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Abstract

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PHYSICS

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X-RAY EMISSION LINES OF THE TITANIUM $K\beta$-GROUP IN CARBIDES

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The question of the nature of the forces of chemical interaction between atoms of a metal and a metalloid in carbides, nitrides, and hydrides of transition elements is of great interest and over many years has repeatedly attracted the attention of researchers. Nevertheless, it still remains among the insufficiently clarified problems.

Concerning the nature of the chemical bond between atoms in these phases ([1−4]), several hypotheses have been put forward, and experimental data characterizing the magnetic, electrical, crystal-chemical, and certain other properties of the group of substances under consideration have been invoked to substantiate them. Ubbelohde ([4]) subjected this question to detailed thermodynamic consideration. However, until recently there were almost no data on the x-ray spectra of atoms in these compounds and on those changes which they undergo in solid alloys of various composition. The first more or less systematic investigation in this field was carried out only quite recently ([5]).

Despite the fact that some of the results of the investigation ([5]) (relating, for example, to titanium hydride) have the character of a preliminary communication and require refinement on chemically more definite material by the fluorescence method, consideration of the data obtained as a whole leaves no doubt that the energy position and fine structure of the lines in the x-ray spectrum of titanium in the oxide, carbides, nitride, and hydride undergo substantial changes that are amenable to reliable measurement and that, with more precise and systematic investigations, may help to illuminate the question of the nature of the forces of chemical bonding and the state of the metal atoms in these compounds from a new point of view.

Table 1

Sample No.	C_{total}, %	C_{free}, %
1	23.7	3.65
2**	22.1	3.92
3	19.0	0.3
4*	18.8	0.1
5**	15.9	0.06
6	14.3	0.1
7**	12.4	0.04
8	8.8	0.18

Note. Alloy No. 1 was prepared from a mixture of carbide No. 3 and carbon black. Alloys Nos. 6 and 8 were prepared from a mixture of carbide No. 3 and titanium.

* Nitrogen was detected in an amount of $\sim 0.03\%$.
** Oxygen was detected in an amount of $\sim 0.4\%$.

The present work is the first in a series of investigations devoted to the x-ray spectroscopic study of carbides, nitrides, and hydrides of transition metals, which are currently being carried out by a group of workers at the Institute of Geochemistry and Analytical Chemistry of the Academy of Sciences of the USSR and the x-ray laboratory of the K. D. Ushinsky Odessa Pedagogical Institute.

The emission lines of the $K\beta$-group of the x-ray spectrum of titanium were studied in a series of specially prepared* alloys of the Ti–C system with metalloid content from 9 to 24%. The designations and compositions of the alloys studied are given in Table 1.

Most of the alloys were prepared by the generally accepted method from a mixture of TiO_2 and carbon black by calcination at a temperature of 1800–2000° in a hydrogen atmosphere. Three alloys were prepared on the basis of specimen No. 3, whose composition is very close to the composition corresponding to the formula TiC. The prepared alloys, chemically analyzed, were subjected to x-ray structural investigation. The lattice constants of the alloys were compared with literature data ([6]), and the agreement proved to be good.

In the single-phase region a linear increase in the lattice period of the carbides was observed (in the interval from 4.28 to 4.32 Å) as the carbon content in them approached 20%, and constancy of this quantity for alloys with a high metalloid content. Metallic titanium was not detected in the alloys.

The work was carried out on a focusing vacuum spectrograph RSD-2 ([7]) with a bent quartz crystal as analyzer. The radius of curvature of the crystal was 1 m. The reflecting planes were $(10\bar{1}0)$. The crystal, ground according to Johansson ([8]), with dimensions 10×50 mm, was bent in a special crystal holder at four points ([9]).

Fig. 1. Lines of the $K\beta$-group of the x-ray spectrum of titanium in carbide No. 1 with maximum C content and in carbide No. 8 with minimum content.

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The titanium spectra were photographed in the second order of reflection on film placed perpendicular to the direction of the x-ray beam. The linear dispersion of the spectrograph in the spectral region considered was 5.7 X/mm. To determine the position of the $K\beta_1$- and $K\beta_5$-lines in the spectra of titanium, the $K\alpha_{1,2}$-lines of vanadium were used as reference lines. The position of the $K\beta''$-, $K\beta_1'''$- and $K\beta_2'''$-lines was measured relative to the $K\beta_5$ line. The substance under study was placed on the copper anode of a powerful demountable x-ray tube. Tube operating conditions: 12 kV and 55 mA. Each spectrogram was photometered on an MF-2 microphotometer at three points along the height of the line, and the measurement results obtained were averaged. From each alloy no fewer than three spectra were obtained, and the reproducibility of the results proved quite satisfactory.

Figure 1 shows, as an example, two spectra containing the $K\beta_5$-, $K\beta''$-, $K\beta_1'''$-, and $K\beta_2'''$-lines of titanium in alloys with maximum (carbide No. 1) and minimum (carbide No. 3 ([8])) carbon content. The positions of the $K\beta_1$-, $K\beta_5$-, $K\beta''$-, $K\beta_1'''$- and $K\beta_2'''$-lines in the titanium spectra shown in Fig. 1, and in alloys with intermediate carbon content, remain unchanged within the limits of measurement accuracy (± 0.2 eV). Only the relative intensity of these lines changes and, first of all, the ratio of the intensity of the maxi-

