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## Abstract

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# On Certain Features of the Structure of the X-ray Emission Spectrum of Titanium in Carbonitrides

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Several years ago a new hypothesis was put forward concerning the nature of the $K_{\beta''}$-satellite in the emission spectrum of atoms in compounds ([1]). It was assumed that the $K_{\beta''}$-satellite arises as the result of a cross transition of electrons from the valence energy levels of the anion to the levels of the metal ion being vacated as a result of $K$-ionization of the 1s level of the absorbing metal ion. Therefore, it could be expected that the intensity and energy position of the $K_{\beta''}$-satellite should depend not only on the properties of the atom that has undergone $K$-ionization, but also on the properties of its partners in the compound, and should be very sensitive to changes in the character and strength of the interatomic interaction in the substances studied. This assumption immediately made it possible to explain a number of observations relating to the properties of this satellite in compounds and, in particular, the dependence of its intensity on the valence of the absorbing atom and its absence in the spectrum of the metal ([2]). Subsequently, the validity of the assumption made was tested in a series of specially designed experiments. First, using examples of titanium emission spectra in oxides, carbides, nitrides, and hydrides, the dependence ([3]) of the intensity of the $K_{\beta''}$-satellite on the nature of the metalloid in these compounds was shown. As was to be expected, the intensity of this line decreased regularly in the indicated series of compounds in going from oxide to hydride. In other experiments, a dependence was established of the intensity of the $K_{\beta''}$-satellite on the valence state of the absorbing atom in the compound ([4,5]). Later ([6]) it was also possible to show that the nature of the anion has a substantial influence on the energy position of the maximum of the $K_{\beta''}$-satellite observed in the titanium emission spectrum in various compounds. It turned out that the distance between the maxima of the $K_{\beta''}$ and $K_{\beta_5}$ emission bands in the titanium spectrum in various compounds is regularly related to the difference between the electronegativities of the anion and cation and, moreover, that this dependence is, to a first approximation, linear. If in titanium carbide, for example, the distance $K_{\beta_5} - K_{\beta''}$ is equal to 7 eV*, then in the nitride it becomes close to 11 eV, and in the dioxide it reaches a value close to 15 eV. This makes it possible to carry out still another experimental test of the validity of the hypothesis on the origin of the $K_{\beta''}$-satellite by studying the X-ray emission spectra of titanium in carbonitrides, which form a continuous series of solid solutions and in which, as follows from an analysis of electrophysical ([9]) and X-ray structural ([10]) data, in going from the simplest nitrides to carbides one may expect a statistical replacement of one metalloid by another.

If the assumptions about the nature of the $K_{\beta''}$-satellite are correct, then in the titanium emission spectrum in carbonitrides one should expect the appearance of not one, of two lines, in accordance with the two kinds of metalloid atoms forming the nearest environment of the titanium atoms in these compounds. At the same time, the study of the emission spectrum of titanium in these compounds and the determination of the degree of correspondence between the observed fine structure and that which might be expected if the additive scheme were valid also have independent significance, since in principle they may make it possible to refine and supplement the information on the nature of the interatomic interaction in these compounds that was obtained in earlier works on the basis of an analysis of electrophysical and magnetic data ([9,11]), as well as of the fine structure of the titanium X-ray $K$-absorption spectra ([12]).

**Table 1**

Relative position $\Delta V$ and width $a$ of the emission bands of the X-ray spectrum of titanium in carbonitrides*

| Sample No. | $C/(C+N)$, % | $K_{\beta_5}$: $\Delta V$, eV | $K_{\beta_5}$: $a$, eV | $K_{\beta''_1}$: $\Delta V$, eV | $K_{\beta''_2}$: $\Delta V$, eV |
|---:|---:|---:|---:|---:|---:|
| 1 | 0 | −2.5 | 4.0 | – | −13.0 |
| 2 | 22 | −2.0 | 4.5 | −8.6 | −12.3 |
| 3 | 26 | −1.4 | 4.4 | −7.8 | −12.5 |
| 4 | 35 | −1.5 | 4.3 | −7.6 | −12.3 |
| 5 | 43 | −0.9 | 4.5 | −7.2 | −12.8 |
| 6 | 100 | 0.0 | 3.7 | −6.8 | – |

* The energy of the maximum of the Ti $K_{\beta_5}$-band in TiC was conventionally taken as the zero of the energy scale.

Powdered carbide, nitride of stoichiometric composition, and carbonitrides* were investigated. The percentage content of carbon atoms among the metalloids in the carbonitrides, $C/(C+N)$, varied from 22 to 43%. Outside this range of carbonitride compositions, observation of all details of the fine structure in the titanium emission spectra proves difficult and cannot be carried out with adequate accuracy.

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* In work ([7]), in which the X-ray emission spectrum of titanium in carbides of various composition was first studied, 7.9 eV was printed. It should read 6.9 eV. (Corrected in a subsequent work ([8]).)

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

The X-ray emission spectra of titanium in all the substances studied were obtained under identical conditions on a DRS-2 spectrograph, using the primary excitation method in the second order of reflection from the $(10\bar{1}0)$ plane of a quartz crystal. The linear dispersion of the instrument in the selected spectral region was $-6.9$ Å/mm. The resolving power of the spectrograph was $\sim 6000$. The anode of the X-ray tube was aluminum. The operating conditions of the X-ray tube were 20 kV and 8 mA. The exposure was 30–50 min. The spectra were recorded photographically. For each compound, 3–5 spectrograms were obtained.

