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STUDY OF CHEMICAL COMPOSITION AND ELECTRONIC STRUCTURE OF HIGH-MELTING COMPOUNDS OF ZIRCONIUM BY ELECTRONIC AES

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Résumé - Les changements de composition et de structure électronique des couches superficielles de carbures ZrC_x et des nitrures ZrN_y dans les domaines d'existence ($0,51 < x \leq 1,0$, $0,76 \leq y \leq 1,0$), produits par chauffage sous bombardement électronique dans une gamme de températures de $300\text{ K} \leq T_h \leq 2300\text{ K}$ sont étudiés par spectrométrie d'électrons Auger.

Abstract - Changes in chemical composition and electronic structure of surface layers of ZrC_x and ZrN_y in areas of homogeneity ($0.51 < x \leq 1.0$, $0.76 \leq y \leq 1.0$) under the action of sample heating by electron bombardment within the temperature range $300\text{ K} \leq T_h \leq 2300\text{ K}$ have been studied using layer-by-layer analysis of sample surface by AES.

Till now study of zirconium nitrides and carbides have been performed in the main using X-ray methods which do not permit to obtain information about composition and electronic structure of surface layers of these materials. Not numerous papers on investigation of zirconium carbide using AES [1,2] gave authors the possibility to carry out semiquantitative analysis of surface elemental composition of stoichiometric ZrC and its change in the course of interaction with oxygen and oxygen-bearing gases. Information obtained from non-differentiated Auger-spectra may be used only indirectly for analysis of chemical state of surface atoms because these spectra are low sensitive to the change of fine structure of Auger-lines comprising valence band. There are available very few papers on study of non-stoichiometric carbides and nitrides of Zr using AES.

We performed analysis of samples of carbide ZrC_x and nitride ZrN_y in areas of homogeneity ($0.51 < x \leq 1.0$ and $0.76 \leq y \leq 1.0$) using AES method in a mode of differentiated Auger-spectra within the temperature range from 300 up to 2300 K when heating samples by electron bombardment in a vacuum of 10^{-9} torr.

Analysis of samples was performed for lines of MNN-series of Zr and KLL-series of C, N and O. Fig. 1 shows Auger-spectra of polycrystalline stoichiometric samples of $Zr_{1.0}$ and $ZrN_{1.0}$ cleaned with heating up to $T_h = 2300\text{ K}$ (curves 1 and 4) as well as spectra of these samples which were after cleaning during 13 hrs in a vacuum chamber under the pressure of residual gases $p = 10^{-5}$ torr (curves 2 and 5). Curve 3 corresponds to $ZrC_{1.0}$ sample heated up to $T_h = 1100\text{ K}$ at $p = 10^{-5}$ torr. $M_{5N_{23}}N_{45}$ -line which is a single line in pure metallic Zr is splitted in both compounds into two lines, splitting value ΔE_{45} being 3 eV

for carbide and 5 eV for nitride. Surfaces of ZrC and ZrN after interaction with residual gases gave similar spectra (curves 3 and 5) differing from spectra of pure samples by even larger splitting value $\Delta E_{45} = 7 \text{ eV}$.

Fig. 1 - Auger-spectra of $\text{ZrC}_{1.0}$ and $\text{ZrN}_{1.0}$. 1, 4 correspond to $\text{ZrC}_{1.0}$ and $\text{ZrN}_{1.0}$, respectively after heating up to 1000 K and the following ion bombardment; 2, 5 correspond to $\text{ZrC}_{1.0}$ and $\text{ZrN}_{1.0}$ after 13 hrs of stay at $p = 10^{-5}$ torr; 3 corresponds to $\text{ZrC}_{1.0}$ after heating up to $T_h = 1100 \text{ K}$ at $p = 10^{-5}$ torr during 10 min.

Fig. 4 - Profiles of Auger-line intensities distribution in depth of ZrN_y samples. a) $Y = 1.0$; b) $Y = 0.85$; c) $Y = 0.76$. The following lines are taken for the elements: Zr - 92 eV, Ar - 215 eV, C - 272 eV, N - 381 eV, O - 509 eV.

