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PHASE TRANSITION OF TITANIUM DIOXIDE UNDER VARIOUS PRESSURES

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SUMMARY

Prepressed TiO_2 specimens (anatase) were studied at pressures from 3.8 to 24 kbars at temperatures from 20° to 1000°C for the anatase–rutile phase transition, using a "belt"-type high pressure apparatus. Discontinuous changes in electrical resistance (a.c. and d.c.) of the TiO_2 at various temperatures under isobaric conditions were used to define the phase diagram at pressures $\gg 1$ bar. Isothermal phase-transition studies at 1 bar pressure were carried out at 880°–950°C. The phase equilibria at this pressure were determined from X-ray diffraction data at high temperatures, and after quenching to room temperature. The irreversible anatase–rutile phase transition was found to follow a slope $dT/dP = -0.02$ degrees bar^{-1}. The enthalpies of transformation, calculated from the slope, were found to decrease with increasing pressures and decreasing temperatures. The irreversibility of the anatase–rutile phase transition at high pressures was confirmed by electrical resistance and quenching methods carried out on rutile specimens.

1. INTRODUCTION

The anatase–rutile phase transition has been studied systematically by CZANDERNA *et al.*[1], and RAO[2]. SULLIVAN AND COLEMAN[3] reported that this phase transformation is favored by the presence of LiCl, while KCl inhibits this transition. YOGANARASIMHAN[4] concluded that the accelerating and inhibiting effect, respectively, of these chlorides may be due to the cations. SHANNON[5] studied the phase transition in air, vacuum, and in hydrogen–nitrogen mixtures, and found appreciable differences in the transformation temperatures, which he explained in terms of the defect structure of TiO_2. From the reported literature on the transition of TiO_2 one can conclude that a rather complex mechanism is involved. The present work was undertaken in order to arrive at a better understanding of this transition in respect of the presence of certain impurities at low and high pressures. In the past, little work has been reported on TiO_2 carried out under pressure. DACHILLE AND ROY[6] reported a new high-pressure modification of TiO_2 formed from anatase at pressures from 15 to 100 kbars and temperatures from 25° to 500°C. These authors further report that this new phase converts

slowly to rutile upon heating between 500° and 700°C by a short-range ordering mechanism.

In solid-state studies at high pressures and high temperatures there is at present no adequate method for the determination of "exact" pressures at high temperatures (above 500°C). Recently[7] the reversible monoclinic–tetragonal phase transition on ZrO_2 was found to follow a linear relationship with a slope $dT/dP = -0.01$ degrees bar^{-1}. This linearity in dT/dP was determined between 3.8 and 60 kbars and temperatures 1200°–800°C for the ZrO_2 transition by discontinuous changes in electrical resistance. It is hoped that the results of the ZrO_2 phase transition and the present work on TiO_2 will help to determine "exact" pressures at high temperatures.

2. EXPERIMENTAL

2.1. High-pressure procedures

The anatase–rutile transition at pressures from 3.8 to 24 kbars and temperatures up to 1000°C was studied with a modified "belt" apparatus*. The pressure source was a hydraulic press with a 200 ton capacity. The resistance-specimen cell (see Fig. 1), using a graphite heating element, was heated at a specific rate and controlled manually and automatically by a Leeds and Northrup power-temperature controller with a high amperage (2000 A), low voltage (2 V) power source. A diagram of

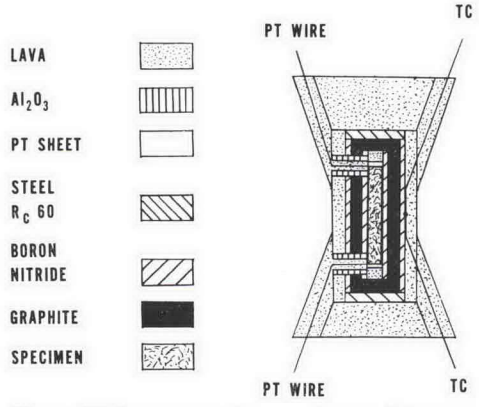


Fig. 1. High-pressure–temperature resistance cell used for phase equilibria study on TiO_2.

