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Abstract

Full Text

PHYSICS

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FINE STRUCTURE OF THE X-RAY K -ABSORPTION SPECTRA OF TITANIUM IN CARBIDES

(Presented by Academician A. P. Vinogradov, May 19, 1958)

A systematic x-ray spectroscopic investigation of carbides and certain other interstitial phases was begun comparatively recently (¹⁻³). These investigations aim at obtaining new experimental material that may shed light on a number of as yet unresolved questions concerning the nature of the forces of chemical bonding and the state of the atoms of transition elements in these compounds. In the work carried out so far, the fine structure of the titanium x-ray K -emission spectrum (^{1,2}) and the molybdenum L -absorption spectra (³) in carbides and a number of other compounds have been studied.

The present work supplements these investigations with data relating to the titanium K -absorption spectra in alloys of the Ti–C system with carbon contents from 12 to 24 wt. %. The method of preparing the alloys and data on their chemical composition have already been given (²). The work was carried out on a focusing x-ray tube spectrograph, the design of which was described earlier (⁴). The radius of curvature of the bent quartz crystal was 260 cm. Reflecting planes: (10 $\bar{1}$ 1). The linear dispersion of the spectrograph was 2.5 X/mm. The spectra were recorded photographically. In determining the wavelengths of individual points of the titanium absorption edge in the compounds, the L_{α_1} Au and K_{α_1} As lines in the second order of reflection were used as comparison lines. The accuracy of the energy determination was ~ 0.2 eV. As was established in a series of preliminary experiments, the optimum absorber density is ~ 5 mg/cm²; it was kept constant for all carbides studied.

The titanium absorption spectra in carbides with different carbon contents, averaged over 6 independent measurements, are shown in Fig. 1. In the same figure, the positions of the last K_{β_5} and $K_{\beta'}$ emission lines (hatched) of titanium in the same alloys are indicated (after (²)), as well as the position and shape of the long-wavelength absorption band (dashed line), identified—

Fig. 1. X-ray K -absorption spectra and K_{β_5} emission lines (hatched) of titanium in carbides with different carbon contents. 1 –24% C; 2 –22% C; 3 –19% C; 4 –16% C; 5 –14% C; 6 –12% C. The dashed line indicates the long-wavelength absorption band.

Figure 1. X-ray K -absorption spectra and K_{β_5} emission lines (hatched) of titanium in carbides with different carbon contents. 1 –24% C; 2 –22% C; 3 –19% C; 4 –16% C; 5 –14% C; 6 –12% C. The dashed line indicates the long-wavelength absorption band.

Figure 1: Figure 1. X-ray K -absorption spectra and K_{β_5} emission lines (hatched) of titanium in carbides with different carbon contents. 1 –24% C; 2 –22% C; 3 –19% C; 4 –16% C; 5 –14% C; 6 –12% C. The dashed line indicates the long-wavelength absorption band.

Fig. 2. Comparison of the X-ray K -absorption spectra of titanium in carbide (1) and dioxide (rutile) (2)

Figure 2: Fig. 2. Comparison of the X-ray K -absorption spectra of titanium in carbide (1) and dioxide (rutile) (2)

...obtained from the experimentally observed absorption edge of titanium in all alloys. This band appears as a result of the transition of the absorbing atom's $1s$ electrons to free $3d$ levels, which partially overlap with the np - and ns -energy levels of titanium atoms in the compounds studied.

Fig. 2. Comparison of the X-ray K -absorption spectra of titanium in carbide (1) and dioxide (rutile) (2)

In Fig. 2 the X-ray absorption spectrum of titanium in carbide is compared with the spectrum of this element in dioxide (rutile).

As can be seen, the fine structure of the titanium absorption spectra in carbides, over the entire range of variation of the carbon concentration in which there exists a single-phase region with a face-centered cubic lattice of metal atoms, remains unchanged. The same applies to the position and shape of the long-wavelength band in the titanium absorption spectrum in the group of alloys studied. Comparison of these spectra with the absorption spectrum of titanium and its dioxide makes it possible to state the constancy of the energy corresponding to the maximum of the long-wavelength absorption band in the spectra of the metal atom in the alloys and dioxide*. This is in good agreement with what was found in previous investigations (¹⁻³), and is a new confirmation that the results of X-ray spectroscopic studies cannot be reconciled with the hypothesis (⁷) according to which, in the formation of carbides of transition elements, a "metallization" of the bond takes place, expressed in the partial filling of the $3d$ -energy levels of the atoms of the transition elements.

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* The splitting of this band observed in the titanium absorption spectra in rutile is connected with the symmetry of the field of the nearest environment of the metal atom in the compound ⁽⁵⁾ and is not observed, for example, in the titanium spectrum in anatase ⁽⁶⁾.

Note: Figure translations are in progress. See original paper for figures.

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