JOURNAL OF SOLID STATE CHEMISTRY 36, 91–96 (1981).

The Investigation of Sodium Titanates by the Hydrothermal Reactions of TiO_2 with NaOH

MAMORU WATANABE

National Institute for Researche in Inorganic Materials, Namiki 1-1, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

Received December 4, 1979; in revised form March 27, 1980

The hydrothermal reactions of TiO_2 with NaOH were performed in the molar range of Na_2O from 0 to 30% between 250 and 530°C. The compounds obtained were TiO_2 (rutile, brookite, and anatase), $Na_2O \cdot nTiO_2$ ($n = 3$, 4, 6, and 9) and Na_xTiO_2, the formation ranges for which are shown in a reaction diagram. The roles of water in this hydrothermal system are investigated, to discuss the differences among the known and the present reaction diagrams and to raise a reliability of diagrams. From the present reaction diagram, phase relations in the system TiO_2–Na_2O are estimated taking account of direct or indirect actions of hydrothermal water on solid phases.

Introduction

There is a series of sodium–titanium mixed-metal oxides with a general formula $Na_2O \cdot nTiO_2$. Some reports have been made on the phase relations in the binary system, TiO_2–Na_2O (*1–4*). Below 25 mole% Na_2O in those diagrams (*1–3*), only two compounds of hexa($n = 6$)titanate (*5*) and tri($n = 3$)titanate (*6*) were described although $Na_2Ti_4O_9$ ($n = 4$) (*7*), $Na_2Ti_5O_{11}$ ($n = 5$) (*8*), and $Na_2Ti_7O_{15}$ ($n = 7$) (*9*) were produced in other works and recently $Na_2Ti_9O_{19}$ ($n = 9$) (*10*) was hydrothermally prepared. For the usual dry synthetic methods, heating at high temperatures above 900 to 1000°C is required in order to allow Na_2O to react with TiO_2. In such a temperature range, hexa- and trititanates are easily prepared and brought back to room temperature. Therefore, compounds with $n = 4$, 5, 7, and 9 may not be found in those diagrams.

Hydrothermal reactions make it possible for Na ions to attack TiO_2 at temperatures much lower than 900°C. For the purpose of studying a series of sodium titanates, the hydrothermal reactions of TiO_2 with NaOH are available since the products are free from contamination with elements other than hydrogen. The hydrothermal reactions were investigated by Keesmann (*11*) and Wefers (*12*). The former tried to prepare the brookite-type TiO_2 and in the paper reported a reaction diagram of TiO_2 and NaOH within the Na_2O molar range from 0 to 30% below 600°C. On the other hand the latter carried out the reactions below 50 wt% Na_2O and 350°C, but his results were considerably different from the former's because hexa- and trititanates occur even at 200°C and at the very low concentration of Na_2O, respectively, and TiO_2 is produced only below about 3 mole%. The discrepancies are considered to depend mainly on the solubility difference between their

0022-4596/81/010091-06-$0.200/0

starting materials. Both diagrams were given in binary systems without consideration for chemical equilibria among solid phases and solution despite hydrothermal reactions.

In this work, water is specified as a component and the roles of water are investigated to describe the system simply in a binary one and to obtain reliable reaction diagrams, and the differences among the previous and the present reaction diagrams are discussed. In the last section, on the basis of the present reaction diagram, phase relations are estimated with the binary system TiO_2–Na_2O below 530°C taking account of the effects of water on solid phases.

Experimental

X-Ray amorphous titanium dioxide gel was used as a starting material to promote mixing of titanium and sodium ions. The gel was prepared by drying below 50°C a hydrolysis product of titanium(IV) tetraisopropoxide in ice-cold water until the water content became 15 to 25 wt%. The gel and NaOH solvent solution within 6 moles dm^{-3} were charged in one end of Pt or Au capsules (5 mm diameter and 35 to 40 mm length). After an excess cavity in the capsule is squeezed another end is welded while the capsule is held in cold water to prevent vapor loss. The capsules are placed in a Morey-type autoclave with 0.14 dm^{-3} net volume as shown in Fig. 1. Temperatures are controlled within an error of ±2.5°C through two thermocouples, the tips of which are inserted into the wells on the autoclave wall (Fig. la). Pressures were usually developed by pumping water into the autoclave through an air-driven intensifier.

