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Abstract

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ELECTRON-DIFFRACTION STUDY OF THE POLYMORPHISM OF ZIRCONIUM DIOXIDE IN THIN FILMS

(Presented by Academician I. P. Bardin, January 21, 1958)

The study of the polymorphism of zirconium dioxide in thin films by the electron-diffraction method is being carried out for the first time and is motivated, on the one hand, by the contradictory nature of the results obtained by various investigators in studying polymorphism in massive specimens of monoclinic ZrO_2, and, on the other hand, by the lack of clarity concerning the structure of the oxide film formed on zirconium during corrosion in oxidizing media.

A detailed survey of the four possible modifications (monoclinic, tetragonal, cubic, and rhombohedral) of ZrO_2, with a description of the conditions of their formation and ranges of existence, is given in Lastman' s monograph (^{1}). According to the X-ray data cited in this review, the lattice of the monoclinic modification of ZrO_2 is a distorted cubic lattice of the CaF_2 type with parameters (in Å): $a = 5.17_4$; $b = 5.26_6$; $c = 5.30_8$; $\beta = 80°48'$. This modification is stable up to 1000°.

Above 1000° the tetragonal modification of ZrO_2 is stable; the parameters of its lattice (in Å) are: $a = 5.07$ and $c = 5.16$.

The cubic modification of ZrO_2 is fixed at room temperature by quenching from 2000° in the presence of an MgO impurity; it has the fluorite structure with parameter $a = 5.098$ Å. It is considered to be stable above 1900°.

After prolonged heating of monoclinic zirconium dioxide at 1900°C, the rhombohedral form of ZrO_2 is formed. It is also represented as a pseudohexagonal form with $a = 3.598$ Å and $\frac{c}{a} = 1.633$.

However, from a number of works (^{2}-^{5}) it follows that, indisputably, there exist two forms of zirconium dioxide: monoclinic and tetragonal, which transform reversibly into one another at temperatures of 1000-1100°. The starting material in the study of polymorphism in the works of the cited authors was sintered or melted monoclinic zirconium dioxide contaminated with hafnium dioxide (up to 2%). Domagala and MacPherson (^{6}) studied the polymorphism of ZrO_2 by the X-ray method on specimens of fused zirconium dioxide practically free of

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hafnium dioxide impurities. Applying heat treatment of the specimens at temperatures of 900, 1210, 1745, and 2315°, followed by quenching, they attempted to fix possible modifications of ZrO_2. The authors note that in all cases only the monoclinic modification was invariably detected.

On the surface of zirconium, when it is oxidized in various media (in oxygen, in air, or in a steam-water medium) under certain conditions and at temperatures from 20 to 800°, oxide films have been found ([1]) consisting of the oxide ZrO_2 with the structure of one of three modifications: monoclinic, tetragonal, or cubic. These data do not agree with the results of the studies of the above-mentioned authors ([2]-[5]), according to which up to 1000° only the monoclinic phase of ZrO_2 exists.

Method. The study of the polymorphism of zirconium dioxide was carried out on specimens in the form of thin zirconium films (400-600 Å thick) by the transmission electron-diffraction method. The use of a special device for heating the specimen (up to 1100°) directly in the electron-diffraction camera made it possible to observe the structural transformations of zirconium dioxide as a function of the temperature and duration of heating without cooling the specimen.

This device consisted of two zirconium strips 0.2 mm thick, with a hole 0.8 mm in diameter in them; the specimen was placed between the strips opposite the hole. These strips were heated by direct current; together with them the specimen, which was in thermal equilibrium with the device, was also heated. The bead of a platinum-platinum-rhodium thermocouple was pressed tightly against the zirconium plates by means of a refractory clamp. When the electron-diffraction pattern was being recorded for 0.5 sec, the current was switched off, since the magnetic field produced by it distorted the diffraction pattern. From experiments on heating and cooling specimens in the electron diffraction apparatus itself, it was established that cooling from a high temperature to room temperature does not introduce changes into the structure of zirconium dioxide characteristic of each heating temperature; therefore, subsequently, electron-diffraction patterns were obtained only from specimens cooled to room temperature. The initial specimens were thin zirconium films obtained by the method of evaporation and condensation in vacuum of zirconium iodide of the second refining, with a purity of 99.9%. As the substrate on which the metal was condensed, NaCl crystals in the form of plates were used. To obtain thin layers of zirconium, a glass high-vacuum apparatus was constructed that made it possible to attain a vacuum of $\sim 10^{-7}$ mm Hg; this vacuum was achieved by using a zirconium getter. The evaporator was a horizontal spiral 2 mm in diameter and 10 mm long, made of tungsten wire 0.2 mm in diameter. The spiral was preliminarily annealed in high vacuum. After this, a zirconium rod 0.2 mm in diameter was placed inside the spiral. Upon attaining a vacuum of 10^{-7} mm Hg, a current of 5-7 A was passed through the spiral until melting of the zirconium rod began.

