Formation of Rutile-Type Ta(IV)O$_2$ by Shock Reduction and Cation-Deficient Ta$_{0.8}$O$_2$ by Subsequent Oxidation

YASUHIKO SYONO, MASAE KIKUCHI, TSUNEAKI GOTO,* AND KIYOTO FUKUOKA

The Research Institute for Iron, Steel, and Other Metals, Tohoku University, Sendai 980, Japan

Ta$_2$O$_5$ is reduced to Ta(IV)O$_2$ with the rutile structure by shock-loading to 50–60 GPa. Tetragonal unit cell parameters at room conditions are measured to be a = 4.7518(5) Å, c = 3.0878(4) Å, c/a = 0.6498(1), and V = 69.72(1) Å^3. The chemical composition is thermogravimetrically determined to be Ta$_{0.97\pm0.04}$O$_2$ by heating shock-reduced products in an oxygen gas flow to 1200°C. In the oxidation process a cation-deficient rutile-type compound Ta$_{0.8}$O$_2$ is found to be metastably formed.

Introduction

The shock-loading process is inevitably accompanied by temperature increase because of its adiabatic (nonisentropic) nature. The temperature increase in shock compression is particularly remarkable when a porous specimen is used for the starting material. It is rather easy to achieve temperatures of several thousand degrees in a specimen with about 50% packing density by shock compression to some 10 GPa *(1)*. Such high temperatures produced by shock compression technique can be utilized for accelerating reactions involving refractory materials, which are otherwise hard to activate *(2, 3)*. Formation of lower oxides of niobium and tantalum by reduction of Nb$_2$O$_5$ and Ta$_2$O$_5$ under shock-loading *(4, 5)* is a typical example.

Tantalum, as the name implies, is one of the most inert metals with high melting temperature and the oxide Ta$_2$O$_5$ is also known to be very stable. Intermediate valence states in the Ta–O system have not been convincingly established. Tantalum(IV) oxides with the rutile structure have been prepared either by oxidation of tantalum metal or carbide *(6, 7)* as well as by shock reduction of Ta$_2$O$_5$ *(5)*. However, this phase has not been isolated in the pure form, and there remains considerable discrepancy in composition and unit cell parameters of tantalum(IV) oxides prepared by different techniques. In the present study, nearly stoichiometric tantalum(IV) oxides with the rutile structure were prepared by the shock reduction technique and compared with previous results. Crystallographic parameters and chemical compositions of these oxides were examined by X-ray diffraction

* Present address: Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106.
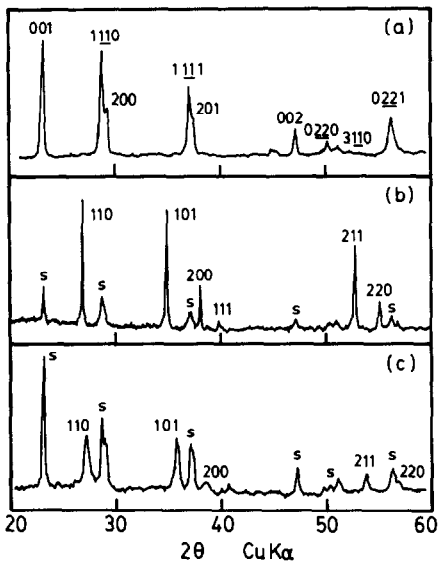
FIG. 1. X-ray powder diffraction pattern. (a) Starting material of the low-temperature form β-Ta_2O_5 (indexed on orthorhombic cell). (b) Rutile-type $Ta_{0.97}O_2$ reduced by shock-loading to 60 GPa (indexed on tetragonal cell) s; starting material. (c) Cation-deficient rutile $Ta_{0.8}O_2$ obtained by subsequent oxidation of shock-reduced product.

analysis and simultaneous thermogravimetry (TG) and thermal differential analysis (DTA), respectively.