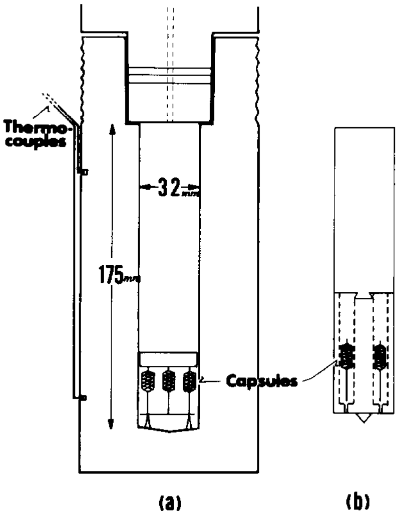

FIG. 1. Autoclave and spacer. The autoclave in (a) is usually used for growing crystals. However, it is useful for performing many reactions at the same time with given T and P. The spacer in (b) is used to reduce an amount of water as a pressure medium and is also effective for decreasing the temperature difference along capsules.

Reaction conditions were give by an empirical factor (α),T,P and C (=$Na_2O/(Na_2O+TiO_2)$ mole%). The α (mg/dm^{-3}) is the ratio of the weight of TiO_2 to the volume of water in a capsule. Usually, 60 mm^3 of water including that in the gel was charged in each capsule, the reaction space of which was about 10 mm in length.

To determine the effect of α in using 60 mm^3 of water, reaction products were systematically checked at 350°C and 65% filling (~46 MPa) and selectively at other temperature. On the basis of these checks, the hydrothermal reactions were performed using α = 800 (or ~48 mg of TiO_2 and ~60 mm^3 of NaOHaq.) in the molar range of Na_2O from 0 to 30% between 250 and 530°C under the pressures corresponding to 65% filling. The constant filling factor was accepted to keep reaction spaces about 10 mm in length at every temperature. Otherwise, an isobaric hydrothermal condition brings about an expansion of reaction space with increasing temperature, resulting in a simple situation in which to induce mass

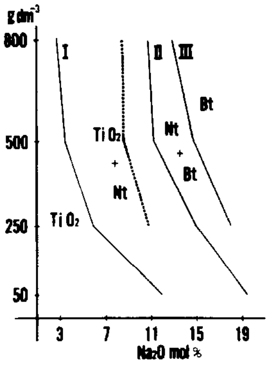

FIG. 2. Shifts of formation ranges with change of α. The reactions were carried out at 350°C and 46 MPa charging ~60 mm^3 of solution in each capsule. Nt = $Na_2Ti_9O_{19}$ and Bt = Na_xTiO_2.

transportation along the thermal gradient. Reaction duration was 10 days at every run and, in some cases, 7 to 30 days. After the desired duration, solvent solutions were ordinarily taken off by releasing an external pressure momentarily to avoid reactions among products and solution during the temperature-decreasing process.

Results

Figure 2 was obtained with the variables α and C after 10 days' duration. After 20 days the dioxide bronze (*13*) began to occur at the lower value of Na_2O shown by the dotted line.

The products obtained between 250 and 530°C after 10 days are shown in Fig. 3. The largest amount of $Na_2Ti_9O_{19}$ (=Nt) is yielded at 10 mole% and the phase is not found below ~3 mole%. In the range from 11 to 13 mole% between 450 and 500°C, there occurs a small quantity of $Na_2Ti_6O_{13}$ (=Ht) in addition to Nt and Na_xTiO_2 (=Bt). In the same temperature range, Ht increases with a decrease of Bt above 14 mole%. $Na_2Ti_3O_7$ (=Tt), which was found at 20 mole%, was produced alone in the molar range from 25 to 30% above ~300°C and at near 30% accompanied by a poorly crystallized phase. Above ~18% at 250°C, tetratitanate (=Tet) is produced with Bt. The titanate had relatively broad peaks in its X-ray powder pattern, but was identified in comparison with the pattern of $K_2Ti_4O_9$ (*14*). Bt is obtained as a monophase between 15 and 17 mole% below ~400°C and in the range from 18 to 22 mole% between 300 and 450°C is accompanied by Nt and Tt. Below 350°C this monophase field is enlarged into the lower percentage up to ~12 mole%. According to the detailed description in (*15*), the Bt field is divided into lower and upper regions by a boundary line along 300 to 350°C. The lower region is occupied by a bronze with a sodium-disordered arrangement and the upper by a sodium-ordered bronze.

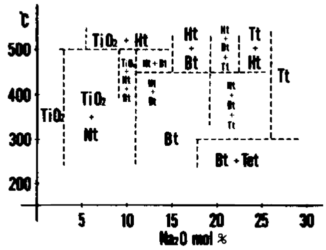

FIG. 3. The reaction diagram of TiO_2 with NaOHaq. Ht = $Na_2Ti_6O_{13}$, Tet = $Na_2Ti_4O_9$ and Tt = $Na_2Ti_3O_7$.