this apparatus is shown in Fig. 2. A similar high-pressure cell was used for the rapid cooling (quenching) experiments from pressure and temperature, except that the two platinum wires and platinum electrodes on the opposite ends of the TiO_2 specimen were omitted. The quenching high-pressure cell for temperature calibration purposes was equipped with two Pt–Pt 10% Rh thermocouples (TC) arranged diametrically to each other. In order to avoid impurity contamination during the quenching experiments the anatase specimens were protected by a cylindrically-shaped platinum sheet 0.005

* A "belt" high-pressure apparatus consists of two truncated conical steel pistons which are pressed into a conical steel die containing the resistance specimen cell (see Fig. 1). The pistons and die are shrunk-fitted for massive support with steel restraining rings forming a "belt" around them. The "belt" apparatus was developed by General Electric Company for the diamond synthesis.

cm in thickness. Another reason for using the quenching cell was to confirm the transition data from the electrical resistance measurements and to determine the possible influence of impurities picked up during the high-pressure study.

2.1.1. Pressure calibration

The belt device was calibrated for actual pressure at room temperature using a similar high-pressure cell against the well-known Bi I–II, Bi II–III, Tl II–III, and Ba II–III pressure transitions at 25.4, 27.0, 36.7 and 60 kbars[8].

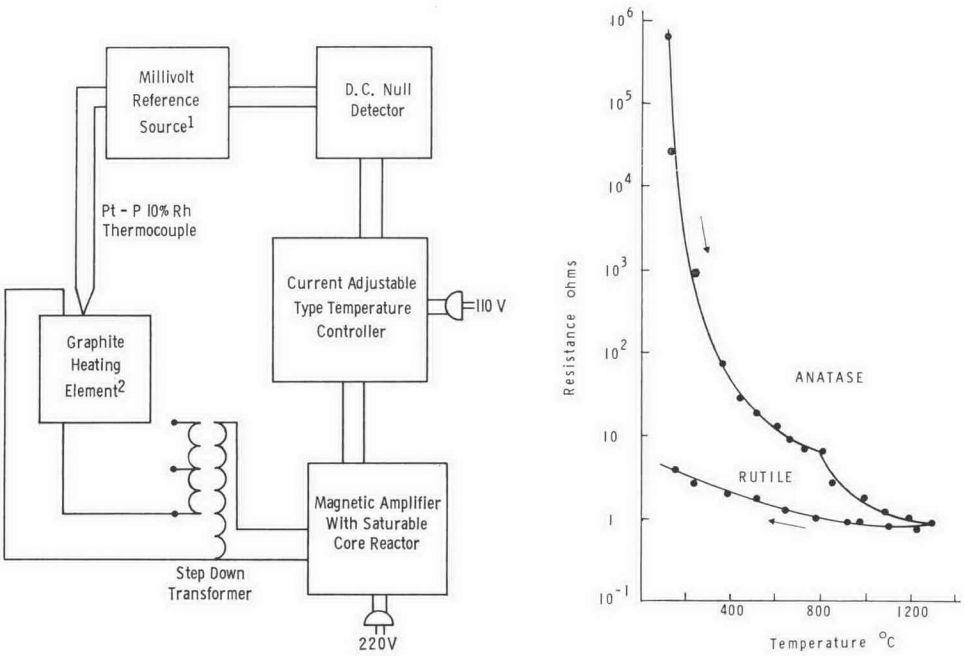


Fig. 2. High-pressure–temperature control and power source. (1) Set-point millivolt-reference source with motor driven set point. (2) High-pressure cell details see Fig. 1.

Fig. 3. Anatase–rutile phase transition at 3.8 kbars.

These data were obtained from discontinuous changes in electrical resistance on the above metals obtained from the National Bureau of Standards. The metal wires (99.999% pure) used for the calibration of the belt device were 0.05 cm in diameter by 1 cm in length. (It should be pointed out that "exact" pressures at high temperatures are not known at present.)

2.1.2. Temperature calibration

A two-thermocouple method was used for the temperature calibration at pressure. One thermocouple bead was placed near the outer boron nitride cylinder (see Fig. 1) and both lead wires brought out through opposite truncated lava ($Al_2O_3 \cdot 4\ SiO_2 \cdot H_2O$) cones. The other thermocouple junction was placed in the center of the specimen inside and the two lead wires brought out in a similar fashion as shown in Fig. 1 (in place of platinum wire for resistance measurements). In other words, the two thermocouple beads were located equidistant from the end of the cell and equidis-

tant with respect to the graphite heater. Actual temperature calibration runs at high pressures were performed up to 24 kbars and 1000°C. A temperature difference of 5°C between the two thermocouples was measured with a Leeds and Northrup potentiometer. The pressure dependence of the e.m.f. was not determined. According to HANNEMAN AND STRONG[9] the temperature correction with regard to applied pressure on Pt–Pt 10% Rh thermocouples would be about 10°C at 1000°C and 20 kbars.

