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Isomorphous Oxidation of Sodium Titanium Dioxide Bronze

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Sodium titanium dioxide bronze is oxidized into a white and nonstoichiometric compound isostructural with itself by being heated upto about 890 K in air. The oxidation means that dioxide bronze converts into a sodium titanate with only a tetravelent state for the Ti ion, retaining the Na_xTiO_2-type structure. The conversion is accompanied by a shrinkage in unit cell volume and a decrease in density. Vegard's law is clearly applicable to the lattice parameters of the oxidized form as well as the dioxide bronze, and the extrapolation of the composition dependency curves of the oxidized form gives the lattice parameters of the new TiO_2 polymorph (R. Marchand, L. Brohan, and M. Tournoux, *Mater. Res. Bull.* **15,** 1129 (1980)). The oxygen uptake also shows a composition dependency proportional to sodium content, and the observed amounts are about 16% less than the theoretical values or a half of Na or Ti^{3+} content in the ideal chemical formula of $Na_xTi_x^{3+}Ti_{8-x}^{4+}O_{16}$. This difference will be discussed on the basis of the estimated chemical formulae of these two phases. © 1986 Academic Press, Inc.

Introduction

Sodium titanium dioxide with a chemical formula of Na_xTiO_2 ($x \leqq 0.25$) or $Na_xTi_8O_{16}$ ($x \leqq 2$) is one of the bronze-type compounds. The bronze has a layered host lattice consisting of TiO_6 octahedra of which Ti/O ratio is 1/2, and eight molecules of TiO_2 are contained in a unit cell (*1*). If a fraction of Ti ions is reduced, then a resultant net charge on the host lattice becomes negative and the other cations like Na^+ are incorporated into interstitial sites so as to neutralize the residual negative charge. It implies the formation of the bronze-type compound of $Na_xTi_x^{3+}Ti_{8-x}^{4+}O_{16}$ in principle. The first preparation of the dioxide bronze was carried out by the reduction of $Na_2Ti_3O_7$ in hydrogen (*1*). Afterwards an empirical nonstoichiometric range of sodium was determined by solid-state reactions of $Na_2Ti_3O_7$, TiO_2, and Ti under low pressure (*2*). The bronze is blue–black in color as expected for trivalent titanium ions in the chemical formula. On this subject, Reid and Sienko (*2*) reported that the compound gave an electronic spectral absorption supporting delocalization of *d* electrons of Ti^{3+} ions and also relatively high electronic conductivity. When Ti ions are all tetravalent, the host lattice has the neutral net charge and requires no interstitial cations, that is, $x = 0$ in the above chemical formula. This situation was realized as the new TiO_2 polymorph prepared through hydrolysis of $K_2Ti_4O_9$ followed by heating (*3*), which was white in color due to no Ti^{3+} content. On the other hand, it was recently found that hydrothermal reactions of TiO_2 gel with NaOH yielded two kinds of compounds isostructural with the dioxide bronze (*4, 5*). These Na_xTiO_2 isomorphous products were

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white in spite of containing a considerable amount of Na ions as indicated by their thermal decomposition into rutile and hexatitanate. So far, no satisfactory interpretations have been given on the nature of these white hydrothermal products.

Watanabe and Fujiki (*6*) prepared sodium and potassium titanium dioxide bronzes by heating mixtures of TiO_2 and alkali carbonate in hydrogen. In their work, blue–black dioxide bronzes were observed to be oxidized into white materials isostructural with themselves by heating in air. This gave an important clue on understanding the above white hydrothermal products. In this paper, therefore, these oxidized forms of dioxide bronze are characterized by thermal analyses, X-ray diffraction techniques, chemical analyses, and so on. This oxidation phenomenon is explained on the basis of chemical formulae and the chemical relation between blue–black and white isomorphous phases is discussed.

In this text, there appear three phases isomorphous with each other which are coupled by oxidation as retaining the Na_xTiO_2-type crystal structure. We conveniently designate these phases B, I, and W, in order with an increasing oxidation degree: for example B phase and B compound.

Experimental

Sodium titanium dioxide bronze which was synthesized according to the previous method (*6*) was used as the starting compound.

