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INVESTIGATIONS ON CERMET ELECTRODES FOR THERMIONIC EMITTERS

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ETUDES SUR LES ELECTRODES EN CERMETS POUR L'EMPLOI DANS LES EMETTEURS THERMIONIQUES

RESUME

On a préparé par compression axiale à chaud Ba_2CaWO_6-W instable, autofournisseur de Ba, aussi bien que des cermetsémetteurs stables en UO_2-Mo qui doivent etre exploités avec une source externe de Ba. Les propriétés utiles de ces cermets, comme la résistance électrique spécifique et la dilatation thermique, sont décrites et comparées aux prédictions théoriques. On discute l'émission électronique de ces matériaux en se réferant aux films formés sur la surface. Ceci donne la base d'une optimalisation du comportement de ces matériaux.

UNTERSUCHUNGEN AN CERMETS ALS EMITTERWERKSTOFFE

ZUSAMMENFASSUNG

Instabile Ba_2CaWO_6-W Cermets mit eigener Ba-Versorgung und stabile UO_2-Mo Cermets für den Betrieb mit externer Ba-Quelle wurden durch axiales Heißpressen hergestellt. Wichtige Eigenschaften für ihren Einsatz als Emitterwerkstoffe (thermische Ausdehnung, spezifischer elektrischer Widerstand) wurden als Funktion der Keramik-Konzentration gemessen und mit theoretischen Voraussagen verglichen. Die Elektronenemission dieser Cermets wurde gemessen und auf die Basis von gebildeten Oberflächenfilmen diskutiert. Damit bietet sich eine Grundlage an, dieses Verhalten zu optimieren.

SUMMARY

Unstable Ba_2CaWO_6-W with their own supply of Ba, as well as stable UO_2-Mo-emitter cermets that have to be operated with an external Ba-source, have been prepared by axial hot pressing. The relevant properties of these cermets such as electrical resistivity and thermal expansion are reported and compared with theoretical predictions. The electron emission of these materials is discussed on the basis of the surface films formed. It provides the basis for optimising the behaviour of these materials.

INTRODUCTION

The useful operating life of emitter materials is primarily affected by the high service temperatures. These in turn determine the chemical stability of the systems as well as greatly increase the vaporisation rate of the materials. As a result, efforts are being made to produce electrodes with ceramics and refractory metals with thus far promising results. The ceramic component decreases the voltage as well as the temperature required for emission, so that instead of point, surface emission takes place. This has significant advantages for the operation of gas discharge lamps. The development is equally important for the design of low temperature Cesium thermionic converters as power sources of high efficiency. The paper outlines the preparation and some relevant properties of the stable UO_2-Mo cermets as well as unstable Ba_2CaWO_6-W cermets. The emitting properties of these materials are discussed on the basis of surface layers formed.

MATERIAL CONSIDERATIONS

The electrode materials should fullfill the following requirements:

a) High current density over long periods of time as well as high electrical conductivity in order to avoid local overheating.
b) Low vaporisation rates to prevent deposition on sensitive neighbouring components as well as changes in the electrode spacing.
c) Low sensitivity for poisoning effects of all types like ionic bombardment or high electrical field.
d) Mechanical and chemical stability despite high thermal cycling and during operation.

In view of these considerations for a given current density the service temperature is limited the equilibrium vapour pressure. Setting this limit as 10^{-5}Torr, it can be seen from Fig.1, that for a given current density, the materials in question can be classified into groups that are suitable for low, medium, and high temperature applications. Ceramics alone however do not meet the requirement of low resistivity and thermoshock stability and have therefore to be combined with metals. In cermet electrodes therefore, Ba or Cs-based ceramics are suitable for low temperature applications, whereas the Rare earth, Thorium or Uranium compounds can be used at medium temperatures.