Experimental

Starting materials were powder specimens of reagent grade Ta_2O_5 (99.99%) obtained from Rare Metallic Company. The diffraction pattern of the starting material (Fig. 1a) was that of the low temperature form of β-Ta_2O_5 (7, 8). A powder specimen was pressed into a pellet of 10-mm diameter and 3-mm thickness by applying a load of 3000 kg/cm^2. Bulk density was found to be 55% of the crystal density. The pellet was encased in a stainless steel container, which was protected from destructive shock effects using a recovery assembly consisting of spalling rings and backing plates (9).

The impact experiments were carried out using a single stage propellant gun capable of accelerating a 20-g projectile to 2.4 km/sec (10). The specimen container was impacted by a 3-mm-thick flyer plate made of stainless steel, which was glued on the front surface of the plastic projectile. The maximum pressure attained in the specimen container was estimated from the measured projectile velocity on the basis of impedance match concept (1). The shocked state in the specimen was considered to be rapidly equilibrated with that of the specimen container via multiple shock reflections between specimen and container interfaces.

The recovered specimen was examined by X-ray diffraction analysis using a diffractometer with Cu$K\alpha$ radiation (Ni filtered). Oxidation experiments of the shock recovered specimen were carried out in an oxygen atmosphere up to 1200°C by means of TG and DTA.

Results

The specimen recovered from shock-loading at 50 to 60 GPa was black, suggesting that reduction took place. X-ray diffraction analysis revealed that the shocked specimen was partially converted to a new phase with the rutile structure (Fig. 1b). No appreciable contamination from the container was noted after careful magnetic separation. The maximum yield of the rutile phase was estimated to be about 70%. Only impact runs which the specimen container was breached were successful, indicating that escape of released O_2 was essential for the completion of shock reduction. When the shocked specimen was completely confined in the container, no rutile phase remained, which is interpreted as recombination of O_2 with the once reduced specimen in the shock-released high temperature state. These observations indicate that the reduction is caused by partial dissociation

TABLE I

Observed and Calculated d Spacings of Shock-Reduced and Subsequently Oxidized Tantalum Oxides with the Rutile Structure

	$Ta_{0.97}O_2{}^a$			$Ta_{0.8}O_2{}^b$		
$h\,k\,l$	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I
1 1 0	3.359	3.360	vs	3.301	3.299	vs
1 0 1	2.589	2.589	vs	2.543	2.543	vs
2 0 0	2.376	2.376	m	2.333	2.333	m
1 1 1	2.272	2.274	w	2.233	2.233	w
2 1 1	1.7502	1.7506	s	1.7191	1.7190	s
2 2 0	1.6797	1.6800	m	1.6507	1.6495	m
0 0 2	1.5435	1.5439	w	1.5165	1.5166	w
3 1 0	1.5023	1.5027	w	1.4752	1.4754	w
3 0 1	1.4095	1.4093	w	1.3832	1.3839	w
1 1 2	1.4031	1.4029	w	1.3782	1.3778	w
2 0 2	1.2946	1.2946	w			
3 2 1	1.2124	1.2121	w			

$a = 4.7518(5)$ Å	$a = 4.666(1)$ Å
$c = 3.0878(4)$ Å	$c = 3.033(1)$ Å
$c/a = 0.6498(1)$	$c/a = 0.6501(2)$
$V = 69.72(1)$ Å³	$V = 66.02(3)$ Å³

^{a} Shocked to 60 GPa.
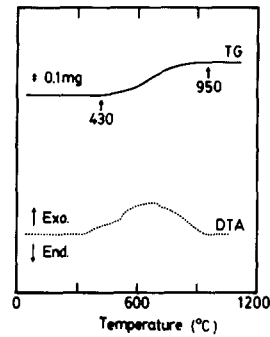^{b} Oxidized in an oxygen gas flow to 1200°C.

FIG. 2. Record of thermogravimetry (TG) and differential thermal analysis (DTA) of shock-reduced product. Heating rate is 15°C/min. Arrows indicate onset and completion of oxidation process.

of Ta_2O_5 upon shock-loading, and not due to presence of the metallic container.

All reflections other than those of the starting material (low temperature form of Ta_2O_5) were assigned to the rutile structure with tetragonal indices, as shown in Table I. Unit cell parameters of the tantalum oxide with the rutile structure were determined to be $a = 4.7518(5)$ Å, $c = 3.0878(4)$ Å, $c/a = 0.6498(1)$, and $V = 69.72(1)$ Å³. Cell parameters were found to be reproducible in several different run products.

