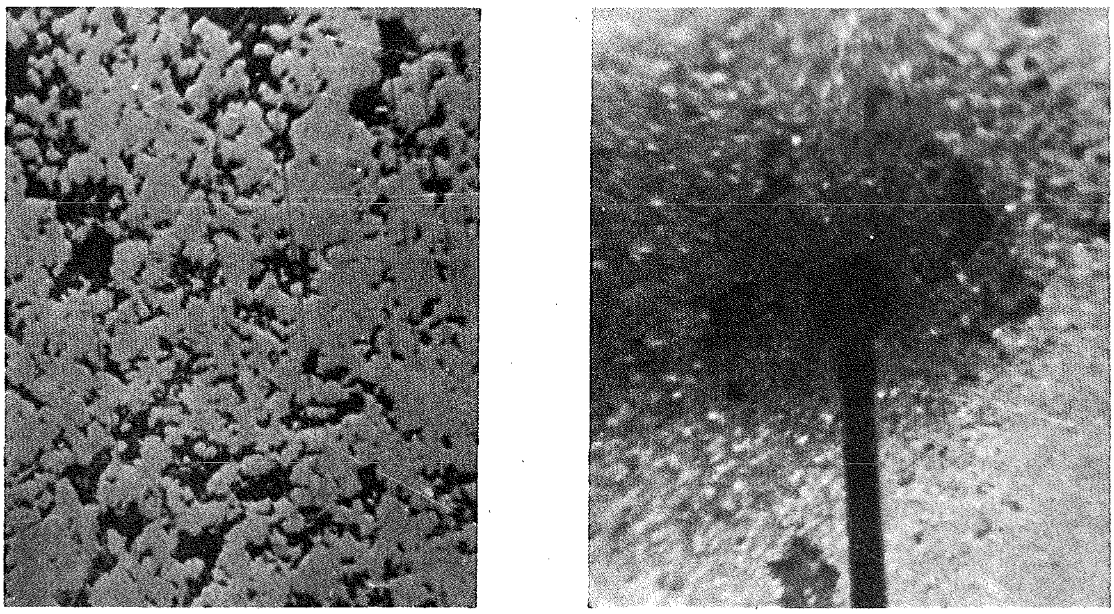

Fig. 6 Pictures of a barium-calcium-tungstate-tungsten cermetelectrode
left side by an optical microscope
right side by an electron emission microscope.

regenerated by migration of the dissociation products along the pore walls. The mechanism exists for example for more than 50 000 h in DC-operation as could be demonstrated recently [4]. Because of the temperature dependency of the two factors diffusion and evaporation the work function of the whole electrode as well as this one of its local parts is seriously affected by the temperature. Due to the fact, that in unstable cermet electrodes the metallic surface is the emitting part, this part should be large. On the other hand, the emitting metal surface has to be totally covered by a ceramic phase film, to give optimum emitting rates. If the metal phase is increased, the ceramic phase is decreased. Above a certain metal concentration the delivery of ceramic phase to the surface becomes too small to guarantee the total coverage of the metal surface. As a result the emission picture is rather patchy (fig.7). The conclusion of this situation is, that an optimum ceramic phase concentration exists for which the current density shows a maximum (fig.5). It should be mentioned that this maximum is also determined by the kind of material used, its stereometric microstructure and the operating temperature.

In addition to these parameters the atmosphere and its composition is an important factor. Especially the oxygen pressure changes the work functions of oxide cathodes to higher values. Therefore it should be noted, that experiments show that reversible behaviour of the cathodes, with varying oxygen content can be obtained in a certain range of oxygen presures [5].

Cesium is another affecting constituent of the atmosphere. This can be seen in fig.8, where the dark parts of the surface become brighter by introduction of cesium to the atmosphere. An equalization state of the surface can be reached at higher cesium-pressures, but this effect slims down again if the cesium pressures become less. This recovering process is temperature dependent and may last for a long period of time if the temperature is very low.

In the contrary to cesium barium addition in the atmosphere leads first to an increased contrast between high and low emitting patches. This is demonstrated in fig.9

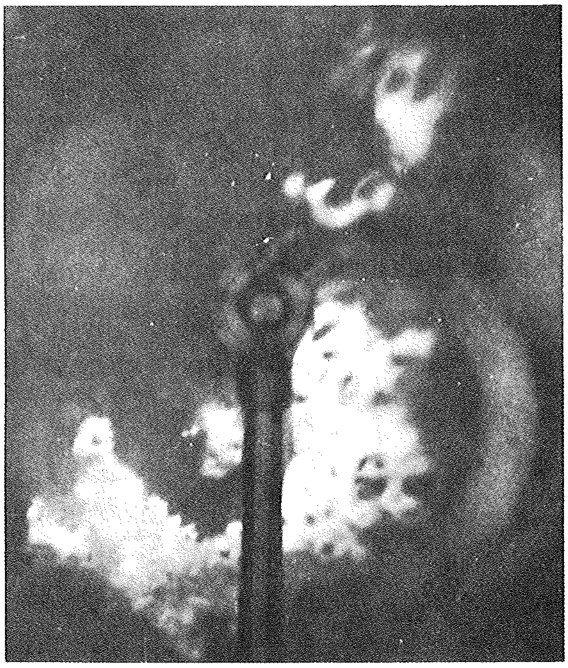

Fig. 7 Emission picture of a barium-calcium-tungstate-tungsten cermetelectrode which is only partially covered by a ceramic phase.