There is also observed difference in energetic position of other lines of MNN-series of Zr and shift towards the lower kinetic energies of electrons is increased with the increase of electronegativity of metalloid atoms in ZrX_y ($X = \text{C}, \text{N}, \text{O}$). In samples of non-stoichiometric carbides and nitrides a value of ΔE_{45} does not change in practice with the change of concentration of metalloid structural vacancies in crystal lattice. At the same time the redistribution of peak intensities in metal doublet takes place. In Fig. 2 there are shown spectra of ZrC_x samples with the surface cleaned by ion bombardment. Nearing the lower boundary of the homogeneity area of carbide a height of long-wave peak is reduced as compared with a height of short-wave one. The situation is similar for ZrN_y samples.

Note, that KL_1L_{23} -line of metalloid in compounds under study is also splitted and splitting value is close to a value of ΔE_{45} in corresponding $\text{M}_5\text{N}_{23}\text{N}_{45}$ - spectrum of Zr.

Successive heating of samples from room temperature up to 2300 K shows that after cleaning the surface from contaminations and oxygen (at $T_h = 1200 \text{ K}$ for ZrN_y and 1600 K for ZrC_x) there are no changes

of energetic position of spectrum lines. There is observed, however, a change in shape of MNN-series lines of Zr as well as a change of relation between line intensities connected with the loss of metalloid atoms in surface layers. In Fig. 3 there are shown Auger-spectra of ZrC_x heated up to $T_h = 1800$ K. Comparing Fig. 2 and Fig. 3 one can see a change of relation between short- and long-wave peaks after the heating and this change is the highest for $ZrC_{0.6}$ sample.

Fig. 2 - Spectra of ZrC_x samples subjected to ionic bombardment. 1 - $X=1.0$, 2 - $X=0.8$, 3 - $X=0.7$, 4 - $X=0.6$; a) - survey spectra, δ) - MNN-series of Zr. Fig. 3 - Spectra of ZrC_x samples heated up to $T_h = 1800$ K. 1 - $X=1.0$, 2 - $X=0.8$, 3 - $X=0.7$, 4 - $X=0.6$; a) - survey spectra, δ) - MNN-series of Zr.

Layer-by-layer analysis of ZrX_y samples shows that the area of changed composition (relative to the volume one) near the surface is of 50 Å and it is the wider the more is the concentration of metalloid vacancies in a sample volume. For nitride this area is approximately twice as wide as for carbide. As illustration in Fig. 4 there are shown intensity profiles of Auger-lines of ZrN_y samples of various composition. Distribution profiles of O, Ar and Zr for ZrC_x samples change in a similar way. Behaviour of distribution profile of the main metalloid in ZrX_y samples is identical.

The splitting of $M_5N_{23}N_{45}$ - line of Zr in compounds under study is apparently connected with the splitting of d-band of Zr in states with the different symmetry of wave functions which according to calculation data [3] should be observed in analyzed metal-like compounds. At the same time according to calculation data for stoichiometric $ZrC_{1.0}$ and $ZrN_{1.0}$ the densities of d_γ -states in occupied part of valence band are considerably higher than densities of d_δ -states near Fermi level. There are always a lot of open bonds on a surface resulting in redistribution of densities of d_γ - and d_δ -states which may be a reason of equalization of Auger-peak heights of $M_5N_{23}N_{45}$ -doublet of Zr as compared with the expected from theory high difference of heights.

The splitting of KL_1L_{23} -line of non-metal is also in good agreement with data of known calculations /3/ where occupied 2p-states of non-metal are splitted. Unvariability of doublet shape in KLL-spectrum of metalloid is apparently connected with unvariability of nearest environment of X atoms by metal atoms (octahedron $\langle Me_6X \rangle$ is always completed).

Intensity decrease of long-wave peak connected with Me-Me interaction is bound up with transition of a part of d_{γ} -electrons of metal to d_{ε} -states in breaking of Me-X bonds. Such an explanation for a shape change of $M_5N_{23}N_{45}$ -doublet of Zr is not contradictory to results of calculation of density histograms of d-states for nitride of isoelectronic analogue of Zr - TiN /4/. The calculation was performed taking into account non-completeness of TiN_6 octahedron for nitrogen.

Known at present data on work function φ of cathodes of ZrX_y compounds are in good agreement with the data obtained in the present study on the surface composition change. So decrease of φ with increase of temperature takes place due to the loss of metalloid atoms by a surface in case of non-congruent vaporization.

Thus the performed studies show that electronic Auger-spectra of surface contain valuable information about features of valence band structure in surface layers of analyzed compounds of ZrX_y type. The most interesting as we feel is the fact that the shape of Auger-spectra comprising valence band may be used for evaluation of chemical bond type of surface atoms as well as for determination of metalloid concentration in homogeneous implantation phases of variable composition.

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