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# Formation of Rutile-type $Nb_{0.94}O_2$ by Shock Reduction of $Nb_2O_5$

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Shock-recovery experiments on $Nb_2O_5$ powder specimens are made in pressure ranges up to 50 GPa using the gun method. "$NbO_2$" with the rutile structure is formed above about 40 GPa when an open recovery fixture is used. The tetragonal unit cell dimensions are measured to be $a = 4.784(2)$ Å, $c = 3.029(2)$ Å, and $V = 69.34(6)$ Å$^3$. The metal-to-oxygen ratio is determined to be $Nb_{0.94}O_2$ by means of thermogravimetry. A comparative study is made on the shock reduction behavior of $Nb_2O_5$ and $Ta_2O_5$. © 1986 Academic Press, Inc.

## Introduction

The niobium–oxygen system has been rather extensively studied for a wide temperature region (*1–3*). Numerous polymorphs of $Nb_2O_5$ have been recognized and several discrete phases have been identified between $Nb_2O_5$–$NbO_2$. $NbO_2$, among others, can also be prepared either by reduction of $Nb_2O_5$ (*3*) or by oxidation of niobium metal (*4*). Even a single crystal of $NbO_2$ was grown by chemical vapor transport (*5*), indicating that the quadrivalent state of niobium ions is relatively stable.

Shock-reduction technique has also been proved to be efficient in obtaining lower oxides of transition metal ions (*6–8*). We observed formation of $TaO_2$ with the rutile structure from $Ta_2O_5$ by applying an intense shock wave to powder specimens (*8*). The synthesis of rutile-type niobium oxides has also been reported by Russian investigators (*6*); they claimed the existence of several rutile polymorphs with different compositions.

In the present study, a reexamination of shock behavior of niobium oxides was planned so as to obtain further information on shock-reduced specimens.

## Experimental

Powder specimens used for shock-loading experiments were guaranteed reagent grade $Nb_2O_5$, which was found to be in the low-temperature form T–$Nb_2O_5$ (*1*) by means of X-ray diffraction analysis (Fig. 1a). Specimens were formed into a pellet form (10 × 3 mm) by applying a load of 3000 kg/cm$^2$. The density of the pellet was about 70% of the crystal density. The pellet specimen was encased in a stainless steel specimen container, which was protected by a conventional momentum trap so as to prevent the destructive effect of shock waves. Small vents were placed in the specimen

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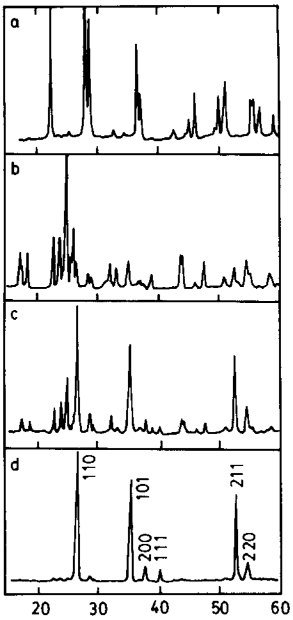

FIG. 1. X-Ray powder diffraction pattern of niobium oxides. (a) Starting material of low-temperature form T-$Nb_2O_5$. (b) Specimen shocked to 37 GPa. (c) Specimen shocked to 44 GPa. (d) Specimen shocked to 53 GPa. Diffraction lines due to the rutile form $Nb_xO_2$ are indexed with tetragonal indices.

container to allow the escape of oxygen produced by decomposition reaction.

Shock-loading experiments were carried out by using a single-stage propellant gun (25 mm bore and 4 m length) (*9*). The specimen container was hit by a stainless steel flyer (24 mm diameter and 3 mm thickness), which was accelerated to a velocity of up to 2.1 km/sec. The velocity was determined by embedding a small magnet in the flyer assembly and measuring the time of flight between two coils placed ahead of the gun muzzle. The pressure was determined by the value achieved in the stainless steel container, estimated on the basis of impedance matching.

Recovered products were examined by X-ray powder diffraction analysis to identify the shock-induced phases using monochromatic Cu $K\alpha$ radiation. The specimen was analyzed by thermogravimetry and differential thermal analysis to determine the chemical composition. Thermal analysis was made in a flowing oxygen gas at constant or increasing temperature. Special care was taken to remove ferroalloy impurities introduced during shock loading by immersing the specimen in HCl solution for a few days. The residual iron impurity was determined to be below 0.1% by wet chemical analysis.

## Results

The first sign of a phase change in shocked $Nb_2O_5$ was observed above about 30 GPa. X-Ray powder diffraction of the shocked product showed it to be mostly the $Nb_{12}O_{29}$ phase with orthorhombic symmetry (Fig. 1b) (*10*). Above about 40 GPa, indication of another new phase, assigned to the rutile structure type, was noticed in the X-ray powder diffraction pattern (Fig. 1c); complete conversion was attained above about 50 GPa, as shown in Fig. 1d. Most of the diffraction lines were successfully assigned on the basis of the tetragonal unit cell, as summarized in Table I. The unit cell dimensions were determined to be $a$ = 4.784(2) Å, $c$ = 3.029(2) Å, $c/a$ = 0.6331(5), and $V$ = 69.34(6) Å$^3$ by the least-squares method. For comparison purposes, the unit cell dimensions of a stoichiometric specimen of $NbO_{2.002}$, offered by S. Kimura, were also measured and tabulated in Table I (*3*).