The symbols of TiO_2 in Fig. 3 represent three polymorphic forms, rutile, brookite, and anatase. The field of each form can be roughly described as follows: rutile occurs above 350°C, brookite above 5 mole% below 350°C, and anatase below 3 mole% and 350°C. However, these boundaries vary with reaction durations.

Nt decomposes into Ht and TiO_2 (rutile) at 940°C in air. For a mixture of Nt and Ht, decomposition takes place at ~650°C. However, decomposition below 650°C and reaction of Ht and TiO_2 into Nt below 500°C have not been observed yet. Tet prepared below 300°C contains 4 to 5 wt% of water and decomposes into Ht and Tt in a molar ratio of about 1:2 at 960°C.

Discussions

The Effect of α

Even compounds which barely react with water below 100°C often have various chemical reactions with hydrothermal water. Sodium ions in nonatitanate crystals are not quite eluted into water at near 100°C. However, the crystals easily elute a number of the ions into hydrothermal solutions. The elution is represented as the following extraction equilibrium:

$$Nt \overset{n\mathrm{H_2O}}{\rightleftharpoons} \{1 - \delta\}Nt + 2\delta\mathrm{NaOH} + 9\delta\mathrm{TiO_2}.$$

Nt is in equilibrium with a solution of about 0.4 mole dm^{-3} of NaOH. When α decreases or the water content increases in a capsule, the phase should release additional sodium ions in order to retain the extraction equilibrium with NaOH solution. Therefore, *Nt* is found at a higher percentage of Na_2O with a decrease in α as shown by boundary line I in Fig. 2, which is located nearly along a concentration curve of 0.4 mole dm^{-3}. With no change of *Nt* into *Bt* due to the reduction of titanium ions, line II is inferred to obey the above equilibrium and line III merges with line II. A similar equilibrium is attained among *Ht*, TiO_2, and $NaOH_{aq}$ at higher temperatures (>500°C).

Comparison of Reaction Diagrams

Keesmann's diagram (*11*) is clearly distinct from the present one (see Fig. 3) in the following two points: (1) the extension of TiO_2-formation range, e.g., up to 14 mole% at 400°C, 17 mole% at 350°C, and 21 mole% at 250°C; and (2) no occurrence of *Nt*. Keesmann's experimental conditions can be estimated to be roughly 200 g dm^{-3} and 550 mm^3 for α and an amount of water charged, respectively. The volume of 550 mm^3 is too large to permit reaction diagrams to be constructed because mass transportation takes place easily in capsules. The first point is explicable as shown with $\alpha \sim 200$ in Fig. 2 and discussed in the previous section. The second point is considered to be the reduction of *Nt* into *Bt* supported by the remarkable structural similarity between the two phases (*13*, *16*). Reduction proceeds with increases in reaction duration, as shown in Fig. 2. However, it has not yet been proved that *Nt* changes completely during a period of about 20 days.

Wefers' diagram (*12*) is quite different from Keesmann's and the present one. His results appear to have been obtained using mainly rutile or anatase as the starting material. Both phases have very small solubilities in comparison with the solubility of TiO_2 gel and hence titanium ions are mixed with sodium ions at a much larger ratio, Na/Ti, than the calculated one. As a result, the *Tt* field is enlarged into the low concentration range (calculated) of Na_2O. According to Wefers' description, the hydrothermal reactions are prevented from progressing further because the starting crystals are covered with sodium titanates. This suggests that the construction of the titanates is done on the surface of the starting crystals. The reaction pass from rutile (or anatase) to each titanate has a particular activation energy. The energy is expected to relate directly to the ease of changing rutile (or anatase) into each titanate between their crystal structure frameworks. The frameworks of *Tt*, *Nt*, and *Bt* can clearly be classified into two types, or *Tt* and *Nt* (or *Bt*), on the basis of their octahedral sharing modes. Wefers' results show that the former pass has a smaller activation energy than the latter. Therefore, it is considered that *Ht* instead of *Nt* occurs at temperatures much lower than 500°C owing to the lower activation energy based on the good structural similarity between *Tt* and *Ht*.

Phase Relations in the System TiO_2–Na_2O

Water often participates directly in

chemical reactions under hydrothermal conditions, resulting in those of extraction, hydration, hydrolysis, and so on. Because of these equilibria among solids and solution, it is expedient to use hydrothermal reactions for the investigation of phase relations in a H_2O-excluded system. In this work, therefore, phase relations in the system TiO_2–Na_2O shown in Fig. 4 were estimated from the reaction diagram in Fig. 3 on the assumption that water slightly modified the relations among stable phases in a system under atmospheric pressure. Extraction reactions have been observed among *Nt* or *Ht*, TiO_2, and NaOHaq. To retain these equilibria, they disappear at the low Na_2O concentration in Fig. 3 and also a trace amount of TiO_2 remains at ~15 mole% above 500°C and at ~11 mole% below 500°C. Hydrolysis and hydration reactions are found for *Tet*. The former results in no yields of the compound above 300°C. Due to the latter, *Tet* becomes approximately monohydrate below 300°C, losing only a few Na ions. The reactivity of $Na_2Ti_4O_9$ with water is expected to be fairly poor compared with that of $K_2Ti_4O_9$, which easily loses K ions in water at room temperature (*14*). However, it is suggested from the X-ray powder pattern that the crystal lattice of the monohydrate is strongly attacked in a hydrothermal atmosphere.