As comparison lines for determining the energy of individual points of the spectrum, the nickel $K_{\alpha_1}$ line in the third order and the titanium $K_{\beta_1}$ line in the second order were used; the constancy of the energy position of the latter in the group of compounds studied was checked specially in a series of preliminary experiments. To prevent overexposure of the $K_{\beta_1}$-line when studying the weaker $K_{\beta_5}$- and $K_{\beta''}$-emission bands in the titanium spectrum in the compounds, its intensity at the maximum was reduced by means of a specially selected aluminum absorber.

The spectra were recorded on a photographic plate with an MF-4 microphotometer. The recording speed was 6 mm/min with a slit width of 0.3 mm. The scale of the photometric curves on the plate was 0.5 eV/mm. Energies were measured from the maximum of the titanium $K_{\beta_1}$-line. In view of the small energy distance between the comparison lines (53.6 eV), the energy scale was taken to be uniform. The accuracy of the energy determination was 0.2 eV.

The spectra were averaged over three independent spectrograms, microphotometered in two sections along the height of the line. Conversion of the curves recorded on the microphotometer to the "intensity—electron-volts" scale was carried out immediately by superposing on the recorded microphotogram a nomographic grid specially prepared for this type of photographic material. The experimental data obtained are presented graphically in Fig. 1. The measurement results are given in Table 1. Consideration of these data makes it possible to draw the following conclusions.

* Obtained and analyzed at the Institute of Cermets and Special Alloys, Academy of Sciences of the Ukrainian SSR.

In accordance with the initial assumptions, in carbonitrides there is a complication of the X-ray emission spectrum of the metal atom and the appearance of two $K_{\beta''}$-bands ($K_{\beta''_1}$ and $K_{\beta''_2}$) instead of one, observed in the spectrum of titanium in binary compounds. This is yet another confirmation of the validity of the hypothesis we have put forward concerning the origin of this band.

Figure 3

Figure 2: Figure 3

**Fig. 1.** Lines of the $K_\beta$-group of the X-ray spectrum of titanium in carbide, nitride, and carbonitrides with different carbon contents. *a*—experimental microphotometric curves (recorded on photographic plates); *b*—the same curves after removal of the background from the $K_{\beta_1}$-line (marked by a dashed line in Fig. *a*) and conversion to intensity. $\dfrac{C}{C+N}$ in %:
1—0; 2—22; 3—26; 4—35; 5—43; 6—100

**Fig. 2.** $K_\beta$-bands of titanium emission in carbonitrides of different composition for the case of additivity of the Ti—N and Ti—C bonds (theoretical curves). $\dfrac{C}{C+N}$ in %: 1—40; 2—35; 3—30; 4—25; 5—18; 6—10

The energy position of the maxima of the $K_{\beta''_1}$ and $K_{\beta''_2}$ satellites in carbonitrides is close to the position of the $K_{\beta''}$-bands, respectively, in titanium carbide and nitride, but does not coincide with them. For the first of these lines, as the carbon content in the carbonitride decreases, a systematic long-wavelength shift of the band maximum is observed. In the complex solid solutions studied, the magnitude of the shift of the $K_{\beta''_1}$-band is, to a first approximation, proportional to the specific concentration of carbon atoms in the alloy.

The $K_{\beta''_2}$-emission band behaves somewhat differently. Its position in carbonitrides differs very little from the position of the corresponding line in the spectrum of titanium in nitride. However, this small shift (on average by 0.5 eV) is already manifested in the spectra of alloys with relatively small-

with higher carbon content and practically does not change further with an increase in the value of C/(C + N).

Noticeable changes in the spectra of titanium in carbonitrides of different composition are also undergone by the $K_{\beta_5}$-emission band. In going from titanium carbide to nitride, a gradual long-wavelength shift of the maximum of this band is observed. The width of this line in carbonitrides is somewhat greater than in the spectrum of titanium in carbide and nitride, and is practically independent of the composition of the complex solid solution.

**Fig. 3.** Dependence of the parameters of the X-ray spectrum of titanium in carbonitrides on the composition of the solid solution for the case of additivity of the Ti—N and Ti—C bonds.
1 —relative position of the maximum of the $K_{\beta_5}$-band; 2 —change in the half-width of the $K_{\beta_5}$-band; 3 —relative position of the maximum of the $K'_{\beta_2}$-satellite; 4 —relative position of the maximum of the $K''_{\beta_1}$-satellite.

Attention is drawn to the considerable deviation of the experimentally observed values of the parameters of the emission lines in the spectra of titanium in the carbonitrides studied, and of the form of their dependence on the composition of the alloys, from those which might have been expected in the case of additivity of the Ti—N and Ti—C bonds in the complex solid solutions studied (Figs. 2 and 3). This applies to all the emission bands studied and especially to the $K_{\beta_5}$ and $K_{\beta_1}$ lines.

Thus, despite the statistical nature of the substitution of one metalloid by another, which apparently takes place ([12,13]) in the formation of titanium carbonitrides, in explaining the properties of these compounds it is necessary to take into account the absence of additivity of the bonds of the metal with each of the metalloids. As follows from the analysis of the data obtained in the present study, the influence of carbon is more significant, and it begins to exert a large influence on the form of the X-ray spectrum of the metal in these compounds already when its relative concentration C/(C+N) does not exceed 30%. With increasing specific concentration of carbon atoms in the carbonitrides, the degree of difference of the experimentally observed X-ray emission spectra of titanium from the additive scheme steadily increases.

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