

THERMIONIC EMISSION CHARACTERISTICS OF PURE AND YTTRIUM-CONTAINING ZIRCONIUM CARBIDE

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Zirconium carbide has a high melting point and a relatively low, compared with other inorganic refractory compounds, evaporation rate [1], and is therefore of considerable practical interest as a material for thermionic cathodes operating at a temperature of $\sim 2000^\circ\text{K}$. The thermionic emission characteristics of zirconium carbide have already been investigated by a number of authors, but the values of work function cited in the literature for this carbide show a large scatter, ranging from 2.5 to 4 eV [2], which may be a result of deviations from the stoichiometric composition within the homogeneity range, differences in methods of preparation, and the presence of impurities.

In this connection, it was considered of interest to study the work functions of zirconium carbide specimens prepared by the following techniques: 1) hot pressing of a zirconium carbide powder synthesized from the elements (in an argon atmosphere at a temperature of $\sim 2200^\circ\text{C}$ and a pressure of $\sim 180\text{ kg/cm}^2$) [3] and 2) chemical vapor-phase deposition from a vapor-gas mixture containing ZrCl_4 , CH_4 , H_2 , and Ar (at a substrate temperature of 1500°C)* [4]. To obtain a basis for comparison, a parallel study was made of the work functions of titanium carbide specimens prepared by the same methods. Some characteristics of the carbides investigated are given in Table 1.

The hot-pressed zirconium and titanium carbide specimens had a porosity of 6-10%. The densities of the carbide specimens prepared by vapor-phase deposition were close to the theoretical densities of the corresponding carbides, and the porosity of these specimens was thus virtually zero. The deposited specimens exhibited a marked growth texture in which their $\{100\}$ faces were preferentially oriented parallel to the deposition surface (at right angles to the direction of measurement of emission current density).

Thermoelectron work function measurements were made, using an apparatus provided with electronic heating, by the thermionic emission (TE) method in a dynamic vacuum below that corresponding to 10^{-6} torr. The specimens - disks of 6-mm diameter and ~ 1 -mm thickness - were initially degassed at a temperature exceeding the maximum operating temperature ($\sim 2000^\circ\text{K}$). It was assumed that the treatment did not significantly alter the composition of the surface layers of the carbide specimens [5] while removing all adsorbed films of residual gases. As regards the latter assumption, it has already been established in an investigation into the surface recombination of hydrogen atoms on refractory carbides [6] that full desorption of residual gases from carbide surfaces occurs already at $T > 1400^\circ\text{C}$ in a vacuum of 10^{-2} torr.

The temperature dependence of the electron work functions of the cathodes investigated is described by the equations

$$\varphi_t = 4.82 - 4.3 \cdot 10^{-4} T \text{ [eV]}$$

for zirconium carbide prepared by chemical vapor-phase deposition and

* Specimens of pyrolytic zirconium and titanium carbides were supplied by V. S. Davydov of the State Institute of Applied Chemistry.

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TABLE 1. Structural and Chemical Characteristics of Specimens of Pyrolytic and Sintered Ti and Zr Carbides

Material	Method of preparation	Chem. composition, wt. %				Comb. C / Zr atomic ratio	Lattice constant a , Å
		Me	total C	free C	N		
ZrC	Hot pressing	87,9—88,0	11,5	N. det.	—	0,97	4,694
ZrC	Chemical deposition	88,6—88,9	11,2—11,4	0,2	0,1—0,2	0,96—0,97	4,698
TiC	Hot pressing	80,6—80,7	19,1—19,2	0,2	—	0,96	4,331
TiC	Chemical deposition	80,6—80,8	18,8—19,0	0,15	0,2—0,3	0,93—0,95	4,3309

TABLE 2. Structural Characteristics and Electron Work Functions of Alloys of the System Zr-C-Y

Alloy composition	Lattice constant a , Å	Electron work function φ , eV		
		CPD method, $\pm 0,05$ eV $\varphi_{300^\circ\text{K}}$, eV	TE method, $\pm 0,04$ eV	
			$\varphi_{300^\circ\text{K}}$, eV	$\varphi_{2000^\circ\text{K}}$, eV
ZrC _{0,97} (hot-pressed)	4,6952 \pm 0,0001	4,28	4,43	3,95
ZrC+0,5% Y	4,6956 \pm 0,0001	5,32	4,12	3,87
ZrC+1,0% Y	4,6965 \pm 0,0002	5,60	4,56	3,70
Zr+C+Y (~2% YC)	4,6966 \pm 0,0001	5,42	4,56	3,70

$$\varphi_t = 4.52 - 2.8 \cdot 10^{-4} T \text{ [eV]}$$

for zirconium carbide produced by hot pressing. It will be seen that the two varieties of zirconium carbide have similar values of φ_t . At $T = 1800^\circ\text{K}$, for example, $\varphi_t = 4.05$ eV for deposited zirconium carbide and $\varphi_t = 4.02$ eV for hot-pressed zirconium carbide. In the case of titanium carbide, it is impossible (within the limits of measurement accuracy) to detect any difference between the two types of specimen, and the temperature dependence of their work function is approximated by the expression

$$\varphi_t = 4.28 - 2 \cdot 10^{-4} T \text{ [eV]}.$$

The value of effective work function found in this investigation for ZrC is larger than that cited in [7] for pyrolytic zirconium carbide deposited on a tungsten core, probably as a result of the use of different temperature conditions in the treatment of specimens before measurements.

