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X-RAY SPECTRAL STUDY OF TITANIUM BERYLLIDES

(Presented by Academician A. P. Vinogradov, 16 VI 1960)

The insufficient study of the question of the nature of the forces of interatomic interaction in beryllides of transition metals, the contradictory views of different investigators (^{1,2}), and the great practical importance that beryllium-based alloys have acquired in modern technology (^{3}), make a comprehensive investigation of this group of substances a very urgent and interesting task.

The present work is devoted to the investigation of the fine structure of the x-ray absorption and emission spectra of atoms of the transition element in titanium beryllides. The phase diagram of alloys of the Ti–Be system has not been studied in sufficient detail and is in many respects controversial. According to Ehrlich (^{4}), at low Be contents in the alloy (up to 9.1 at. %) it forms substitutional solid solutions with titanium, with a hexagonal lattice close to the lattice of the initial titanium. Single-phase regions were also observed by the author for alloys containing about 43 and 66 at. % Be. Ehrlich was unable to determine the lattice type of the first of these phases. The second, corresponding to the intermetallic compound $TiBe_2$, is, according to Mish (^{5}), isomorphous with $MgCu_2$ and belongs to the so-called Laves phases (^{6}). It forms a complex cubic lattice with $c/a = 6.42$ and 24 atoms in the cell, which may be represented as two interpenetrating sublattices containing only titanium or beryllium atoms. The beryllium atoms lie at the vertices of tetrahedra joined by their corners. Each of them is surrounded by six titanium atoms, so that the total coordination number for beryllium is 12. Each titanium atom in the lattice is surrounded by four atoms of the same name and, at a somewhat shorter distance, by 12 beryllium atoms. The total coordination number for it is therefore 16. The phase composition of alloys with a high beryllium content (more than 80%) is very complex. There are indications that new intermetallic compounds are formed here. One of them, according to (^{7}), may be described by the formula $TiBe_{12}$. On the other hand, according to the data of P. I. Kripyakevich and E. I. Gladyshevskii,* a compound is formed here whose composition should be described by the formula Ti_2Be_{17}. The structure of this compound belongs to the Th_2Zn_{17} type and is close to the structure of the $ThMn_{12}$ type, a derivative of which, according to (^{7}), is characteristic of the compound $TiBe_{12}$.

In the present work, two firmly established and best-studied phases, close in composition to intermetallic compounds of the TiBe and $TiBe_2$ types, were subjected to x-ray spectral investigation. They were prepared at the Institute of Metal Ceramics and Special Alloys of the Academy of Sciences of the Ukrainian SSR and kindly placed at our disposal by G. V. Samsonov, to whom the authors express their gratitude. Both alloys were obtained by sintering powders of metallic (iodide) titanium and beryllium. The appropriately calculated charge was thoroughly mixed for 2 hours, passed through a sieve, and pressed into briquettes under a pressure of 1000 kg/cm^2. The resulting briquettes were placed in a resistance furnace with a quartz tube and held in an argon atmosphere for one hour at 1200°. Control chemical analysis of the prod—

* Private communication of the authors.

···of sintering revealed good agreement between the actual beryllium content in the alloys and the calculated content. The content of impurities in the alloys and in the initial titanium, recorded by optical spectral analysis, is given in Table 1.

The structure of the alloys was checked by comparing the results of X-ray structural analysis of the samples studied with literature data (^{4}).

Table 1

	Mg	Al	Si	Mn	Fe	Cu
Ti_{met}	0.01	0.01	0.01	–	0.02	0.0001
TiBe	0.01	0.03	0.01	0.003	0.03	0.01
$TiBe_2$	0.03	0.03	0.02	0.003	0.05	0.01

The apparatus and method of the X-ray spectral investigation were described earlier (^{8,9}). Both the fine structure of the absorption spectra and the fluorescence spectra of titanium were studied. In the first case, spectrograms of satisfactory quality were obtained at a regime of 15 kV, 40 mA for 4-6 h; in the second, in studying the fine structure of the $K\beta_5$-emission line of titanium in these alloys, at a regime of 15 kV and 70 μA and an exposure time of 20–40 h. Under the selected experimental conditions, no noticeable effect of reabsorption was found in the fluorescence spectra. When recording the absorption spectra a gold anode was used; when recording the fluorescence spectra, a chromium anode. The absorber density when recording the titanium absorption spectra in the beryllides was 5 mg/cm^2. The spectrograms were photometered point by point and, after averaging, were presented as a graph of quantities proportional to the absorption coefficient versus the energy of the X-ray quanta in electronvolts. The accuracy of the energy determination was 0.2 eV.