Results of thermogravimetry to determine the chemical composition of the rutile form $Nb_xO_2$ are shown in Fig. 2. When the temperature was increased at a constant rate of 5°C/min, the weight increase due to oxidation became very noticeable above 700°C, and nearly zero around 1100°C (Fig. 2a). The oxidation product was found to be $Nb_{12}O_{29}$ by X-ray powder diffraction analysis. The orthorhombic unit cell dimensions were determined to be $a$ = 28.78(2) Å, $b$ =

TABLE I

OBSERVED AND CALCULATED *d* SPACINGS OF SHOCK-REDUCED $Nb_{0.94}O_2$ AND STOICHIOMETRIC $NbO_{2.002}$

| | $Nb_{0.94}O_2$ | | $NbO_{2.002}$[a] | |
|---|---|---|---|---|
| *h k l* | $d_{obs.}$ (Å) | $d_{calc.}$ (Å) | $d_{obs.}$ (Å) | $d_{calc.}$ (Å) |
| 1 1 0 | 3.383 | 3.383 | 3.433 | 3.429 |
| 1 0 1 | 2.560 | 2.559 | 2.548 | 2.548 |
| 2 0 0 | 2.395 | 2.392 | 2.424 | 2.425 |
| 1 1 1 | 2.258 | 2.257 | 2.257 | 2.256 |
| 2 1 1 | 1.748 | 1.748 | 1.7567 | 1.7566 |
| 2 2 0 | 1.690 | 1.692 | 1.7148 | 1.7145 |
| 3 1 0 | 1.512 | 1.513 | 1.5337 | 1.5335 |
| 0 0 2 | | 1.515 | 1.4974 | 1.4975 |
| 3 0 1 | 1.412 | 1.411 | 1.4221 | 1.4225 |
| 1 1 2 | 1.384 | 1.382 | 1.3724 | 1.3723 |
| | $a = 4.785(2)$ Å | | $a = 4.8494(5)$ Å | |
| | $c = 3.029(2)$ Å | | $c = 2.9949(3)$ Å | |
| | $c/a = 0.6331(5)$ | | $c/a = 0.6176(1)$ Å | |
| | $V = 69.34(6)$ Å$^3$ | | $V = 70.43(2)$ Å$^3$ | |

[a] Synthesized by S. Kimura (*3*).

3.825(2) Å, $c = 20.661(1)$ Å, and $V = 2274(2)$ Å$^3$, in good agreement with the previously reported values (*10*). The chemical composition of the rutile form $Nb_xO_2$ thus determined was $x = 0.94$. On the other hand, when the specimen was held at constant temperature of 850°C, the weight increase was saturated after a lapse of 6 hr, indicating completion of the oxidation process (Fig. 2b). The final product was found to be B-$Nb_2O_5$ (*11*). The chemical composition of the rutile form $Nb_xO_2$ was again estimated to be $x = 0.94$.

## Discussion

The tetragonal unit cell volume of $Nb_{0.94}O_2$ obtained by shock reduction in the present study is significantly smaller than that of the stoichiometric $NbO_{2.002}$ synthesized in a reducing atmosphere (*3*). The dimension of *a* of the former is considerably smaller than that of the latter, while *c* is unchanged, thus resulting in a sizeable increase in the *c*/*a* ratio. The unit cell dimensions as well as the chemical composition of the shock-reduced rutile were found to be quite reproducible for relatively wide shock-loading conditions, in contrast to previous observation by Adadurov *et al.* (*6*), who claimed formation of a series of rutile-type compounds with different metal-to-oxygen ratios, i.e., from $NbO_{2.003}$ to $Nb_{0.83}O_2$. However, in spite of a seemingly systematic variation of the unit cell dimension of *a* and *c* with the composition, they observed only a very small difference in the unit cell volume normalized for two formula units. This is rather difficult to understand because the difference in the metal-to-oxygen ratio implies a difference in the amount of lattice vacancies, and hence should be reflected as a considerable change in the unit cell volume.

Two different explanations for nonstoichiometry exist in terms of either a metal deficient dioxide or an oxygen-excess

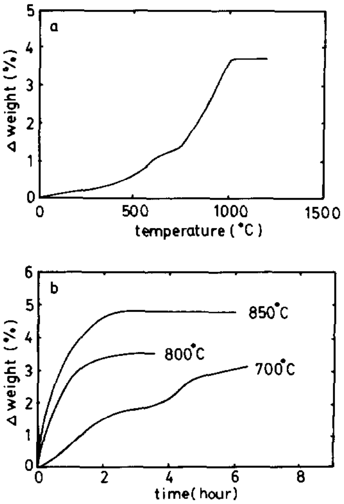

FIG. 2. Results of thermogravimetric analysis of shock-reduced $Nb_xO_2$ with the rutile structure. (a) Mass increase with temperature when the specimen was heated with an increasing rate of 5°C/min in an oxygen gas flow. (b) Mass increase with time when the specimen was kept at a constant temperature in an oxygen gas flow.