2.1.3. Electrical resistance measurements at pressure

The best way to describe an electrical resistance measurement is by describing an actual experimental run under constant pressure and temperature. Fisher reagent-grade powder (anatase, 99.96% pure, average particle size 0.3 μ) was prepressed at room temperature at 1 kbar into cylinders of 0.4 cm in diameter by 1 cm in length. These specimens were placed in the high-pressure resistance cells which in turn were put in the "belt"-type high-pressure device. The TiO_2 samples were enclosed in direct contact with the inner cylinder of boron nitride (see Fig. 1), using lava or boron nitride end-plugs. In order to decrease impurity contamination, boron nitride end-plugs were primarily used. The platinum contacts on the end surfaces of the specimens were insulated from the graphite plugs by the previously mentioned flat cylinders of lava or boron nitride. The platinum resistance lead wires (0.05 cm in diameter) were brought out by each of the lava cones. The specimens were pressed isobarically at 3.8, 10, 15, 20, and 24 kbars, respectively, and heated to temperatures from 20° to 1000°C .The electrical resistance measurements were made simultaneously with the temperature measurements, after apparent temperature equilibrium was reached. The a.c. measurements were made with an Industrial Instruments Inc. impedance bridge at 60 and 1000 c/sec to avoid electrode polarization effects. The a.c. measurements were checked with a calibrated Wheatstone bridge, the data being considered to be accurate to within $\pm 1\%$. It should be noted that at these high pressures no apparent polarization effects were observed, as indicated by the good agreement between the a.c. and d.c. resistance readings. The heating and cooling cycles for the various pressures were kept constant as nearly as possible. This rate was about 200°C/h. Resistivity or conductivity values could not be calculated because of the unknown diameter-to-thickness ratios at pressure and temperature.

2.1.4. Rapid-cooling (quenching) experiments at pressure

The type of cell used for this work was quite similar to the resistance cell. The main differences were pointed out in part 2.1 above. Similar pressure and temperature ranges were used in order to determine the phase equilibria between anatase and rutile. Three heating and cooling rates were used to check on the transition data received from the resistance measurements: (a) A similar heating and cooling cycle as described under 2.1.3; (b) 500°C/h heating and rapid cooling; and (c) 100°C/min heating followed by rapid cooling. The rates described under (a), (b), and (c) were used in order to check on the sluggish transformation rate observed at 1 bar pressure, and for the purpose of determining impurity contaminations. Rapid cooling was achieved by power cut-off and by increasing the water cooling rate. (The die of the "belt" apparatus is surrounded by a suitable water cooling jacket.)

2.2. Experimental procedure at 1 bar pressure

For preliminary investigation on the temperature range of transition with respect to time high-temperature X-ray diffraction was undertaken with a TEM-

PRES X-ray diffractometer in air, at temperatures ranging from 800° to 950°C*. The anatase and rutile phases were monitored by X-ray scanning of the two most intense *d*-spacings (anatase $d=3.515$ Å, and rutile $d=3.245$ Å) using CuKα radiation.The results of this study indicated that rather slow transformation rates exist for temperatures below 950°C.

The slow transformation rates observed by high-temperature X-ray diffraction were confirmed by electrical resistance measurements between 800° and 950°C in air by a.c. and d.c. measurements. Isothermal transition studies were undertaken in air atmosphere at 1 bar pressure, using a resistance furnace. A 2 kVA-power temperature controller, similar to the one shown in Fig. 2 was used to maintain uniform temperature. The anatase specimens prepressed at 1 kbar in steel dies were placed in platinum boats in the hot zone of the furnace. The tube furnace was equipped with radiation shields to help maintain a homogeneous temperature distribution. The hot zone of the furnace showed an average temperature deviation between 880° and 950°C of about ± 2°C. After specimens were placed into the furnace about 15 min were needed to obtain apparent temperature equilibrium. The transition of TiO_2 was studied at constant temperatures at 880°, 910°, 930°, and 950°C. The amount of anatase to rutile transformation which had occurred at a given temperature was determined from the ratio of the integrated peak height X-ray intensities of the *d*-spacings mentioned above after rapid cooling of the specimens. Samples were heated at constant temperature for up to 64 h. A number of anatase specimens were heated at similar constant temperatures, placed in direct contact with boron nitride inside the platinum boats to determine boron and nitrogen contamination. Negligible amounts of boron (0.005%) and nitrogen (0.003%) were detected by chemical analysis. It should also be noted that prepressing of anatase specimens in steel dies resulted in 0.005–0.007% iron contamination. Other impurities, such as nickel, chromium, and molybdenum, amounted to about 0.0005% each.

