Physics

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1961

SovietRxiv

Abstract

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Physics

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FINE STRUCTURE OF THE X-RAY K-ABSORPTION SPECTRA OF TITANIUM IN COMPLEX SOLID SOLUTIONS OF THE TiC–TiN SYSTEM

(Presented by Academician A. P. Vinogradov on May 6, 1961)

The study of the properties of refractory compounds of transition metals and of the connection between practically the most important of these properties—hardness, heat resistance, and chemical stability—and the electronic structure of the substance and the character of the interatomic interaction in it is at present attracting the attention of an ever wider circle of investigators ([1,2]).

It is being carried out with the aid of the most diverse modern methods of physical and physicochemical investigation of matter. Particularly detailed and comprehensive study in recent years has been devoted to the carbides and nitrides of transition metals (and, in particular, of titanium), for which numerous and systematic data have been obtained on their electrical, magnetic, and mechanical characteristics ([3–6]), and interesting theoretical calculations have also been performed ([7]). Recently, the results were published of an x-ray spectroscopic investigation of titanium carbides and nitrides ([8–12]) over a wide range of variation of their composition within the homogeneity region. These results made it possible to reveal certain differences in the structure of the x-ray spectra of the transition metal in these two closely related classes of compounds and to bring them into correspondence with the features of the electronic structure and properties of carbides and nitrides. For further deepening and broadening these investigations, it seemed advisable to turn to the study of the x-ray spectra of titanium in the TiC–TiN system, which forms a continuous series of solid solutions.

The investigation was carried out on alloy specimens kindly placed at our disposal by G. V. Samsonov, who, together with his collaborators, had recently ([6]) used them to study various electrical properties of alloys of the TiC–TiN system (specific electrical resistivity, Hall constant, thermoelectric-power coefficient, and thermal coefficient of resistance) and to calculate the effective concentration and mobility of current carriers. Many other physical characteristics of carbonitrides are now known from the work of other investigators ([1,13–16]).

The method of obtaining the carbonitrides is described in (6). The alloy specimens studied in our work were cut by the electrospark method from the core of blanks sintered by hot pressing; the charge of these blanks, consisting of a mixture of TiC and TiN, contained, respectively, 25, 33, 50, 67, and 75% of one of the components. In addition to the binary alloys, the original TiC and TiN preparations of stoichiometric composition were again studied. To establish the phase composition of the alloys, they were subjected to x-ray structural phase analysis, which in all cases showed the presence of only one phase with a lattice of the NaCl type and with parameters in good agreement with literature data (17). The elemental composition of the preparations was checked by chemical analysis. In some carbonitrides small amounts of free carbon were found, which, however, is not,

as is known (10), is an obstacle to carrying out X-ray spectral investigations.

The titanium K-absorption edge was recorded photographically in the first order of reflection on a vacuum X-ray tube spectrograph with focusing by the Johann method (18). The analyzer was a bent quartz crystal with reflecting plane $(10\bar{1}1)$. The radius of curvature of the crystal in a series of parallel experiments was 2600 and 1650 mm. The accuracy of determining the energy of the X-ray photons was 0.3 eV. The optimum absorber density, established experimentally, was 4.5 —5 mg/cm^2 for all alloys of the TiC—TiN system.

In Fig. 1 are presented the K-absorption edges of titanium in the carbide, nitride, and five intermediate carbonitrides, averaged over three independent spectrograms. The points indicate the course of the theoretical curves obtained from the formula

$$\mu(\lambda) = \mu_1(\lambda)x + \mu_2(\lambda)(100 - x),$$

in which μ_1 and μ_2 are the absorption coefficients of titanium, respectively, in TiC and TiN, and x is the percentage content of one of the phases in the complex solid solution.

Consideration of the experimental results permits the following conclusions to be drawn.

1. As the relative concentration of one of the components of the complex solid solution in the TiC—TiN system increases, there is a gradual change in the structure of the X-ray absorption spectrum of the transition metal. At the same time, the fine structure of the spectrum observed experimentally agrees well with the theoretical one, obtained under the assumption of a gradual change in the nearest octahedral environment of the metal atom in the complex solid solutions and of the statistical replacement of one metalloid by another in passing from the simplest nitrides to carbides. Such a process, as is known, is accompanied only by a slight (of the order of 3%) change in the lattice constant of the compound and by a monotonic decrease in the concentration of current carriers (6). Consideration of the

Figure 1

Figure 1: Figure 1

structure of the main absorption edge of titanium in the alloys studied and of the course of its change as a function of the concentration of the metalloids again confirms the conclusions we made earlier about the small degree of filling (10,12) of the $3d$-band of the metal in carbides and nitrides and the insignificant role played in these compounds by donor-acceptor interaction of the titanium $3d$-electrons with the valence electrons of the metalloids. The degree of filling of the $3d$-band of the transition metal and the character of its interaction with the corresponding metalloid atoms in the complex solid solutions studied and in the original simplest phases do not undergo, as is evident from consideration of the X-ray spectra, any substantial changes. This conclusion is in good agreement with the conclusions (6) following from an analysis of the electrical properties of alloys of the TiN—TiC system and indicating that they, like the properties of titanium carbide and nitride, are determined mainly by the behavior of the $4s$-electro-

Fig. 1. X-ray K-absorption spectra of titanium in a series of alloys of the TiN —TiC system. Points indicate the course of the theoretical absorption curves. 1 —TiC; 2 —75% TiC + 25% TiN; 3—66.6% TiC + 33.4% TiN; 4 —50% TiC + 50% TiN; 5 —33.3% TiC + 66.7% TiN; 6 —25% TiC + 75% TiN; 7 —TiN.

titanium and the valence electrons of the corresponding metalloids and are only to a very small extent connected with the hole contribution of the $3d$-band. Analysis of the data on the Hall coefficient (6), the thermoelectric-power coefficient (6), and the change in magnetic susceptibility of the group of alloys under consideration (14, 15) also leads to analogous conclusions concerning the role of the $4s$-electrons and the degree of participation of the $3d$-band in these processes.

2. Along with the gradual change in the structure of the main absorption edge, a regular change in the far fine structure is also observed in the series of carbonitrides studied. These changes, as well as the changes in the long-wavelength structure of the edge, are monotonic in character and are expressed chiefly in a change in the amplitude of successive fluctuations of the absorption coefficient. The positions of the extrema of the far fine structure, which are very close to one another in the titanium spectrum in the carbide and in the nitride, are preserved, within the accuracy of the measurements, also in carbonitrides of different composition. However, as the relative carbon content in the sphere of the nearest environment of titanium in the compound increases, the sharpness of the fine structure increases. In accordance with modern concepts (19), this seems entirely regular and may be connected with a gradual change in the scattering power of the metalloid atoms forming the first coordination sphere around

the absorbing titanium atoms.

The degree of agreement of the additive theoretical absorption curves with those observed experimentally may be considered quite satisfactory, which indicates the statistical character of the substitution of atoms of one metalloid by the other in the transition from the pure carbide to the nitride.

The authors express their gratitude to Corresponding Member of the Academy of Sciences of the Ukrainian SSR G. V. Samsonov for providing the carbonitrides studied and for his attention to the work.

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Received
28 IV 1961

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