To study the effects of alloying additions upon the thermionic emission characteristics of zirconium carbide, measurements were made of the electron work functions of zirconium carbide specimens containing various amounts of yttrium. Specimens were produced by sintering mixed powders of zirconium carbide (containing 88.15% Zr, 11.53% total C, 0.5% free C, and 0.3% nitrogen) and metallic yttrium (prepared by grinding yttrium shavings in an agate mortar at the liquid nitrogen temperature). The presintering of the alloys was performed for 4 h at a temperature of 1800°C in a vacuum, at a residual pressure of no more than $5 \cdot 10^{-5}$ torr (the rate of a temperature rise was 300°C/h). The presintered alloys were ground to powder (of 10- to $20\text{-}\mu$ particle size), from which cylindrical specimens were prepared by pressing and sintering for 1 h at a temperature of $2100\text{--}2200^\circ\text{C}$ (the rate of temperature rise being 500°C/h) and a residual pressure of $5 \cdot 10^{-5}$ torr. Yttrium was added to the zirconium carbide in amounts of up to 5 wt.%, but emission spectral analysis revealed that the yttrium content of the sintered specimens did not exceed 1.5%. A similar result was obtained in experiments in which alloy specimens were remelted in a nonconsumable-electrode arc furnace provided with a He atmosphere subjected to adsorption purification (under a pressure of 1.5 atm).*

* Melting was performed by V. V. Smirnov at the I. A. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR.

Thus, in contrast to the fairly wide range of homogeneity of the solid solution in the system $\text{TiC}-\text{ScCx}$ [8], the solubility of yttrium in zirconium carbide is very small, which may be due to the fact that the difference between the atomic radii of Zr and Y is greater than that between the atomic radii of Ti and Sc. In addition to the $\text{ZrC} + \text{Y}$ alloys, a $\text{Zr} + \text{C} + \text{Y}$ alloy was prepared (under the same process conditions) by direct synthesis from the elements, which were taken in amounts calculated to give a $\text{ZrC} + 2\% \text{ YC}$ solid solution. According to data yielded by x-ray phase analyses, only one phase - zirconium monocarbide - was present in all the specimens examined. In diffraction pictures obtained with the aid of a DRON-1 diffractometer (copper radiation), the relevant lines showed a good resolution of the $K_{\alpha_1}-K_{\alpha_2}$ doublet.* Excess yttrium had apparently been removed by evaporation during sintering or melting. The lattice constants of the zirconium carbide alloys investigated are given in Table 2. In alloys prepared from charges containing more than 2% Y, metallographic examinations revealed the presence of a small amount of a gray phase, probably yttrium oxide.

Electron work function measurements were made, in a vacuum of not less than $1 \cdot 10^{-8}$ torr, by both the TE method and Anderson's variant of the contact potential difference (CPD) method [9]. The results of these measurements are presented in Table 2. It will be seen that the values of φ_{CPD} differ from those of φ_{TE} . The reason for this is that different heat treatments, resulting in different surface layer compositions, were applied to the specimens in these two methods: In the CPD method, the specimens were held at a temperature of not more than 1200°K, whereas in the thermionic emission method a much higher temperature ($\sim 2000^\circ\text{K}$) was employed. Heating at such a high temperature may lead to the appearance of an yttrium film on the surface of a zirconium carbide alloy and decrease the latter's work function. An indirect confirmation of this is provided by the fall in φ_{TE} exhibited by high-yttrium alloys at high temperature (see Table 2).

The marked increase in φ_{CPD} brought about by the addition of yttrium to zirconium carbide might perhaps be regarded as surprising, since the work functions of both metallic yttrium and yttrium oxide (if one assumes their presence on the alloy surface) are much less than the work function of ZrC [2, 10]. However, this result can readily be explained by assuming that yttrium occurs on the alloy surface only as a substitutional solid solution in the metallic sublattice of the carbide.

In an investigation of the composition of specimens made with a Kwiescan electron microprobe fitted with an Edax attachments,† spectrograms of the alloys were found to exhibit two peaks corresponding to the L_{α} lines of Zr and Y. However, the positions of these lines did not coincide with those of the L_{α} lines of metallic Zr and Y, indicating that the yttrium in such an alloy is in a combined state. Replacement of some of the zirconium atoms by yttrium, which has a lower statistical weight of atoms with the stable configurations (SWASC) d^5 compared with zirconium and hence a higher donor capacity [1, 11], leads to a stabilization of the electronic configuration d^5 and sp^3 , respectively, in the atomic spheres of both the zirconium and carbon (the effect is particularly marked in the latter). This is confirmed by the fact that spectrograms of alloy specimens show a long-wave shift of the L_{α} line of Y and a small short-wave shift of the L_{α} line of Zr. Such an increase in the SWASC sp^3 , whether caused by a change in the stoichiometry of a carbide [5] or by alloying additions, leads to a decrease in the total energy of the valence electrons in the carbide and hence to a growth in φ .

As a result of this investigation, it has been established that alloys of the system $\text{Zr}-\text{C}-\text{Y}$ exhibit different mechanisms of electron emission in different temperature ranges. Heat treatment at high temperatures may lead to the appearance on the alloy surface of fairly large areas of metallic yttrium which reduce the value of work function. In those cases where the energy of the chemical bond between the carbon and metal atoms is increased (as a result of a change in stoichiometry or an alloying addition), the formation of such a surface metal film is hindered. During heat treatment at moderate temperatures (up to $\sim 1200^\circ\text{K}$), no surface metal film is formed, and the value of work function recorded is a characteristic of the alloy itself.

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