For the purpose of determination of the chemical composition of the shock-converted tantalum oxides, simultaneous TG and DTA were performed. About 20 mg of the shocked specimen was heated at 15°C/min to 1200°C in an oxygen gas flow and the increase in weight was measured. A typical example of TG and DTA results is reproduced in Fig. 2. Gradual increase in weight started at 430°C and was completed at about 950°C, being accompanied by a broad exothermic signal in DTA. Since complete conversion to the rutile form was not attained in the present experiment, apparent volume fraction (x) of the rutile form produced by shock-loading relative to the starting material was estimated from the measured area of the diffraction profiles of the rutile (110) and β-Ta_2O_5 (001) lines. The weight increase measured for several shocked specimens with different degrees of conversion to the rutile form was plotted against x in Fig. 3. The chemical composition of pure tantalum oxide with the rutile structure, estimated from the weight in-
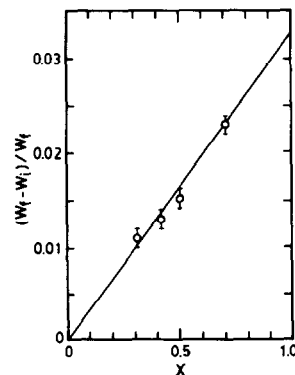

FIG. 3. Relation between weight increase obtained by thermogravimetry and apparent volume fraction x of rutile form TaO_2 ($x = TaO_2/(TaO_2 + Ta_2O_5)$). W_i and W_f are initial and final values of weight.

TABLE II

Comparison between Unit Cell Parameters of Tantalum Oxides and the Rutile Structure
Prepared by Various Methods

Composition	$a(\text{Å})$	$c(\text{Å})$	c/a	$V(\text{Å}^3)$	Method of preparation	Reference
"TaO$_2$"[a]	4.709	3.065	0.651	67.96	Oxidation of TaC	Schönberg (6)
"TaO$_2$"[a]	4.721	3.078	0.652	68.60	Reaction of tantalum with CuO	Terao (7)
Ta$_{0.83}$O$_2$	4.768	3.069	0.644	69.77	Shock reduction	Breusov et al. (5)
Ta$_{0.97}$O$_2$	4.7518	3.0878	0.6498	69.72	Shock reduction	Present study
Ta$_{0.8}$O$_2$	4.666	3.033	0.6501	66.02	Oxidation of shock-reduced product	Present study

[a] Composition was not given.

crease extrapolated to $x = 1$, is Ta$_{0.97\pm0.04}$O$_{2.00}$, indicating near-stoichiometry of quadrivalent tantalum.

X-ray diffraction analysis of the specimen heat-treated to 1200°C in an oxygen gas flow revealed that the shock-converted tantalum oxide was metastably oxidized to Ta$_2$O$_5$ composition, keeping the rutile structure as shown in Fig. 1c. The volume fraction x was found to be conserved during oxidation, i.e., apparent decrease in peak height is compensated by line broadening. The unit cell parameters of the metastable Ta$_{0.8}$O$_2$ with the rutile structure were determined to be $a = 4.666(1)$ Å, $c = 3.033(1)$ Å, $c/a = 0.6501(2)$, and $V = 66.02(3)$ Å^3, showing considerable volume decrease as a result of omission of a fifth of tantalum atoms from the rutile structure.

No significant change was noticed in the position of diffraction lines of coexisting β-Ta$_2$O$_5$, unreacted starting materials, in either the shock reduction or the subsequently oxidized specimens.

Discussion

In Table II, tetragonal unit cell parameters of "TaO$_2$" with the rutile structure prepared by various methods are summarized. Unit cell parameters obtained in the present study are comparable to those of Breusov et al. using a similar shock reduction technique (5): We find a is slightly smaller, and c is slightly larger, but there is excellent agreement for the unit cell volume. However, considerable disagreement is noticed for the metal to oxygen ratios. The reported composition of Ta$_{0.83}$O$_2$ by Breusov et al. (4) strongly deviates from stoichiometry and is rather close to that of the cation deficient rutile Ta$_{0.8}$O$_2$ metastably prepared by heat treatment in an oxygen gas flow in the present study, while the unit cell parameters of the latter are much smaller than those of the former. Unfortunately no detailed description as to the determination of the chemical composition of the shock-treated specimen was given by Breusov et al. (5).