Fig. 1. X-ray K-absorption spectra and $K\beta_5$—emission lines of titanium in the metal (1), mono- (2), and diberyllide (3)

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In Fig. 1 the X-ray absorption and emission spectra of titanium in the beryllide, close in composition to TiBe, and in the diberyllide (in first order of reflection) are compared with the corresponding spectra of the transition metal. The origin on the energy scale is chosen, conditionally, to coincide with the position of the maximum of the titanium $K\beta_5$-emission band in the metal. As can be seen, on going from the metal to its alloys with beryllium, the titanium $K\beta_5$-emission band and its K-absorption edge undergo a short-wavelength shift, the magnitude of which is different for the $K\beta_5$-band and for the individual characteristic points of the absorption edge. An idea of the scale of this shift can be obtained from consideration of the data given in Table 2. Since the magnitude of the short-wavelength shift of the emission band more than triples the corresponding value for the initial region of absorption, in the beryllides there is observed a much stronger overlap of the short-wavelength tail of the emission band and the absorption spectrum of titanium than in the pure metal, and a noticeable decrease in the distance between the maximum of the $K\beta_5$-band and point m in the absorption spectrum. At the same time, in going from metallic titanium to the beryllides, a sharp increase is observed in the width of the $K\beta_5$ emission band and an increase in its asymmetry index, as well as a change in the relative intensity of different portions of the main titanium absorption edge, associated with transitions of the metal $1s$-electrons into different regions of the generalized $3d, 4sp$ energy band of the alloys. The energy of the absorption maximum (A) increases considerably (~ 5 eV) in the beryllides, which arises in the spectrum upon transition of the photoelectron into the region of the hybridized energy band of the alloy, possessing predominantly p-symmetry. It is very probable that the mentioned increase in the energy of the titanium $4p$-states in the alloys is a consequence of the considerable decrease, observed in the beryllides of this metal, in the Ti—Ti distance compared with pure titanium

Table 2

	Relative position on the energy scale, eV	Relative position on the energy scale, eV	Relative position on the energy scale, eV
	max. $K\beta_5$	point m	point A
Metal	0	6.7 ± 0.2	17.8 ± 0.5
TiBe	3.8 ± 0.2	7.5 ± 0.2	23.0 ± 0.3
$TiBe_2$	3.8 ± 0.2	7.2 ± 0.2	22.6 ± 0.3

(0.15 Å, which amounts to about 5% of this distance in the pure metal). The short-wavelength shift of point A in the titanium absorption spectra in the beryllides is also associated with the general increase in the width of the K-edge observed in these alloys. In contrast to what was said above, the position and shape of the K-absorption edge in the so-called region of initial absorption (from the beginning of the K-edge to point m), which according to current ideas is associated with the transition of a K-electron into the unfilled part of the hybridized $3d$ energy band of titanium, undergoes practically no change in going from the metal to the beryllides. Point m in this case is only slightly (0.5–0.8 eV) shifted to the short-wavelength side, while the corresponding absorption maximum in the diberyllide is somewhat reduced in intensity. The latter is evidently a consequence of the decrease in the degree of overlap of the *dsp* energy levels of titanium and beryllium atoms in this alloy compared with the alloy having a smaller beryllium content, and of the consequent decrease in the probability of transition of the photoelectron into this region of the generalized energy band. As for the degree of screening of the nucleus by the electrons of the titanium $3d$-shell in the metal and in both beryllides, judging from the position of the long-wavelength maximum in the edges investigated, it does not undergo noticeable changes and gives no grounds for supposing that, in the process of alloy formation, the valence electrons of beryllium penetrate into the $3d$-shell of the transition metal. On the contrary, the entire body of observations concerning the structure of the x-ray spectra of titanium in these compounds, in good agreement with the physical properties of the alloys and with the ratio of the electronegativities of titanium and beryllium atoms, argues in favor of the concept of a substantially metallic character of the bonding in these compounds and of collectivization of the valence electrons of both atoms. In this case the role of donor–acceptor interaction of the titanium $3d$-electrons with the beryllium $2s$-electrons must be small.

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