When zirconium melts, droplets form on several turns of the spiral, from which the zirconium evaporates intensely. The thickness of the films is limited by the evaporation time and the distance of the substrate from the evaporator.

On a cold substrate, zirconium crystallized in a fine-crystalline state, as evidenced by the very blurred diffraction lines in the electron-diffraction patterns (see the electron-diffraction pattern in Fig. 1). Therefore we heated the substrate to a temperature of 200–250°. The heater was made of strips of zirconium foil 0.05 mm thick, through which current was passed.

Experiments showed that evaporation of zirconium must be carried out with great care, with special attention paid to the vacuum in the system, since zirconium in the molten state reacts actively with residual gas, and films obtained in the case of insufficient vacuum (10^{-5} mm Hg) are partially oxidized. Therefore, before evaporation it is necessary to degas the substrate thoroughly, which we did by heating it to 600° for 1 hour. Air was admitted into the system after the film had been obtained only some time after the pumps were switched off; this ensured gradual passivation of the zirconium film by residual oxygen and protected it from deep oxidation when air was admitted.

The film was separated from the NaCl substrate by gradual immersion in distilled water. The separated film was then washed free of NaCl in several baths of distilled water. Pieces of zirconium film floating on the surface of the water were fished out onto zirconium strips and onto platinum frames with a hole 0.8 mm in diameter. These thin zirconium films were then heated in pure oxygen at a temperature of 270°, at which, as had been established beforehand, appreciable oxidation of zirconium begins, i.e., at this temperature the metal lines in the electron-diffraction patterns disappear and oxide lines appear.

The electron-diffraction studies were carried out with an electron diffraction apparatus designed at the Institute of Metallurgy of the Academy of Sciences of the USSR. Its resolving power is 0.005 Å over 0.2 mm at a diffraction-space length of 500 mm.

Fig. 1. Electron diffraction pattern of a thin Zr layer condensed on a cold substrate (18°)

a

b

c

d

e

Fig. 2. Electron diffraction patterns of a thin zirconium layer heated at different temperatures in oxygen: *a* –18°, *b* –300°, *c* –700°, *d* –850°, *e* –1000°

The electron-diffraction constant $2\lambda L$ was determined in each case from electron-diffraction patterns of a standard specimen—a thin aluminum film.

The specimens were heated in air (in an ordinary muffle electric furnace), in oxygen, and in vacuum (in a special apparatus and in the electron-diffraction camera itself) at temperatures from 275 to 1300° with intervals of 25°. The temperature was determined by a thermocouple with an accuracy of ±10°.

The **results of the investigation** are presented in the form of electron-diffraction patterns in Fig. 2 and in the corresponding calculation tables (Tables 1 and 2).

From electron-diffraction pattern 2a, obtained from a thin layer of zirconium, and from the corresponding Table 1, it is evident that the values of the interplanar spacings of the crystal lattice of this layer correspond to α-zirconium; however, in comparison with X-ray data they are increased by 2–3%. The line intensities coincide with the intensities determined from X-ray

Table 1

Results of the calculation of the electron-diffraction pattern from a thin layer of α-Zr, obtained by evaporation in vacuum (10^{-6} mm Hg)

Ring No.	Ring diameter, mm	Ring intensity	$d/n_{\text{exp.}}$	$d/n_{\text{X-ray}}$	Ring No.	Ring diameter, mm	Ring intensity	$d/n_{\text{exp.}}$	$d/n_{\text{X-ray}}$
1	21,3	s.	2,85	2,78	7	40,95	weak	1,48	1,46
2	23,0	med.	2,64	2,56	8	43,1	weak	1,41	1,36
3	24,4	v. s.	2,49	2,44	9	44,3	med.	1,37	1,34
4	31,5	weak	1,92	1,88	10	48	v. weak	1,26	1,22
5	34,0	v. weak	1,78	–	11	57,8	med.	1,05	1,038
6	37	s.	1,64	1,61	12	61,4	weak	0,99	0,97

Note: Here and in Table 2: s. –strong, med. –medium, weak –weak, v. s. –very strong, etc.

Table 2

Interplanar spacings and relative line intensities on electron-diffraction patterns obtained from ZrO_2 as a function of the heating temperature