DTA–TG analyses were performed in air over the temperature range of 288 to 1273 K using about 100 mg of each sample previously dried at 523 K and α-Al_2O_3 as a reference material. I and W compounds, obtained by oxidation before the decomposition into rutile and hexatitanate, were cooled to room temperature, and weighed in order to confirm an increment in a TG curve and identified by X-ray powder diffraction technique. Lattice constants of the two phases were calculated by applying the least-squares program (*7*) to reflection data collected in the 2θ range of 10 to 60°($CuK\alpha$) as the internal standard of rutile. Data collection was made by a 2θ–θ scanning method with a scan rate 0.125°/min. Densities were determined by measuring the bouyance acting on 500 to 800 mg of powder in CCl_4 at 293 K. The accuracy and precision of the density by this method was checked by measuring silicon powder, resulting in 2.331 ± 0.003 at 293 K for four independent measurements. On the other hand, the precision for the present compounds was within ± 0.005.

Chemical analyses of Na and Ti in B and W compounds were performed by atomic absorption spectrometry and weighing a metal–cupferron precipitate, respectively. Samples were washed in advance with dilute hydrochloric acid to remove sodium ions isolated, if any. The analytical error was ±0.1% for Ti and ±0.5% for Na. Hydrogen contents of W compounds were semiquantitatively analyzed by using a high temperature gas chromatograph equipped with a small furnace. A specimen was preheated for 15 min at 475 K in argon flow, and successively heated for 10 min at 1353 to 1363 K in argon atmosphere, and then argon gas flow was started again at a rate of 20 ml/min in order to carry its sample gas into a column and a detector of the gas chromatograph. A calibration curve and a retention time were determined by the injection of hydrogen gas under the same conditions. Mass spectrometry was also used for checking gaseous products released while heating from room temperature to about 1500 K.

Isomorphous Oxidation

DTA and TG curves obtained for dioxide bronzes are shown in Fig. 1. The DTA

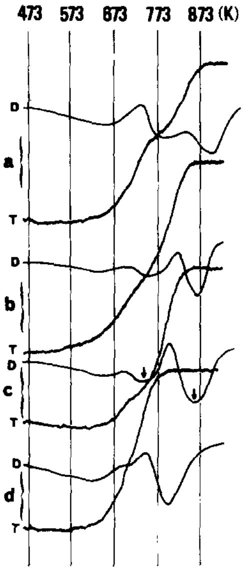

FIG. 1. DTA and TG curves: (a), (b), (c), and (d) were taken for the compounds with 0.181, 0.2, 0.222, and 0.235 in the ratio of Na/Ti, respectively. The exothermic direction is upward and D and T indicate DTA and TG curves, respectively.

curves have two exothermic peaks between 570 and 890 K. Each peak corresponds to an increment in a TG curve. These heat and weight changes were brought about by the oxidation of dioxide bronze. In the Na/Ti ratio less than 0.222, two peaks were clearly separated as displayed in Figs. 1a–c, and an intermediate (I) phase could be isolated by cooling from the temperature between two peaks and a white (W) phase from temperatures higher than the second peak. The second peak seems to make a large approach toward the first one with an increasing cation ratio from 0.222 to 0.235. Near and above 0.235, no I compound could be isolated due to overlapping of the two peaks (see Fig. 1d), but a W compound obtained alone. X-Ray powder patterns in Fig. 2 taken for the bronze with 0.222 and its ashes cooled from the temperatures marked on the DTA curve in Fig. 1c reveal that an isomorphous relation is retained