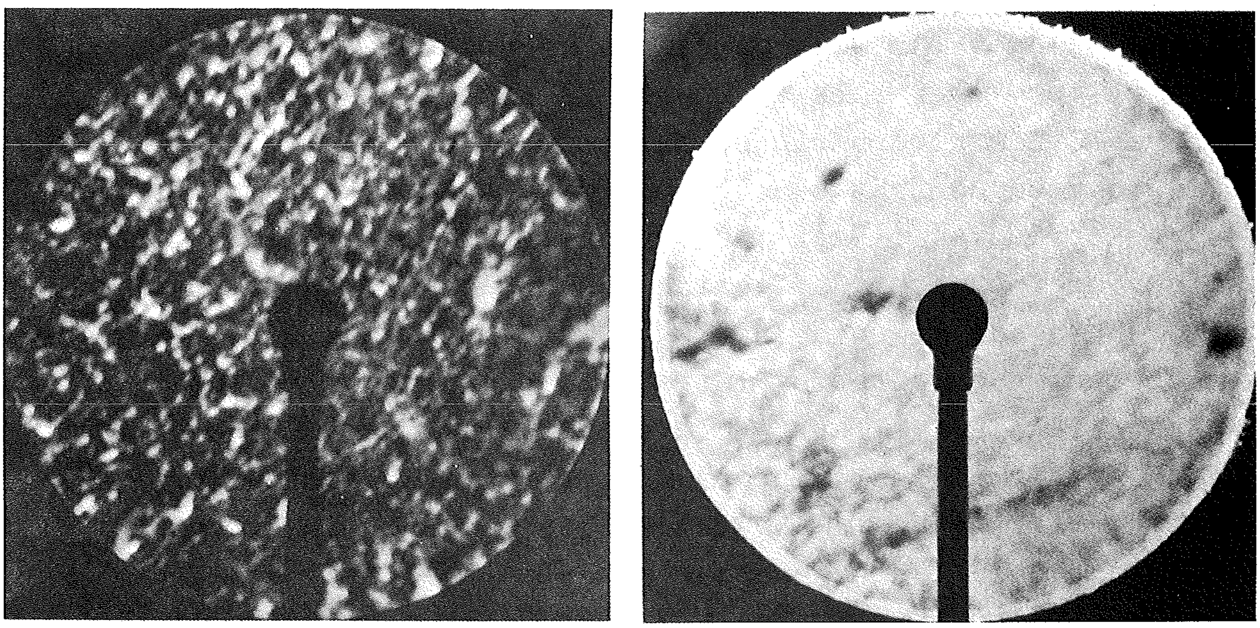

Fig. 8 Influence of cesium on an unstable cermetelectrode
left side without cesium supply
right side with cesium supply.

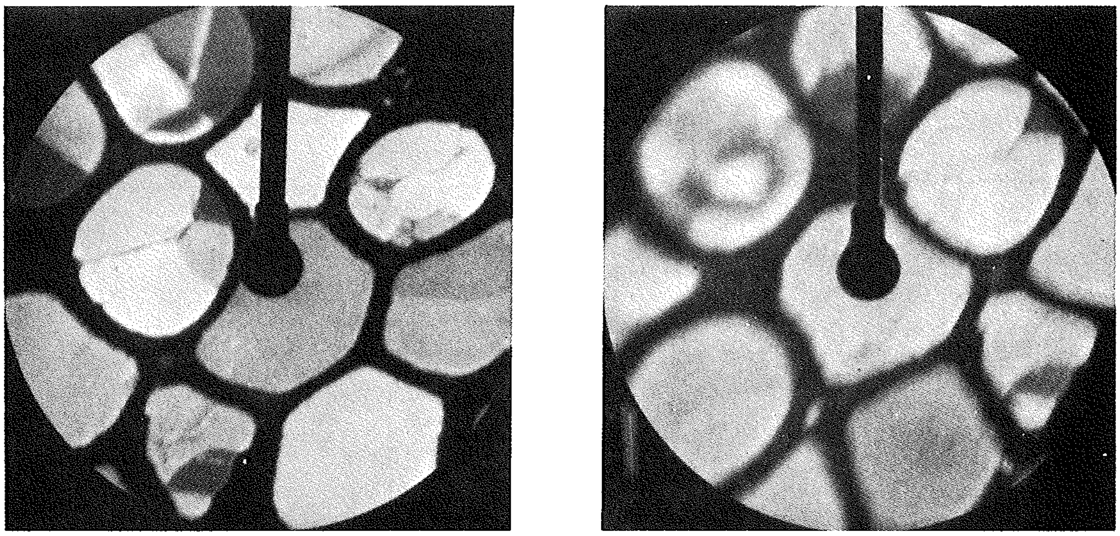

Fig. 9 Influence of barium on a stable cermetelectrode at low barium coverage
left side without barium supply
right side with barium supply.

and caused by the preferential adsorption of barium in the UO_2 - parts of the surface. These results confirm similar experiments published in the past [6].

References

[1] WEIMAR, P., THÜMMLER, F., BUMM, H.,
J. Nucl. Mat. 31 (1969) 215.

[2] ONDRACEK, G., SPLICHAL, K.,
Berichte der DKG 48 8 (1971) 343.

[3] GEBHARDT, E., ONDRACEK, G.,
J. Nucl. Mat. 13 2 (1964) 220.

[4] AEG-TELEFUNKEN ULM,
private communication (1972).

[5] SCHMIDT, D., AUER, H., RIEGEL, W.,
BMBW-FB W 71-55 (1971)

[6] GOOD, R. H., MÜLLER, W., "Field emission" Handbuch der Physik Bd XXI (Flügge, S.) Springer, Berlin (1956)