EXPERIMENTAL RESULTS

1. Preparation of specimens

As part of a long term experimental programme, cermet electrodes with UO_2-Mo, Ba_2CaWO_6-W among others were prepared with the aid of powder metallurgical techniques. The objective was the preparation of samples with high density and homogeneous distribution of the ceramic phase in the metallic matrix. Axial hot pressing in graphite dies with Al_2O_3 inserts was adopted to prepare all specimens. The powder mixture of Ba_2CaWO_6 (ca.10 µm) and W (ca.1 µm) were hot pressed in vacuum (10^{-5} Torr) at 1473 K at a pressure of 2000 N/cm^2 for 1 hour. The specimens attained a density of 90% TD. The UO_2 (80 µm) and Mo (3 µm) powder mixtures were hot pressed at 1873 K at a pressure of 3000 N/cm^2 for 15 min in inert gas. The densities attained were also about 90% TD. Typical microstructures of the specimens can be seem in Fig.2.

Fig. 1: Current density of various materials as a function of temperature ($p = 10^{-5}$Torr)

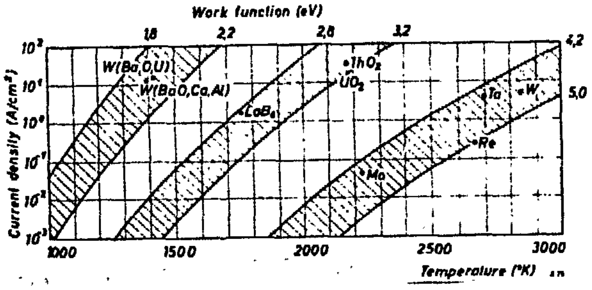
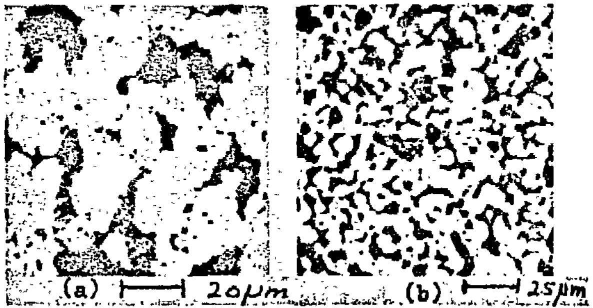


Fig. 2: Microstructure of hot pressed of UO_2-Mo (a) and Ba_2CaWO_3-W(b) cermets (Metalcontent 70 vol%)



2. Properties of Ba_2CaWO_6-W and UO_2-Mo cermets

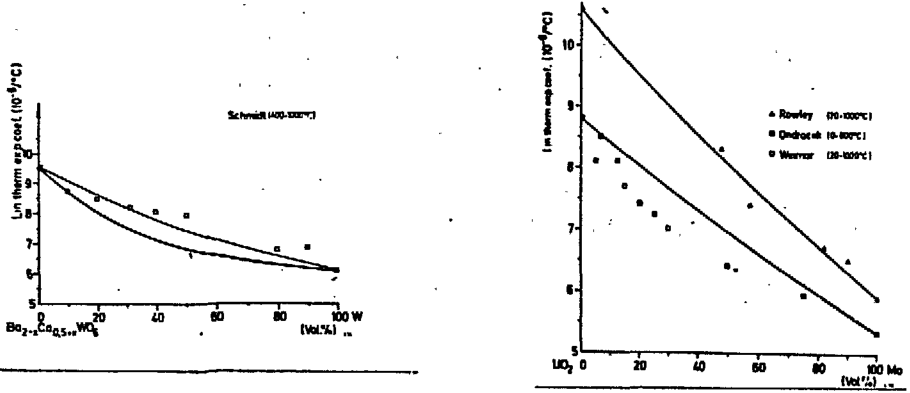
For the use of these cermets as electrode materials, the thermal expansion coefficients as well as the electrical resistivity are important properties. Plotted in Fig.3 are the linear thermal expansion coefficients as a function of the concentration of the ceramic phase. The measured thermal expansion coefficients have also been compared with theoretical predictions. These are derived by considering the elastic restraint imposed on the matrix phase owing to the presence of dispersed particles with a different expansion coefficient (for details of the derivation see (1)).