2.3. Analytical procedures

Specimens obtained from the various pressure and temperature studies were studied by total chemical, emission spectrographic, and by X-ray techniques, as to composition, impurities, and phases present. Selected samples from the high- and low-pressure studies were polished and etched to determine grain size and imperfections if present. Polished specimens were etched with a mixture of 1 H_3PO_4:1 H_2SO_4 solution at temperatures between 130° and 165°C. A Unitron Metallograph and a JEM-6A electron microscope were used for the optical studies.

3. DISCUSSION OF RESULTS

3.1. Phase relations at high pressure

The resistance of prepressed specimens measured with the impedance bridge and using platinum electrodes was 10^{12} ohm. A large drop in resistance to 10^7 ohm was observed at high pressure and room temperature. Anatase specimens pressed at 3.8–24 kbars, respectively, showed no significant differences at a constant pressure

* It should be mentioned that the Brookite phase of TiO_2 was not detected by X-ray diffraction on quenched or slow cooled samples after being heated to respective temperatures at pressures ranging from 1 bar to 24 kbars.

and room temperature, the resistance remaining at 10^7 ohm. A larger resistance drop (10^5–10^6 ohms) was observed under pressure on heating from 20°C to approximately 400°C at a constant rate of 200°C/h. From 400° to 1000°C the resistance drop was found to range from 10 to 50 ohms. For decreasing temperatures from maximum temperatures reached to 100°C a decrease of up to 10 ohms was observed. Since the TiO_2 specimens were in immediate contact with boron nitride cylinders, it was necessary to determine any influence of the resistance of boron nitride on the resistance of TiO_2. Therefore, separate resistance experiments at pressure using similar heating rates were undertaken on boron nitride samples. These measurements showed that at 1000°C the resistance of boron nitride was 10^6 ohms, and therefore can be ignored with respect to the resistance of TiO_2.

Figure 3 shows the results of the phase transformation of TiO_2 at 3.8 kbars. The discontinuous resistance change was found at 790°C. With increasing pressures this discontinuous change in resistance (shown by a sudden increase followed by a continuous decrease in resistance) became more pronounced. This was observed at 10, 15,

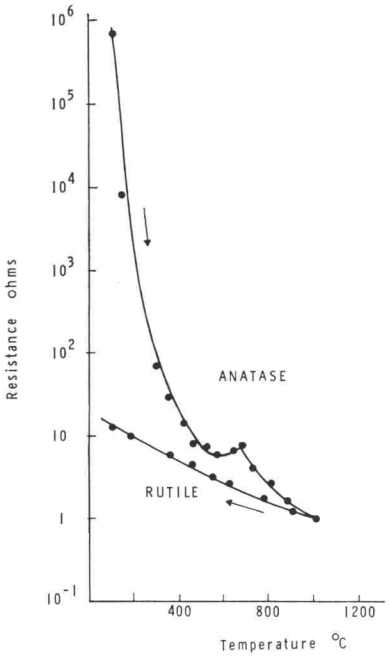


Fig. 4. Anatase–rutile phase transition at 10 kbars.

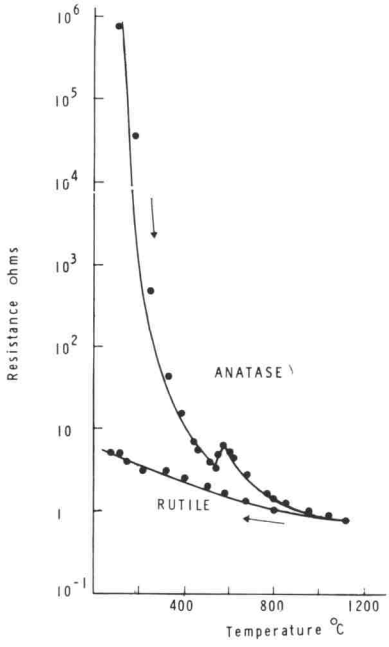


Fig. 5. Anatase–rutile phase transition at 15 kbars.

and 20 kbars applied pressure. At 24 kbars the temperature of transformation could not be accurately determined, because of erratic changes in resistance. The transformation at 24 kbars was determined from quenching experiments at pressure (*cf.* Table I). The reproducibility of the resistance measurements at constant pressures and various temperatures can be noted by comparison of Figs. 3–6. Furthermore, four resistance experiments were conducted at each pressure for confirmation of transition temperatures and slopes. X-ray diffraction showed only the rutile phase present after cooling.