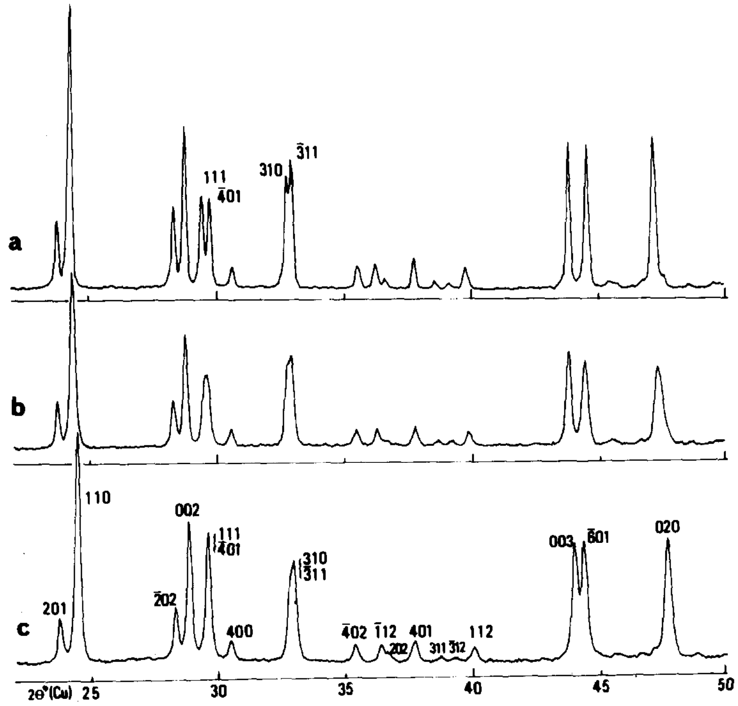

FIG. 2. X-Ray powder diffraction patterns: (a) B, (b) I, and (c) W Phases. They are coupled by oxidation and have the same cation ratio of 0.222.

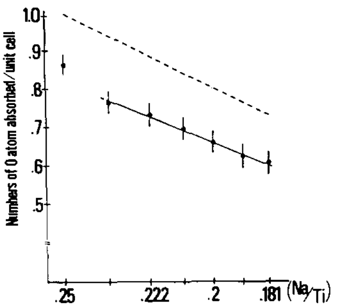

FIG. 3. Oxygen absorption amounts. The solid curve gives the relation of total amounts of oxygen absorbed in the change from B to W phase vs the Na/Ti ratio. The dotted line indicates the theoretical numbers of oxygen absorbed when an ideal chemical formula of $Na_xTi_x^{3+}Ti_{8-x}^{4+}O_{16}$ is perfectly oxidized.

through the oxidation process although a little lattice distortion accompanies it. This relationship was observed over the experimental range from 0.181 to 0.25 in Na/Ti, but it is unknown at the present stage if W phase has a superstructure or not as detected in the hydrothermal products (*5*). Among these phases, B and I phases show blue–black and W phase is white in color.

The oxygen uptake amount was different for every compound and every oxidation step. Total absorption amounts, by which B phase is perfectly oxidized into W phase, were obtained by weighing isolated W compounds and were plotted in Fig. 3. The scatter in uptake amount was less than ±0.03 atom/unit cell for more than three independent measurements.

Lattice Distortion

All of observed reflections could be completely indexed by the known lattice type, *C*2/*m*, and lattice parameters were well refined. The parameters of I and W compounds are plotted in Figs. 4a–e in comparison with those of B compounds. Vegard's law is clearly applicable to the relation between each parameter and the cation ratio. Every phase has the contractions of unit cell volume and *b* axis and an elongation of the c axis with increasing Na content. Only the *a* axis gives opposite trends between white and black phases. In connection with this composition dependency, it is worthwhile to note the lattice constants of the new TiO_2 polymorph (*3*). Its volume and *b* axis are 282.5 Å^3 and 3.735 Å are in fairly good agreement with 282.7 Å^3 and 3.740 Å obtained by extrapolating the above composition dependency curves of the W phase in Fig. 4. Ratios of the observed to the extrapolated values are 0.999, 0.999, 0.998, and 1.004 for *V*, *b*, *a*, and *c*, respectively. Namely, the new polymorph is regarded to be more closely related to W than B phase in structural similarity.

Density and Analytical Results

As to the oxidation couples of B and W compound, the latter has always a smaller volume than the former. Considering the

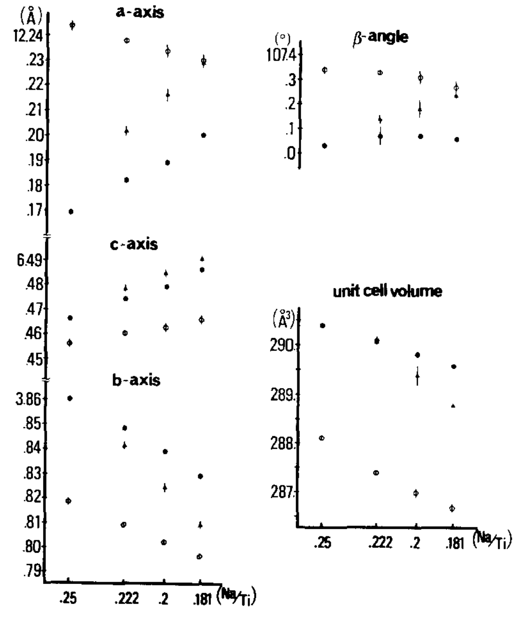

FIG. 4. Composition dependency of lattice parameters: open circles, W phase; triangles, I phase; dark circles, B phase. Small bars indicate standard deviations.