We get:

$$\alpha_C = \frac{\dfrac{\alpha_D \cdot V_D \cdot K_D}{3K_D + 4G_M} + \dfrac{\alpha_M \cdot V_M \cdot K_M}{3K_M + 4G_M}}{\dfrac{V_D K_D}{3K_D + 4G_M} + \dfrac{V_M K_M}{3K_M + 4G_M}} \qquad (1)$$

with: α = linear thermal expansion coefficient
K, G, = bulk and shear modulus
Indices C, M, D = composite, matrix, dispersed phase respectively

This equation gives two bounds, one valid when the metallic phase is the matrix and the other when the ceramic phase is the matrix. Depending on the elastic constants and the thermal expansion coefficients these bounds are close as can be seen in Fig.3a. In the case of UO_2-Mo cermets (Fig.3b), the theoretical curve shown is valid for the Mo-matrix only. As can be seen the measured values are in good agreement with theoretical predictions.



(a)   (b)

Fig. 3: Linear thermal expansion coefficient of Ba_2CaWO_3-W (a) and UO_2-Mo cermets (b) as a function of concentration
lower bound - W-matrix   upper bound - ceramic matrix

The room temperature electrical resistivity of these cermets is shown as a function of concentration in Fig.4. Also included are measurements cited in the literature (5). The measured values are again compared with theoretical predictions which are derived with the aid of the continumm theory (for details see 6).

Its application for cermets prepared by conventional powder metallurgy has to take into account that 3 different types of microstructure will exist in practice.

1. Metallic matrix with ceramic dispersed phase. For this case we have

$$\Phi_C = \Phi_M (1-c_D)^{\frac{\cos^2 \alpha_D}{2F_D-1} - \frac{1-\cos^2 \alpha_D}{F_D}} \quad \text{for} \quad \left(\frac{\Phi_M}{\Phi_D} \ll 1\right) \qquad (2)$$

2. Ceramic matrix with metallic dispersed phase. For this case we have

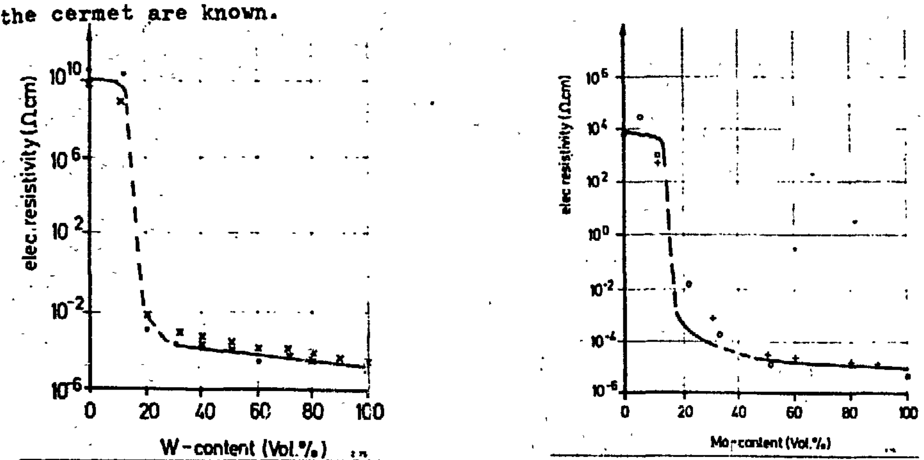
$$\Phi_C = \Phi_M (1-c_D)^{\frac{\cos^2 \alpha_D}{2F_D} - \frac{1-\cos^2 \alpha_D}{F_D-1}} \quad \text{for} \quad \left(\frac{\Phi_M}{\Phi_D} \gg 1\right) \qquad (3)$$

3. Both phases are continuous. For this case we have:

$$\Phi_C = \frac{\Phi_m}{5}\left[\pm \sqrt{(4,5\,c_K-2)^2+5\,(1-c_K)}-4,5\,c_K+2\right] \quad \text{for} \quad \left(\frac{\Phi_K}{\Phi_m} \to 0\right) \qquad (4)$$

The symbols mean:
ϱ = electrical resistivity
α_D = orientation angle to the field direction
F_D = Formfactor, C = concentration.
Indices C, M, D = composite, matrix, dispersed phase respectively.