TABLE I

RESULT OF HEATING AND RAPID-COOLING STUDY ON TiO_2 PHASE TRANSITION AT VARIOUS PRESSURES

Phase (before)	*Pressure (kbars)*	*Temperature at pressure (°C)*	*Time at temperature (min)*	*Phase (after)*
Anatase	3.8	820	30	Rutile
Anatase	3.8	775	30	Anatase
Anatase	3.8	785	30	Rutile and trace of anatase
Anatase	10	710	30	Rutile
Anatase	10	650	30	Anatase
Anatase	10	680	30	Rutile and trace of anatase
Anatase	15	620	30	Rutile
Anatase	15	600	30	Rutile
Anatase	15	580	20	Rutile and anatase
Anatase	16	590	20	Rutile
Anatase	16	560	20	Rutile
Anatase	16	550	20	Rutile and anatase
Anatase	16	520	20	Anatase
Anatase	20	540	20	Rutile
Anatase	20	510	20	Rutile
Anatase	20	490	20	Rutile and anatase
Anatase	24	450	30	Rutile
Anatase	24	430	30	Rutile
Anatase	24	425	30	Rutile
Anatase	24	420	30	Rutile and trace of anatase
Anatase	24	380	30	Anatase

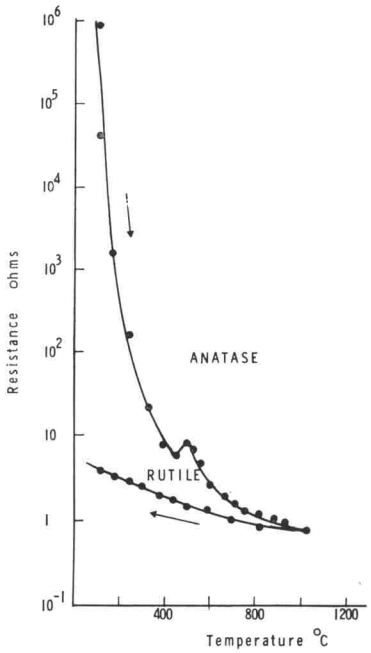


Fig. 6. Anatase–rutile phase transition at 20 kbars.

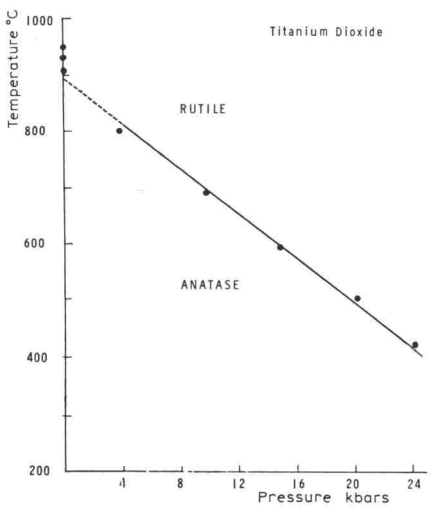


Fig. 7. Anatase–rutile phase diagram as a function of pressure and temperature up to 24 kbars.

Slow heating and cooling (200°C/h) at pressures from 3.8 to 24 kbars and above transition temperatures (see Figs. 3–6) were undertaken in the high-pressure cell with the specimens inclosed in platinum. The results confirmed the findings of the resistance experiments. Quenching experiments at pressure were undertaken using heating rates of 100°C/min and 500°C/h. The specimens were kept at temperature for 10 min–1 h prior to rapid cooling. Complete anatase–rutile transformation had occurred after quenching from above transition temperatures at pressures from 3.8 to 24 kbars. Table I shows the results of heating anatase specimens at a rate of 500°C/h followed by rapid cooling, on the TiO_2 phase transition at various pressures. From this table and previous data by resistance measurements, the phase equilibrium between anatase and rutile could be determined. The above data show a pressure-temperature dependence on the transition rather than a time-temperature dependence (*cf.* CZANDERNA *et al.*[1]). In Fig. 7 the anatase–rutile transition is plotted as a function of pressure and temperature.