uptake of oxygen in the phase change, the volume contraction attracts our attention. In this regard, observed densities are compared in Table I among W, I, and B phases with the same cation ratios, and in Table II, Na and Ti contents are shown for three couples of W and B phases. The volume contraction makes us expect an increase in density due to oxygen absorption. The fact, however, gave about 2.6% decreasing as shown in the table. According to Table II, the Ti content in W phase is significantly less than that in the corresponding B phase and Na seems to have a similar trend, too, but the differences are not more than the analytical error. As a result, a cation ratio appears to remain almost equal to the initial value throughout the phase change.

By the high-temperature gas chromatography, B compounds were estimated to contain a trace amount to about 0.25 hydrogen atom per unit cell at the maximum, which had an increasing tendency with a decreasing Na/Ti ratio (*6*). In comparison with the B phase, the W phase was found to contain a negligible small amount of hydrogen. On the other hand, mass spectra measured as heating W compounds upto about 1300 K displayed slight increases at the mass numbers 17 and 18 in the temperature range of 600 to 700 K, which were not observed at all for B compounds. Notably, the W compound with 0.181 showed the most remarkable water emission among them. Accordingly, most of the hydrogen atoms in B phase are inferred to escape as the water molecules in the oxidation process, in particular, into the I phase. It should be noted that the release of water molecules has no effect on real weight changes. In this paper, therefore, hydrogen is not put down in B phase formulae for simplification.

TABLE I

COMPARISON OF OBSERVED DENSITIES AMONG THREE PHASES COUPLED BY OXIDATION

	Phase		
Na/Ti	B	I	W
0.222	3.847	3.834	3.749
0.181	3.831	3.800	3.735

TABLE II

Ti AND Na CONTENTS

	Phase	
Na/Ti	B	W
0.25	55.7	54.8
	6.5	6.5
0.2	56.5	55.4
	5.7	5.6
0.181	56.8	55.8
	5.0	4.9

Discussions

The change of B to W phase is considered to be a system conversion of Na_2O–Ti_2O_3–TiO_2 to Na_2O–TiO_2 as basically retaining the Na_xTiO_2-type structure. In principle, the number of oxygen absorbed is correlated to the Ti^{3+} content in the B phase. When the phase includes a formula

TABLE III

ESTIMATED AND IDEAL CHEMICAL FORMULAE OF B AND THE CORRESPONDING W COMPOUNDS

Na/Ti	Chem. formula (estimated)	Chem. formula (ideal)	d_c
0.222	$Na_{1.75}Ti_{7.89}O_{15.91}$	$Na_{1.77}Ti_8O_{16}$	3.891
	$Na_{1.66}Ti_{7.48}O_{15.79}$	$Na_{1.68}Ti_{7.58}O_{16}$	3.800
0.181	$Na_{1.44}Ti_{7.92}O_{15.96}$	$Na_{1.45}Ti_8O_{16}$	3.855
	$Na_{1.37}Ti_{7.53}O_{15.75}$	$Na_{1.39}Ti_{7.65}O_{16}$	3.789

Note. Upper and lower formulae for B and W phase, respectively.

of $Na_xTi_x^{3+}Ti_{8-x}^{4+}O_{16}$ in a unit cell, the theoretical uptake amount should be a half of x, which is illustrated in Fig. 3. The observed amounts, however, are about 16% less than the theoretical. As further oxidation has not been detected, it is suggested that the Ti^{3+} content in the starting B phase would be actually less. This oxidation phenomenon, therefore, is discussed below on the basis of estimated chemical formulae. It is worthwhile to note the density lowering (~2.6%) from the B to the W phase. Provided that the present measured densities imply the true crystallographic densities within the experimental deviation as confirmed for Si powder, the lowering can be regarded to be due to an escape of some components from each unit cell. The above analytical data do not show an isolation of only Na or Ti with respect to this density decrement. Therefore, assuming (1) charge neutrality, (2) content of only Ti^{4+} for Ti ions, and (3) constant Na/Ti ratio throughout oxidation, chemical formulae are derived for the W compounds with 0.222 and 0.181 whose densities were known. The formulae obtained (Table III) are $Na_{1.66}Ti_{7.48}O_{15.79}$ and $Na_{1.37}Ti_{7.53}O_{15.75}$, corresponding to 1/9 and 1/11 in Na_2O/TiO_2 ratio, respectively. The precision of composition is mainly dependent on density and unit cell volume. In this case, these were ± 0.005 for density and ± 0.2 for volume, converted to ± 0.03 in composition. Then they are compared with the corresponding B phase formulae in Table III which were obtained using the Ti^{3+} contents from real oxygen absorption numbers. Each unit cell in the B phase is seen to release small amounts of Na, Ti, and O as the excess atoms in the change to a W phase cell; for example 0.09 Na, 0.41 Ti, and 0.12 O from $Na_{1.75}Ti_{7.89}O_{15.91}$ to $Na_{1.66}Ti_{7.48}O_{15.79}$. Unless these released ions are separated as the other compounds, they must be converted to a final W phase composition. This conversion can be formulated as

