The Solubility of Oxygen in, and the Oxides of, Tantalum

BY R. J. WASILEWSKI

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The purpose of the work described below was to determine the solid solubility of oxygen in tantalum and the existence of any intermediate structures in the range 0–18.11 weight per cent. of oxygen, particularly at the composition corresponding to the formula Ta_2O_4 (15.03% oxygen), since the existence of this oxide had not been definitely established.

Previous Work.—The structure of tantalum metal is body-centered cubic, and the lattice parameter values varying from 3.337 to 3.272 Å. have been reported. The value $a_0 = 3.3026 \pm 0.0003$ Å., as given by Neuburger,[1] has been accepted as the most accurate.

There are very little data on the tantalum–oxygen compounds, apart from that on the pentoxide. The X-ray diffraction pattern of the latter is given in the A.S.T.M. Index,[2] but although it is stated to be orthorhombic, the structure has not been determined. Recently, Lagergren and Magneli[3] have reported the existence of a high temperature form of the pentoxide, the transition taking place at 1310°. The reported existence of Ta_2O_4, said to be formed by the reduction of the pentoxide by carbon or magnesium at high temperatures, or by electrolysis of tantalum salts, has been questioned.[4]

Since tantalum is closely related to columbium, some similarities can be expected between the oxides of the two metals. Grube, *et al.*,[5] investigated the reduction of Cb_2O_5 by hydrogen. They reported the existence of different structures corresponding to the compositions Cb_2O_5, Cb_2O_4, CbO and Cb_2O, while the sesquioxide was found to be a mixture of the mono- and dioxide. A later investigation by Brauer[6] confirmed most of the above data. He was unable, however, to observe the suboxide structure, and concluded that the pattern reported for it must have been caused by impurities. The pentoxide he found to exist in three temperature dependent modifications, the transition temperatures being approximately 950° and 1100°.

Experimental Procedure

Materials.—1, MUREX, Grade A tantalum powder, prepared by sodium reduction of K_2TaF_7. This powder contained less than 0.1% each of oxygen and columbium, and traces of SiO_2 and CaO. 2, Secondary tantalum powder, containing approximately 0.7% oxygen, 0.1% each of Cb and Fe. 3, MUREX tantalum pentoxide, analyzing 99.85^{+}% Ta_2O_5.

For the determination of the lattice parameter of the pure metal, filings from a melted end of an oversintered bar were used. This material was spectroscopically pure, and gave the theoretical gain in weight on ignition (22.11%).

Preparation of the Specimens.—A small quantity of the metal powder was heated at 1000–1050° in a molybdenum boat, in an atmosphere of electrolytic hydrogen containing traces of oxygen and water vapor. There was no detectable pick-up of molybdenum from the boat. The oxidation of tantalum was slow and fairly uniform, so that by varying the heating time the extent of oxidation could be easily controlled. The powder could be oxidized to pentoxide within 24 hours.

When oxidized, the sample was cooled in hydrogen, then ground in an agate mortar, and annealed for 72 hours at 1050° at a pressure below 5×10^{-4} mm. This annealing period was sufficient to remove the hydrogen absorbed during the previous heating, and to ensure the homogeneity of the powder. The oxygen content was determined on 1-g. samples by gain in weight on ignition. Powder diffraction patterns were taken using CuK radiation and a standard 9-cm. diameter camera, although in a few cases CrK radiation and a 19 cm. diameter camera were used.

Experimental Data

The parameter values corresponding to varying oxygen content are shown in Table I. The value found for the gas-free metal agrees well with that reported by Neuburger, and corresponds to an X-ray density of 16.671 g. cm.$^{-3}$, taking as unit atomic weight 1.6603×10^{-24}.[7]

TABLE I

TANTALUM LATTICE PARAMETER WITH INCREASING OXYGEN CONTENT

Material	Oxygen wt. %	X-Ray method	Lattice parameter, Å.
Annealed wire	Nil	Powder	3.3026 ± 0.0002
Melted bar tip	Nil	Back reflection	3.3026 ± .0002
Filings	Nil	Powder	3.3026 ± .0003
Electrolytic powder	0.22	Powder	3.3055 ± .0003
Murex, oxidized	0.65	Powder	3.3124 ± .0003
Murex, oxidized	0.84	Powder	3.3157 ± .0003
Murex oxidized	0.93	Powder	3.3163 ± .0002
Murex, oxidized	1.96	Powder	3.3163 ± .0003

The solubility limit of oxygen in tantalum at 1050° is thus found to be 0.9% by weight. The parameter increase is linear with the oxygen content, within the accuracy of the oxygen determination. As will be mentioned later, however, there are indications that the solubility is considerably higher at higher temperatures.