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300° intensity of ring	300° $d_{\text{exp.}}$, Å	300° $d_{\text{X-ray}}$, Å	700° intensity of ring	700° $d_{\text{exp.}}$, Å	700° $d_{\text{X-ray}}$, Å	850° intensity of ring	850° $d_{\text{exp.}}$, Å	850° $d_{\text{X-ray}}$, Å	1000° intensity of ring	1000° $d_{\text{exp.}}$, Å	1000° $d_{\text{X-ray}}$, Å
v. s.	2,94	2,94	v. s.	2,94	2,94	weak	5,12	5,10	med.	5,16	5,10
med.	2,54	2,54	med.	2,59	2,57	med.	3,67	3,69	med.	3,69	3,69
weak	2,10	—	med.	2,53	2,53	med.	3,16	3,19	v. s.	3,17	3,19
s.	1,80	1,80	weak	2,09	—	v. s.	2,94	2,94	s.	2,86	2,85
med.	1,54	1,53	s.	1,80	1,80	med.	2,83	2,85	med.	2,63	2,63
weak	1,46	1,47	med.	1,55	1,55	weak	2,57	2,58	med.	2,55	2,55
weak	1,27	1,27	med.	1,52	1,52	weak	2,53	2,53	weak	2,34	2,34
med.	1,17	1,17	weak	1,47	1,47	weak	2,31	2,34	weak	2,29	—
v. weak	1,15	1,14	weak	1,35	—	weak	2,19	2,21	med.	2,22	2,21
med.	1,04	1,04	v. weak	1,29	1,29	weak	2,02	2,01	weak	2,01	2,01
weak	0,98	0,98	med.	1,26	1,26	s.	1,80	1,80	med.	1,85	1,85
			med.	1,175	1,165	weak	1,70	1,70	weak	1,80	1,81
						weak	1,65	1,65			
						med.	1,55	1,55			
						s.	1,52	1,52			
Cubic	Cubic	Cubic	Tetragonal	Tetragonal	Tetragonal	Tetragonal + monoclinic	Tetragonal + monoclinic	Tetragonal + monoclinic	Monoclinic	Monoclinic	Monoclinic

studies. The increase in the lattice constant is evidently associated with the dissolution of oxygen in the zirconium film. The electron-diffraction pattern in Fig. 2a is characteristic of thin zirconium films obtained on heated substrates.

Analysis of the electron diffraction pattern (Fig. 2b and Table 2) from a zirconium film heated at 300° shows that this film was completely oxidized, and the diffraction pattern corresponds to the cubic modification of zirconium oxide ZrO_2 (with one extra line present, $d = 2.10$ Å). The value of the lattice constant of this modification was found to be $a = 5.10$ Å, which agrees well with the value of this quantity determined by the X-ray method [1]. The somewhat increased width of the diffraction lines in the electron diffraction patterns in Figs. 2a and 2b indicates that both α-Zr and ZrO_2 in this case are fine-grained.

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When heated from 300 to 600°, the interference rings in the electron diffraction patterns from the zirconium dioxide film become increasingly sharp and correspond to the indicated cubic modification; beginning at 650°, splitting of some rings is observed (for example, the ring from the (002) plane of cubic ZrO_2), which indicates the appearance of a new modification of ZrO_2 in the layer. Calculation of the electron diffraction pattern from it showed that it has a tetragonal lattice, the interplanar spacings of which, as is seen from Table 2, coincide with their X-ray values. A characteristic electron diffraction pattern obtained at 700°, on which the split rings are visible, is presented in Fig. 2e.

In the present case it is difficult to speak of the simultaneous existence of two forms of ZrO_2—cubic and tetragonal—since their parameters are very close; but, apparently, the transition process from the cubic to the tetragonal form proceeds gradually, as evidenced by some electron diffraction patterns obtained from the layer at 500°, on which splitting of lines from planes with the corresponding indices begins to appear. In the temperature interval from 750 to 800°, in the electron diffraction patterns, along with the lines of the tetragonal modification of ZrO_2, lines of the monoclinic modification of the oxide appear; with increasing heating temperature these become increasingly intense, while the lines of the tetragonal modification gradually disappear, and at 1100° a purely monoclinic modification of ZrO_2 is observed, the interplanar spacings of which coincide with tabulated data (see Fig. 2b and Table 2). This monoclinic modification of zirconium dioxide was preserved on heating up to 1300°.

Thus, upon oxidation of a thin zirconium layer at a temperature of 270°, the cubic modification of ZrO_2 is formed; on heating, it undergoes polymorphic transformations of the monotropous type: the cubic lattice is stretched along one axis and becomes tetragonal, and then, with increasing heating temperature (700–1100°), it is distorted still more, transforming into a monoclinic lattice.

As indicated above, polymorphism was studied by heating a thin film of cubic ZrO_2 in vacuum, in oxygen, and in air. In all these cases identical regular transformations of the cubic modification into the tetragonal, and of the latter into the monoclinic, were found in the same temperature intervals. The results obtained therefore make it possible to assert that the polymorphic transformations observed are intrinsic to zirconium dioxide, and are not a consequence of dissolution of oxygen in ZrO_2 or of the oxide ZrO_2 reaching an exact stoichiometric composition; atmospheric nitrogen likewise played no role in this case. In conclusion, it should be noted that our data and the results reported by Domogala and McPherson make it possible to consider monoclinic ZrO_2 the stable form of zirconium oxide, the final product of the transformation of ZrO_2 in the temperature range 300–1300°.

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