Adadurov et al. (3) reported to have prepared a variety of lower oxides of niobium with the rutile or rutile-related structure, whose compositions were claimed to range from NbO$_{2.003}$ to Nb$_{0.83}$O$_2$. However, cell volumes (normalized for two formula units) of these compounds had only very small differences, in spite of wide distribution in compositions, which is rather unlikely. Reexaminations of shock-reduced products of "NbO$_2$" are necessary to settle these problems.

Unit cell parameters of the rutile form "TaO$_2$" prepared by oxidation of TaC or reaction of tantalum with CuO are found to fall between the values for Ta$_{0.97}$O$_2$ and Ta$_{0.8}$O$_2$ obtained in the present study, indicating intermediate average valence states between Ta(IV) and Ta(V). This suggests existence of a complete solid solution between TaO$_2$ and Ta$_{0.8}$O$_2$ with the rutile structure. The X-ray densities of Ta$_{0.97}$O$_2$ and Ta$_{0.8}$O$_2$ are computed to be 9.884 and 8.890 g/cm^3, respectively. The X-ray density obtained for β-Ta$_2$O$_5$ is 9.045 g/cm^3 (7), which is comparable to that of the cation-deficient rutile Ta$_{0.8}$O$_2$ and much smaller than that of the stoichiometric rutile TaO$_2$.

The ionic radius r for the octahedral Ta^{4+} ion is estimated to be 0.68 Å, using the unit cell volume versus effective ionic volume (r^3) for the rutile structure (11), which is in agreement with that obtained by Shannon using systematics for ionic radius vs oxidation state (12).

Acknowledgments

References

1. R. G. McQueen, S. P. Marsh, J. W. Taylor, J. N. Fritz, and W. J. Carter, "High-Velocity Impact Phenomena" (R. Kinslow, Ed.), p. 293, Academic Press, New York, 1977.
2. B. Morosin and R. A. Graham, "Shock Waves in Condensed Matter—1981" (W. J. Nellis, L. Seaman, and R. A. Graham, Eds.), p. 4, AIP Conference Proceedings, No. 78, 1982.
3. S. S. Batsanov, "Shock Waves in Condensed Matter—1981" (W. J. Nellis, L. Seaman, and R. A. Graham, Eds.), p. 14, AIP Conference Proceedings, No. 78, 1982.
4. G. A. Adadurov, O. N. Breusov, A. N. Dremin, V. N. Drobyshev, A. I. Lazarev, and S. V. Pershin, Dokl. Akad. Nauk USSR 202, 864 (1972); Dokl. Phys. Chem. Engl. Trans. 202, 89 (1972).
5. O. N. Breusov, A. N. Dremin, V. N. Drobyshev, and S. V. Pershin, Russ. J. Inorg. Chem. 18, 157 (1973).
6. N. Schönberg, Acta Chem. Scand. 8, 240 (1954).
7. N. Terao, Japan J. Appl. Phys. 6, 21 (1967).
8. R. S. Roth, J. L. Waring, and H. S. Perker, J. Solid State Chem. 2, 445 (1970).
9. Y. Syono, T. Goto, Y. Nakagawa, and M. Kitamura, "High-Pressure Research: Application in Geophysics" (M. H. Manghnani and S. Akimoto, Eds.), p. 477, Academic Press, New York, 1977.
10. Y. Syono and T. Goto, "Shock Waves in Condensed Matter—1981" (W. J. Nellis, L. Seaman, and R. A. Graham, Eds.), p. 701, AIP Conference Proceedings, No. 78, 1982.
11. R. D. Shannon, Solid State Commun. 6, 139 (1968).
12. R. D. Shannon, Acta Crystallogr. Sect. A 32, 751 (1976).