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···of the line $K\beta''$ to the maximum of the line $K\beta_5$. A representation of the change in the ratio $IK\beta''/IK\beta_5$ as a function of the percentage content of carbon in the alloy is given by curve 1 in Fig. 2. Curve 2 shows how the integral intensity of the total $K\beta''$—$K\beta_5$ band changes in comparison with the intensity of the line $K\beta_2'''$, conventionally chosen in each of the spectrograms as an internal intensity standard ([5]). The half-width of the $K\beta_5$ line remains constant for alloys with a higher carbon content and tends to increase in the spectra of titanium in low-carbon carbides. The intensity of the $K\beta_2'''$ line on average amounts to about 25% of the intensity of the $K\beta_5$ line. The intensity of the $K\beta_1'''$ line is on average 5 (± 0.8) times smaller than the intensity of the $K\beta_2'''$ line and tends to decrease as the carbon content in the alloy decreases. In some spectra of titanium in these alloys the line $K\beta_1'''$ is in general hardly

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

distinguishable against the overall background of the spectrogram.

Fig. 2. Dependence of $IK\beta''/IK\beta_5$ (1) and of the relative intensity of the $K\beta''$—$K\beta_5$ X-ray emission band (2) of titanium in carbides on the carbon content in the alloys

Consideration of the experimental data obtained makes it possible to draw certain general conclusions.

1. The position of the $K\beta_1$ and $K\beta_5$ lines in the spectra of titanium in carbides with different carbon contents from 9 to 20% remains unchanged. The same also applies to the short-wavelength boundary of the $K\beta_5$ line.
2. The distance between the maxima of the $K\beta''$ and $K\beta_5$ lines in the X-ray spectra of carbides of different composition is equal to 7.9 eV. These two lines essentially form a single emission band with two clearly distinguishable maxima. In this respect this spectrum differs qualitatively from the spectrum of titanium in its dioxide, in which the $K\beta''$ band is separated from the $K\beta_5$ line of titanium by a considerably greater distance ([5]) and, apparently, represents an independent line.
3. As the carbon content in carbides increases, the relative intensity of the $K\beta''$ line, or of the long-wavelength maximum of the common $K\beta''$—$K\beta_5$ absorption band of titanium in the alloy, increases. The rate of this increase noticeably exceeds the increase in the relative intensity of the $K\beta''$ line that might have been expected on the basis of data on the increase in the relative carbon content in these alloys and the assumption that the probability of the corresponding radiative transition in carbides of different composition remains unchanged. The regular change in the probability of the radiative transition under consideration in alloys with different carbon contents, with which we apparently are dealing here, is in the first place

Fig. 3. On the origin of the line $K\beta_x$ in the X-ray spectrum of titanium in low-carbon carbides

may be due to two causes: the difference in interatomic distances in alloys of different composition and the change in the degree of overlap of the wave functions of the atoms in these compounds. From this point of view one could also explain the dependence of the integral intensity of the $K\beta'' - K\beta_5$ emission band in the titanium spectrum in carbides on their carbon content.

To refine and verify conclusions about the nature of the bonding forces in alloys, which could be drawn on the basis of analysis of the experimental material obtained, the X-ray absorption spectra of the same carbides are now being studied.

In the study of the fine structure of the emission spectra of titanium in some low-carbon carbides (Nos. 7 and 8), certain complications were observed, expressed in the appearance of two weak additional lines. One of them was readily identified as the $K\beta''$ line of titanium in its dioxide, which, apparently, was present in the specimen under study as an impurity. The origin of the other line ($K\beta_x$ on curve I in Fig. 3) has not yet been fully clarified. Its appearance cannot be explained by the presence of foreign impurities in the sample,* but is connected with some processes occurring in the carbide at high temperatures ($\sim 1800°$) and considerably weakening at lower ones ($\sim 500°$). The results of the following experiment support this conclusion. Powders of TiO_2 and TiC, the titanium spectra of which did not contain the $K\beta_x$ line, were mixed with each other in a ratio of 1 : 3. Part of the mixture was immediately placed on the anode of the X-ray tube and radiographed; in this process it could be heated to a temperature not above 500°. The spectrogram obtained under these conditions (Fig. 3, III) was the result of superposition of the titanium spectra in both substances and did not contain the $K\beta_x$ line. The other part of the mixture, before being studied, was calcined in a carbon crucible for one hour at 1850° and a pressure of 0.1 mm Hg, and only then was it radiographed. A microphotogram of the spectrum obtained is shown in Fig. 3, III. As can be seen, the traces of TiO_2 have practically completely disappeared, and the curve on which the $K\beta_x$ line appeared resembles the spectrogram from a low-carbon carbide (Fig. 3, I).

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REFERENCES CITED

1. D. Bernal, *Metallophysics*, trans. from English, Moscow, 1933.
2. Ya. S. Umanskii, *Carbides of Hard Alloys*, 1947.
3. S. A. Nemnonov, *ZhTF*, **18**, 246 (1948).
4. A. P. Ubbelohde, *Uspekhi Khimii*, **7**, 1692 (1933).
5. E. E. Vainshtein, Yu. N. Vasil' ev, *DAN*, **114**, No. 1 (1957).
6. Ya. S. Umanskii, S. S. Khidekel' , *ZhFKh*, **15**, No. 9 (1941).

7. K. I. Narbutt, E. E. Vainshtein, A. B. Gil' varg, L. M. Belyaev, *Izv. AN SSSR, ser. fiz.*, **20**, 152 (1956).

8. T. Johansson, *Zs. f. Phys.*, **82**, 507 (1933).

9. A. B. Gil' varg, *DAN*, **72**, 489 (1950).

* Including nitrides, whose $K\beta_5$ line is located in the longer-wavelength region of the spectrum.

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