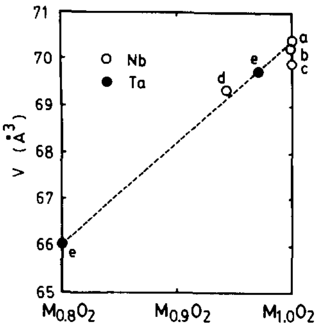

FIG. 3. Variation of the unit cell volume with composition for rutile form $Nb_xO_2$ and $Ta_xO_2$. (a) Kimura (*3*), (b) Adadurov *et al.* (*6*), (c) Terao (*4*), (d) This work, (e) Syono *et al.* (*8*).

rutile. The correct model for niobium dioxide could be established from density measurements. However, these data are not available for the present specimens. We tentatively prefer the metal-deficient model to the anion-excess model because the unit cell volume decreases with increasing nonstoichiometry. This trend has also been clearly demonstrated in tantalum dioxide (*8*). The contrary tendency might be anticipated for the oxygen-excess model. The tetragonal unit cell volume of the rutile form $Nb_xO_2$ and $Ta_xO_2$ is plotted against composition, $x$, in Fig. 3. The composition dependence of the unit cell volume is approximately represented by a straight line, common for both niobium and tantalum oxides of the rutile type. This relationship may be understood in terms of the same ionic radii of $Nb^{5+}$ and $Ta^{5+}$, and presumably, $Nb^{4+}$ and $Ta^{4+}$ (*12*). The observed linear decrease in volume with $x$ should be correlated to the increase in the cationic vacancy.

The shock reduction behavior of niobium and tantalum oxides, is summarized in Table II. In the case of tantalum oxides, shock-reduced rutile phase has a composition close to stoichiometry, although the yield of the rutile phase remains 70% at best. In the course of subsequent oxidation, the rutile form of $TaO_2$ was continually oxidized to $Ta_{0.8}O_2$, with no change in crystal structure.

On the contrary, shock-reduced niobium oxides have greater nonstoichiometry although complete conversion to the rutile phase is generally attained. Oxidation of the rutile phase $Nb_{0.94}O_2$ leads to formation of either $Nb_{12}O_{29}$ or B-$Nb_2O_5$, depending on the heating condition, in contrast to the case of oxidation of $TaO_2$. This discrepancy may be related to a relative difference in reactivity of niobium and tantalum oxides. Because of the high melting point of $Ta_2O_5$

TABLE II

COMPARISON OF SHOCK-REDUCTION BEHAVIOR OF $Nb_2O_5$ AND $Ta_2O_5$

| Starting materials | Shock reduction<br>Intermediate | <br>Final products (50 ~ 55 GPa) | Products of subsequent oxidation in $O_2$ |
|---|---|---|---|
| T-$Nb_2^VO_5$ | $Nb_{12}O_{29}$<br>~40 GPa | Rutile<br>$Nb^{IV}_{0.94}O_2$<br>$V = 69.34$ Å$^3$<br>Yield = 1.0 | $Nb_{12}O_{29}$: heating rate 5°C/min, ~1200°C<br>B-$Nb_2^VO_5$: kept at 850°C for 6 hr |
| $\beta$-$Ta_2^VO_5$ | — | Rutile<br>$Ta^{IV}_{0.97}O_2$<br>$V = 69.72$ Å$^3$<br>Yield = 0.7 | Rutile: $Ta^V_{0.8}O_2$;<br>$V = 66.02$ Å$^3$; heating rate 15°C/min, ~1200°C |

(1870°C), oxidation temperature up to 1100°C would be insufficient to reconstruct a more stable crystal structure associated with the valence change from $Ta^{4+}$ to $Ta^{5+}$. This explains why the shock-reduced rutile $Ta_{0.97}O_2$ has been oxidized to $Ta_{0.8}O_2$ without change in crystal structure. However, in the case of niobium oxides, oxidation treatment up to 1100°C, or even at 850°C in the thermogravimetry experiment at constant temperature, seems sufficient for changing the crystal structure from rutile to $Nb_{12}O_{29}$ or B–$Nb_2O_5$, respectively, probably due to a higher reactivity as revealed by the lower melting point of $Nb_2O_5$ (1490°C).

The mechanism that leads to the fast reduction of $Nb_2O_5$, accompanied by oxygen release during a short duration of shock is not yet established. Recently we observed a similar shock reduction of $Nb_2O_5$ single crystal to the rutile form $Nb_xO_2$. Shock temperatures in the case of single crystals should be much lower than for the powder specimens because of zero porosity (*13*). This strongly suggests that shock reduction is essentially related to the shock-loading or -unloading processes, rather than simply to high-temperature effects. The decomposition reaction in the decompression stage, which was observed in vanadium hydride and deuteride (*14*), might have some relevance to the decomposition reactions observed in transition metal oxides under shock processes.

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