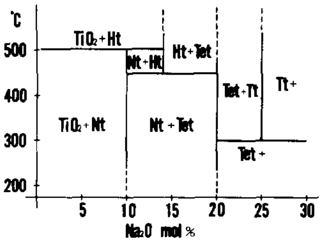

FIG. 4. Phase relations in the system TiO_2–Na_2O. The extension of the *Tet* field over 300°C, although hydrothermally prepared only below 300°C, is based on the fact that *Tet* is synthesized at 460°C in air (*7*) and decomposes into *Ht* and *Tt* at 960°C. At near 30 mole% *Tet* and *Tt* seem to coexist with dititanate $Na_2Ti_2O_5$, taking account of other works (*3*, *12*). $Na_2Ti_7O_{15}$ is not prepared in this reaction system.

Water has an indirect effect on solids. In a typical example, redox states are different in reaction systems with and without water. In this work, it is proved by the appearance of titanium dioxide bronze. This phase, in which a number of Ti ions are reduced, belongs to the ternary system TiO_2–Ti_2O_3–Na_2O and hence is omitted from the diagram. The reduction takes place by increases of the partial pressure of hydrogen in capsules. Hydrogen is produced concomitantly by the oxidation of Co, Ni, etc., and supplied into capsules which themselves (Pt or Au) act as a semipermeable membrane (*17*, *18*). These transition metals are the main components of the alloys forming the autoclave and the spacer.

Acknowledgments

The author is grateful to Drs. Y. Fujiki and T. Mitsuhashi, National Institute for Researche in Inorganic Materials, for valuable discussions on the hydrothermal method and to Dr. I. Shindo, National Institute for Researche in Inorganic Materials, for allowing him to use the hydrothermal apparatus.

References

1. P. P. BUDNIKOV AND S. G. TRESVYATSKII, *Dokl. Akad. Nauk. SSSR*, 374 (1956).
2. R. BOUAZIZ AND M. MAYER, *C.R. Acad. Sci. Paris Ser. C* **272**(23), 1874 (1971).
3. E. W. WASHBURN AND E. N. BUNTING, *J. Res. Nat. Bur. Stand. USA* **12**, 239 (1934).
4. C. GICQUEL, M. MAYER, AND R. BOUAZIZ, *C.R. Acad. Sci. Paris Ser. C* **275**(23), 1427 (1972).
5. S. ANDERSSON AND A. D. WADSLEY, *Acta Crystallogr.* **15**, 194 (1962).
6. S. ANDERSSON AND A. D. WADSLEY, *Acta Crystallogr.* **14**, 1245 (1961).
7. M. DION, Y. PIFFARD, AND M. TOURNOUX, *J. Inorg. Nucl. Chem.* **40**, 917 (1978).
8. E. K. BELYAEV, N. SH. SAFIULLIN, AND N. M. PANASENKO, *Inorg. Mater.* **4**, 78 (1968).

9. A. D. Wadsley and W. G. Mumme, *Acta Crystallogr. Sect. B* **24**, 392 (1968).
10. M. Watanabe, Y. Bando, and M. Tsutsumi, *J. Solid State Chem.* **28**, 397 (1979).
11. I. Keesmann, *Z. Anorg. Allg. Chem.* **346**, 30 (1966).
12. K. Wefèrs, *Naturwissenschaften* **54**, 19 (1967).
13. S. Andersson and A. D. Wadsley, *Acta Crystallogr.* **15**, 201 (1962).
14. Y. Fujiki, F. Izumi, T. Ohsaka, and M. Watanabe, *Yogyo-Kyokai-Shi* **85**(10), 475 (1977).
15. M. Watanabe and E. Watanabe, *J. Solid State Chem.* **32**, 233 (1980).
16. Y. Bando, M. Watanabe and Y. Sekikawa, *Acta Crystallogr. B* **35**, 1541 (1979).
17. H. P. Eugster, *J. Chem. Phys.* **26**, 1760 (1957).
18. S. Hirano and S. Somiya, *J. Cryst. Growth* **35**, 273 (1976).