X-RAY SPECTRAL INVESTIGATION OF THE HOMOGENEITY REGION OF TITANIUM NITRIDE

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Translated from Poroshkovaya Metallurgiya, No. 5 (23), pp. 57-64, September-October, 1964
Original article submitted October 27, 1963

Articles [1-4] provide the results of systematic x-ray spectral investigations of titanium carbide and titanium nitride in the homogeneity region of the phase characterized by face-centered cubic lattices of the NaCl type. Investigations have shown that the fine structure of the absorption spectra of titanium in carbides does not depend on the carbon percentage, and that it remains unchanged throughout the entire concentration range with the exception of the absorption spectrum in one of the subcarbide phase (9 mass % carbon). In this initial low-carbon portion of the homogeneity region of titanium carbide and in the subcarbide phases, a certain reduction in the relative intensity of the Kα*-satellite in comparison with the intensity of the Kα*-line was observed [4]; in the rest of the homogeneity region of the carbide, this intensity was unchanged and independent of the carbon concentration.

The constancy of the spectrum of titanium carbide in its homogeneity region, which was established with respect to data from absorption and emission spectra (which, in the first approximation, reflect the distribution density of electron states in the free and the filled portions of the conductivity and the valence bands of carbides, respectively), positively indicates that the character of the bond in the carbide lattice is the same throughout the entire homogeneity region. This makes it possible to assume that the metallic bond component, which is expressed by the number of collective electrons in the lattice, does not increase with higher carbon percentage in titanium carbide; the general covalent-metallic character of the bond in titanium carbide does not change.

In the titanium-nitrogen system, as well as in the titanium-carbon system, there exists an extensive homogeneity region of the nitride (from 30 to 50 at.% nitrogen) which is characterized by a face-centered cubic lattice, similar to the titanium carbide lattice. As was shown in [3], the concentration dependence of the fine structure of the initial absorption region of the K edge of titanium in nitrides has a complex character, in contrast to carbides, which gave reason to assume (before studying the emission spectra) that considerable changes in the character of the bond in titanium nitrides belonging to the above homogeneity region take place with changes in concentration.

Later, a rather far-reaching parallelism between changes in many physical properties (according to T. S. Verkhoglyadova’s investigations [5]) and changes in the fine structure of x-ray spectra was detected. On analyzing these data in [3], an assumption was formulated concerning the presence of a considerable ion bond component in the nitride and its reduction with transition from phases deficient in nitrogen to compounds with stoichiometric compositions. Certain additional pertinent data can be extracted from the results, published here for the first time, concerning an experimental investigation of the K emission spectra of titanium in the same nitride specimens that were investigated earlier with respect to absorption spectra [3].

The method for producing the alloys and certain data on their chemical and phase compositions were given earlier [5]. Figure 1 shows the line diagrams of the x-ray reflections of certain phases in the titanium-nitrogen system: pure titanium, the solid solution of nitrogen in titanium, and titanium nitride in the extensive homogeneity region [5]. They are also compared with the diffraction reflections of the face-centered cubic lattice of titanium nitride with a = 4.32 A, which were calculated theoretically.

It is obvious from Fig. 1 that the investigated titanium nitride specimens (from 14 to 22.4 mass % nitrogen) do not contain free titanium, the α-solid solution of nitrogen in titanium, titanium oxides, or any other phase, at least in amounts detectable by means of x-ray structural analysis. We also investigated a subnitride phase with 12.8 mass % nitrogen, whose roentgenogram, along with the lines of the face-centered cubic lattice with a = 4.32 A, also contained a system of lines belonging to the lattice of solid nitrogen in α-titanium (not shown in the line diagram). This
was done for the purpose of comparing the spectra of titanium in the subnitride phase with similar spectra in the subcarbide phases mentioned earlier.

The experiments were performed by means of a focusing x-ray telescope spectrograph of a design commonly used at the present time. The curvature radius of the curved crystalline quartz plate, used as the x-ray analyzer, was 180 cm. The reflecting planes of the plate were cut from a quartz monocrystal parallel to the (1011) plane. Under these conditions, the spectrograph's linear dispersion was 3.5 μm/μm, while its resolving power was about 7000. Considering the high chemical stability and the high melting point of titanium nitride, the primary method of x-ray excitation was used in the investigations: the specimen under investigation was rubbed into the copper anode of a high-power demountable x-ray tube. The operating conditions of the tube were: 10 kV; 30 mA.

A series of preliminary experiments have shown that, according to the previous assumption, titanium nitride does not decompose as a result of electron bombardment and heating of the anode material to 700-800°C. A comparison between the spectra of a nitride with stoichiometric composition that were obtained in this series of experiments with spectra of the same nitride obtained earlier by using the fluorescent (secondary) method [6], did not reveal any difference in the shape and position of the group of Kβ lines in the titanium emission spectrum, with the exception of the short-wave satellites KβIII and KβIV, which were present in our spectra, but were absent in the fluorescent spectra. Subsequently, they were not considered.

Each titanium nitride specimen was photographed three to five times, while the exposure and the development conditions were identical. By increasing the cut angle of the anode mirror to 20°, it was possible to secure a considerable exposure gain, thereby obtaining blackenings in the range from 0.5 to 0.7 in one hour. The reproducibility of the spectra was satisfactory. Each of the spectrograms was measured by means of an MF-2 microphotometer at three places along the height of the line under investigation, after which the measurement data were averaged.

The K-spectrum of purest titanium iodide was photographed under perfectly similar experimental conditions. As is known, the KβII -satellite is absent in the emission spectra of pure metals of the first transition period, including titanium spectra. This simplified considerably the process of graphic separation of the satellite on the descending short-wave slope of the KβI line in nitrides with different compositions, whereby this process was transformed into a simple and exact operation. The described method was proposed in [8]. Figure 2 shows the mutually superimposed elements of the Kβ-emission spectrum of titanium in one of the nitrides and in metallic titanium. The reference points for comparison was the superposition of the positions of the KβI lines in both spectra which, as was mentioned above, can be considered as constant for metallic titanium and all its compounds within the limits of experimental accuracy (± 0.2 eV).

*As is known [7], the origin of these satellites is not connected with the chemical characteristics of the material under investigation, but with the physical process of excitation of x-ray photons by the electron bombardment of the anode, which is not used in the secondary method.