The metal lattice persists up to approximately 3.9 weight % oxygen content, the first lines of a new structure, however, were obtained at 1.8% oxygen. This structure appeared homogeneous at 4.2% oxygen. The homogeneity range of this structure appears to be very narrow, since no difference in the spacing of the planes giving rise to the highest angle reflection could be detected within the range 3.0–8.0% oxygen.

A third structure appeared at just below 8%, and was found to be homogeneous above 17% oxygen content. This structure was found to be that of the pentoxide, as confirmed by comparing its pattern with that of the commercial Ta_2O_5. The diffraction pattern of this structure is very complex, and the high angle reflections are very diffuse.

Since no pattern was found corresponding to the composition Ta_2O_4, attempts were made to reduce the pentoxide by heating with carbon at 1770°. The pentoxide became black after heating for 90 minutes, and the total loss in weight corresponded very closely to that expected, had the reduction to Ta_2O_4 taken place. A new diffraction pattern was obtained from this sample, but the maximum intensity line of the suboxide was also observed. In a second experiment, Ta_2O_5 was heated at 1770° with tantalum. Again the new pattern, together with that of the suboxide, were found.

Neither of the diffraction patterns observed so far corresponded with that given for Ta_2O_5 in the A.S.T.M. Index.[2] An investigation was therefore made concerning the existence of other forms of the oxide. It was found that the precipitated oxide, containing some 40% moisture, is amorphous, as stated by Huttig and Konig.[8] However, a crys-

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[1] M. C. Neuburger, *Z. Krist.*, **93**, 312 (1936).

[2] A.S.T.M. Index of X-ray diffraction patterns.

[3] S. Lagergren and A. Magneli, *Acta Chem. Scand.*, **6**, 444 (1952).

[4] B. S. Hopkins, "Chemistry of the Less Familiar Elements," Stipes, Chicago, 1939, Chapt. 15, p. 16.

[5] G. Grube, O. Kubaschewski and K. Zwiauer, *Z. Elektrochem.*, **45**, 885 (1939).

[6] G. Brauer, *Z. anorg. allgem. Chem.*, **248**, 1 (1941).

[7] C. S. Smithells, "Metals Reference Book," Butterworths, London, 1949, p. 48.

[8] G. F. Huttig and A. Konig, *Z. anorg. allgem. Chem.*, **193**, 100 (1930).

talline pattern, although indicating poor structure, was found for a hydrated oxide approximating to the composition $Ta_2O_5 \cdot 4.28H_2O$. The structure observed for the oxide heated between 650° and 1300° is identical with that obtained for the commercial oxide, and was found to be isomorphous with the low temperature modification of Cb_2O_5 reported by Brauer.[6] When heated to higher temperatures, the pentoxide was found to transform, and the pattern obtained was that observed previously for the "reduced" oxide. The low temperature structure persisted up to 1300°, the high temperature structure having been obtained after heating to 1350°, in agreement with the findings of Lagergren and Magneli.[3]

The transition of the pentoxide appeared to involve considerable structural changes, judging from the diffraction patterns. The high temperature structure remained unchanged after heating at 1300° for 48 hours. Neither of the diffraction patterns obtained corresponded to that given in the A.S.T.M. Index,[2] and the attempts at growing single crystals of the oxide, suitable for rotation photographs, were unsuccessful.

Discussion of Results

The discrepancies in the values reported for the tantalum lattice parameter previously are thought to have been due to oxygen present in the metal used. Andrews[9] and Myers[10] have observed the increase of the metal lattice parameter on addition of oxygen. While it has been stated,[11] that hydrogen also causes a lattice expansion, a slight expansion only was found by Burgers and Basart[12] in the metal prepared under conditions facilitating the solution of hydrogen. During the author's experiments the expansion was found to be small, a far more marked effect of the absorption having been the widening of the diffraction lines, consistent with high stresses being set up in the metal lattice.