The theoretical curve shown in Fig.4 was calculated with the aid of the equations (2,3,4) in the range of concentration where they are valid. As can be seen, the measured values are in good agreement with theoretical predictions. These can therefore be used to calculate the resistivity of the cermets, once the data of the components and their microstructure in the cermet are known.



(a) (b)

Fig. 4: Electrical resistivity of Ba_2CaWO_3-W (a) and UO_2-Mo (b) cermets as a function of concentration

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3. Electron emission behaviour

The cermets prepared by the method outlined before, were tested with regard to their emission properties with the aid of an emission microscope. The total emission current was measured in vacuum ($<10^{-9}$Torr) as a function of the ceramic concentration (Fig.5). In the case of the unstable Ba_2CaWO_6-W - which generates a thin surface film with Barium by slow in situ decomposition of the ceramic - the emission current is high, increases with concentration and attains a maximum value. In contrast the stable UO_2-Mo cermet shows a linear dependence of emission current with concentration. Higher current densities can only be attained in the presence of Ba vapour.

For the understanding and extrapolation of the behaviour of these electrodes for long periods of time, it is necessary to investigate the surface phenomena in microscopic regions. This was again accomplished with the aid of the emission microscope. The UO_2-Mo specimens were tested in flowing Ba-vapour. Fig.6a shows a series of micrographs of the cermet at various temperatures along with corresponding micrographs of polycrystaline Molybdenum. With decreasing temperature and consequent increase in surface coverage with Barium vapour, preferred grains with originally low electron emission (6a) reverse their behaviour completely (6e), whilst going through all intermediate emission stages as coverage increases (5b,c,d). This behaviour is reflected in the emission current characteristics shown in the figure. As a consequence for a given cermet combination, there is an optimum Ba coverage, that results in high emission currents. Since an increase to higher temperatures also increases the Ba-vaporisation rate, optimum coverage can be an complished by increasing the Ba-supply. In the case of Ba_2CaWO_6-W cermets which generate their Ba-vapour coverage by in situ decompensation, the coverage is determined by the dissociation and transport to the surface. In this case for a given temperature, the surface coverage can only be influenced by changing the content and the microstructure of the material.

Fig. 5: Total emission current density of Ba_2CaWO_3-W and UO_2-Mo cermets

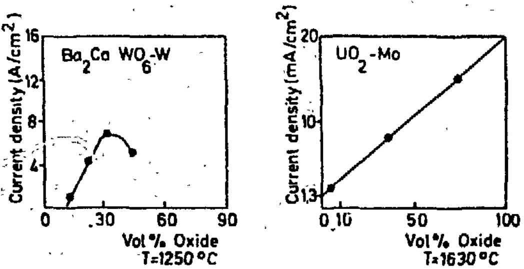
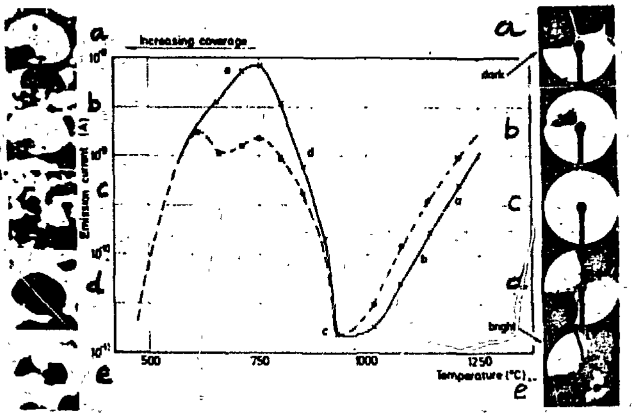


Fig. 6: Emission micrographs and current of UO_2-Mo cermet at various temperatures and stages coverage



CONCLUSIONS

1. Cermet emitter materials have the advantages of low work functions, along with high electrical conductivity and dimensional stability.
2. Unstable combinations (Ba_2CaWO_6-W) that generate their own supply of Ba can be optimised with regard to their ceramic content.
3. Stable combinations (UO_2-Mo) have to be operated with an external Ba-source and could be optimised by adjusting this supply.

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