$$Na_{0.09}Ti_{0.41}O_{0.12} + 0.37O_2^{ex} \rightarrow \sim 1/18.3[Na_{1.66}Ti_{7.48}O_{15.79}].$$

Similarly, the following equation is given for the other pair:

$$Na_{0.07}Ti_{0.39}O_{0.21} + 0.30O_2^{ex} \rightarrow \sim 1/19[Na_{1.37}Ti_{7.53}O_{15.75}].$$

The terms "O_2^{ex}" represent oxygen numbers per unit cell which must be externally supplied in order to convert the excess atoms into a desired W phase composition. In other words, the equations mean that an additional unit cell of the W phase is newly formed from excess atoms excluded by about 20 unit cells and oxygen atoms externally supplied (ex. $0.37O_2 \times \sim 20$ unit cells). These calculated values of O_2^{ex} are in good agreement with the total amounts of oxygen actually absorbed (see Fig. 3). This consistency shows that the estimated chemical formulae can explain a composition conversion between B and W phase as the other important aspect of the oxidation phenomenon.

Comparing the estimated compositions of B phase and the ideal chemical formula of $Na_xTi_8O_{16}$, for instance, $Na_{1.75}Ti_{7.89}O_{15.91}$ and $Na_{1.77}Ti_8O_{16}$, the present bronze includes vacancies on 1.0 to 1.5% and 0.2 to 0.6% of Ti and O sites, respectively. This composition deviation is inferred to be attributable to preparation conditions such as calcination temperature, hydrogen flow rate, starting material species, and so on, i.e., to depend on kinetic factors related to these conditions. On the other hand, vacancies in W phase extend to 6.0–6.5% and 1.3–1.6% for Ti and O sites, respectively, which can be divided into two kinds: the vacancies which came into from the original B phase; and those newly introduced in order to retain the same type structure framework in the phase change. The present analysis of oxidation process suggests that even if the starting *B* phase contains no vacancies to keep the formula of

$Na_xTi_8O_{16}$, the second type vacancies still occur in its W phase.

The occurrence of W phase suggests that the Na_xTiO_2 isomorphous hydrothermal products (*4*) are not of bronze, but like the W phase. Simultaneously, it gives a reason appropriate for the white color of the products. In contrast with a series of stoichiometric titanates having a general chemical formula $Na_2Ti_nO_{2n+1}$ (n: integer), the W phase which ranges from 8 to 11 in n is probably the first nonstoichiometric sodium titanate with only a tetravalent state for Ti. In the above composition range, nonatitanate $Na_2Ti_9O_{19}$ was hydrothermally prepared as a stoichiometric compound (*8*). Its crystal structure is very similar to the Na_xTiO_2 configuration (*9*). The clear difference between the two structures is exhibited by a thin bridging layer interleaved every two Na_xTiO_2 unit cells in nonatitanate. These layers seem to be much looser in comparison with the bronze unit. In fact, the observed density of nonatitanate (3.67) is considerably smaller than that of the dioxide bronze (3.85 in average), and W phase has an intermediate value (3.75). The Na_xTiO_2-type framework normally consists of a linkage of —$[Ti_nO_{2n}]$—, and hence it is unfavorable to that of —$[Ti_nO_{2n+1}]$—. From a crystallographic viewpoint, it may be said that the W phase is a metastable phase in an oxidative decomposition process from the bronze into a system containing a certain normal titanate like nona- or hexatitanate. In this connection, the existence of bridging layers in nonatitanate seems to be suggestive of the stabilization of the W phase whose vacancies make a contribution also by associating mutually and forming local configurations analogous to those in the layer.

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