The solubility of oxygen in the metal appears to be higher at temperatures of the order of 2000°, as found during an investigation of a sintered metal bar, showing considerable surface oxidation. Both the suboxide and the body-centered cubic metal patterns were obtained from this specimen, the parameter of the latter, however, was found to be 3.340 Å.; *i.e.*, considerably higher than that found for the maximum oxygen content at 1050°. This solubility must, however, decrease with further temperature increase, since the oxygen or the oxide is expelled by heating above about 2200° *in vacuo*.[9,10,13]

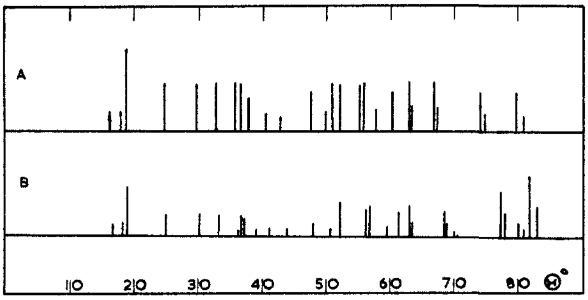

Fig. 1.—Debyograms of Cb_2O (A), from Kubaschewski[5,14] and tantalum suboxide (B). The relative intensities were estimated visually (A), and by means of a microphotometer (B).

The photogram of the pattern obtained with tantalum containing 4.2% oxygen was compared with that given by Kubaschewski for Cb_2O.[14] Figure 1 shows the similarity of the patterns, and consequently the structure is thought to correspond to the composition Ta_2O. An attempt was made to determine the symmetry of the unit cell, following the method of Jacob and Warren.[15] It was found that an orthorhombic cell of $a = 5.29$, $b = 4.92$ and $c = 3.05$ Å. would account for all the lines present. The experimental density being 15.52 g. cm.$^{-3}$, the cell contains two formula units of Ta_2O, the corresponding X-ray density being 15.8 g. cm.$^{-3}$.

It is evident that no confirmation of the existence of the dioxide has been found, and it is doubtful whether, in fact, any structure intermediate between Ta_2O and Ta_2O_5 exists, since the first new pattern obtained on the reduction of the pentoxide is that of the suboxide. Thus the "dioxide" appears to be a mixture $Ta_2O \cdot 3Ta_2O_5$, obtained by partial reduction of the pentoxide.

The reaction of the pentoxide with tantalum metal appears to be very rapid in the temperature range 1700–2200°. This indicates that the diffusion of oxygen through the metal must be rapid, which would account for the difficulty in obtaining oxygen-free metal, if it is cooled slowly through this critical range after sintering.

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[9] M. R. Andrews, THIS JOURNAL, **54**, 1845 (1932).

[10] R. H. Myers, *Metallurgia*, **41**, 301 (1950).

[11] E. Pietsch and H. Lehl, *Kolloid Z.*, **68**, 226 (1934).

[12] W. G. Burgers and J. C. M. Basart, *Z. anorg. allgem. Chem.*, **216**, 223 (1934).

[13] "Tantalum, The Metal," Fansteel Metal Corporation, 1939.

[14] O. Kubaschewski, *Z. Elektrochem.*, **46**, 284 (1940).

[15] C. W. Jacob and B. E. Warren, THIS JOURNAL, **59**, 2588 (1937).

SCHOOL OF MINES
COLUMBIA UNIVERSITY
NEW YORK 27, N. Y.

The Partial Hydrolysis of Chlorosilanes

BY ROBERT WEST

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Schumb and Stevens have shown that hexachlorodisiloxane can be prepared in fair yield by the partial hydrolysis at −78° of silicon tetrachloride dissolved in ether.[1] We have extended this work by studying the partial hydrolysis of trichlorosilane,[2] dichlorosilane and methyltrichlorosilane, under similar conditions. With trichlorosilane, 5 to 10% yields of 1,1,3,3-tetrachlorodisiloxane (a new compound) are obtained, but with dichlorosilane and methyltrichlorosilane only traces of partially-hydrolyzed products could be isolated. The reason for the diminished yields is not known; however, recent unpublished work in this Laboratory indicates that among these chlorosilanes the tendency toward the formation of addition compounds with amines[3] falls off in the same order.

In the titration of 1,1,3,3-tetrachlorodisiloxane (in acetone solution) with standard alcoholic sodium

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[1] W. C. Schumb and A. J. Stevens, THIS JOURNAL, **69**, 726 (1947); **72**, 3178 (1950).

[2] The complete hydrolysis of trichlorosilane has been studied recently; see G. H. Wagner and A. N. Pines, *Ind. Eng. Chem.*, **44**, 321 (1952).

[3] W. R. Trost, *Can. J. Chem.*, **29**, 877, 1075 (1951).