The authors express their gratitude to V. G. Bessergenev and S. A. Gromilov for providing and testing the samples and T. I. Guzhavina for assistance in treatment of the experimental results.

LITERATURE CITED


ELECTRONIC STRUCTURE AND CHEMICAL BONDING IN
NONSTOICHIOMETRIC ZIRCONIUM NITRIDES

D. L. Novikov, Yu. M. Yarmoshenko,
A. L. Ivanovskii, and V. A. Gubanov

X-ray emission spectra were taken and band calculations using the Green function LMTO method and cluster calculations using the discrete variational Xo method were carried out for the electronic structure and chemical bonding parameters for nonstoichiometric zirconium nitrides containing metallic and metalloid vacancies. The existence of structural defects leads to a redistribution of the occupancies of the major sub-bands of the nitride valence spectrum and the formation of a new group of states between the p--d- and d-like bands of ZrN1.0.

Zirconium nitride belongs to an extensive class of refractory compounds with extended homogeneity regions. However, in contrast to most cubic carbides and nitrides of d and f metals, which usually have lattice vacancies only in the nonmetallic sublattice [1], zirconium nitride with B1 structure may have both anionic and cationic defects.

In the present work, we studied the effect of metalloid and metallic vacancies on the electronic structure and interatomic distances in ZrN using x-ray emission spectroscopy and quantum chemical calculations.

The Zr Lβ3,15 spectra (2p → 4d transition) were obtained on a FRSKD-2 spectrometer [2]. Quartz (10 10 plane, R = 1.5 m) was used as the analyzer crystal. The spectra were accumulated up to an intensity of about 2000 pulses over 3 h. We studied the spectra of three monophasic and isostructural (B1 type) samples with unit cell parameters: a = 4.589 Å (ZrN1.0), a = 4.595 Å (ZrN1-x), and a = 4.596 Å (Zr1-xN), where x ~ 0.10.

Self-consistent nonempirical calculations were carried out with the Green function LMTO method [3] for the band structure of ideal ZrN1.0 and also for zirconium nitrides containing isolated N and Zr vacancies. The rearrangement of the individual interaction types upon the introduction of an anionic defect into the ZrN bulk was examined in greater detail in the framework of the fragment model. The complete nitride is described by an [NZr6N18] cluster, while the nitride containing an N vacancy (●), is described by the [Zr6N18] group. The calculations were carried out by the nonempirical Xα discrete variational method in a basis of numerical atomic orbitals (AO) with self-consistency relative to charge and metal atom configurations and renormalization of the nitrogen atom charges in each


766 0022-4766/89/3005-0766$12.50 ©1990 Plenum Publishing Corporation
Fig. 1. Total state density for ZrN$_{2p}$ (broken line) and energy distributions of the "vacancy" states for single N and Zr defects. The LSD are given below for the nitrogen and zirconium atoms in the complete nitride (solid line) and near the crystal defect (dashed line).

iteration cycle [4]. The boundary conditions were taken into account by the introduction of a 98–atom pseudocrystal [5]. The vacancy was simulated by replacement of the central nitrogen atom by a pseudoatom with effective $s,p$ wave functions localized in a radius of ~1 Å about the center of the defect with a starting occupancy of 0.003 e. The cluster charges were determined using the formal valence of the component atoms and condition of electroneutrality for the crystal [6].

The band structure of defectless ZrN (GF–LMTO calculation) is shown in Fig. 1. In accord with previous calculations [6], it contains a subvalence band for the N 2s states with slight additions of the Zr $s,p$, and $d$ orbitals (not given in Fig. 1), separated by forbidden gap (~0.36 Ry) from the major valence band. In turn, the major valence band is composed of two bands formed by hybridized N 2$p$, Zr 4$d$, Zr 4$s$, and metallic 4$d$, 4$s$, and 4$p$ functions, separated by a deep state density (SD) minimum. The Fermi level is located in the lower part of the metallic band.

Figure 1 also gives the local state densities (LSD) for single N and Zr vacancies. The LSD of the nitrogen defect has a single $s$-type maximum located near the bottom of a $d,s,p$-like band. The LSD of the cationic vacancy contains two maxima, the lower of which corresponds in general to the SD profile of the $p–d$ band, while the other is a strong resonance in the vicinity of the upper edge of the hybrid band.

The nature of the formation of these "vacancy" states, which reflect the extent of the sphere of the defect of the electronic states coordinating its atoms, may be established by analyzing the perturbation effect of the defect on the SD of an ideal crystal $(\delta n(E))$, which is calculated in the framework of the model employed [3] as

$$\delta n(E) \sim \frac{1}{4\pi} \text{Im} \left\{ \sum_L \frac{p_{ql} - p_{0ql}}{1 + (p_{ql} - p_{0ql}) T_{0LL}^{pq} + T_{0LL}^{pq} + T_{0LL}^{pq}} \right\},$$

where $\dot{T}_{0}$ is the derivative of the $T$ matrix of the defectless system relative to energy, and $p$ and $\dot{p}$ are the potential parameter and its derivative relative to energy [3, 6]. Then, assuming that the perturbation effect of a vacancy is reflected only in the states of its first coordination sphere (which appears quite justified for ZrN, which belongs to the group of refractory phases, the chemical bond system in which is composed mainly of close-lying metal—metalloid covalent interactions [6]), we may evaluate the change in the SD of the Zr and N atoms near the vacancy $(n'(E))$ by the following expression

$$n'_{Zr,N}(E) \sim n_{Zr,N}(E) + \frac{1}{Q} \delta n(E),$$