3.2. Phase transition at 1 bar in air

In Fig. 8 the results of the anatase–rutile transition at 1 bar are shown. It can be seen that the transition at 1 bar in contrast to 3.8–24 kbars is strongly time and temperature dependent, as earlier reported by CZANDERNA *et al.*[1]. At 880°C approximately 45% of the anatase phase was transformed to rutile after 64 h. At 910° and 930°C approximately 90% was transformed to rutile after 64 h; only the rutile phase was present at these temperatures after heating for 100 h as confirmed by X-ray

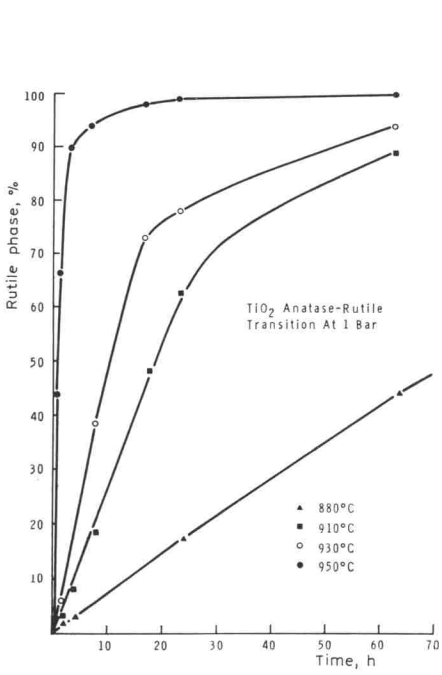


Fig. 8. Isothermal transition of TiO_2 at 1 bar.

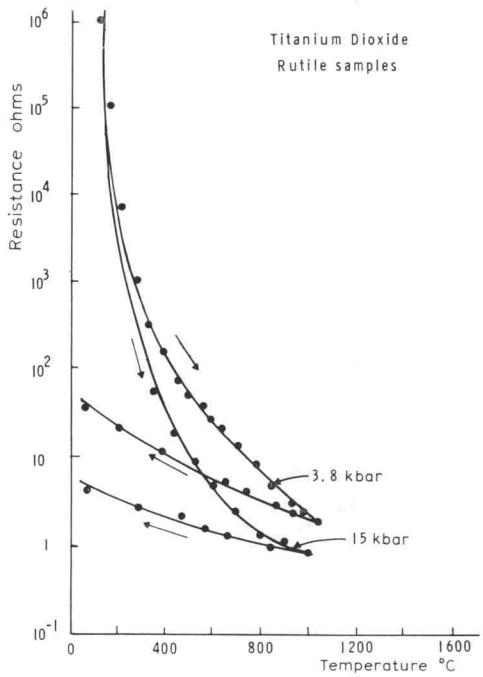


Fig. 9. Electrical resistance measurements on rutile at 3.8 and 15 kbars.

diffraction. At 950°C the anatase–rutile transition is essentially complete after 23 h. It should be mentioned that after 160 h at 880°C about 80% was transformed to rutile.

The 910°, 930°, and 950°C transition temperatures at 1 bar were incorporated into Fig. 7. Since these transition rates are strongly time-dependent and therefore cannot be directly related to high-pressure experiments, a dotted line was drawn from 3.8 kbars to 1 bar.

3.3. Phase transition and enthalpies of transformation

From the high-pressure data, a $dT/dP = -0.02°$/bar relationship was determined between 3.8 and 24 kbars. The extrapolated transition at 1 bar at 910°C, using the same slope, resulted in the calculation of ΔH_{tr} at 1 bar. A ΔH_{tr} value for 950°C based on the same slope was added to indicate the range in transition temperature actually observed at 1 bar. In Table II the transition temperatures and enthalpies of transformation at various pressures are presented. The ΔV_{tr} value represents the molal volume relative to the densities of anatase (3.84 g/cm³) and rutile (4.26 g/cm³) determined by pycnometric and X-ray methods.

TABLE II

PHASE TRANSITION TEMPERATURES AND ENTHALPIES OF TRANSFORMATION FOR TiO_2 AT VARIOUS PRESSURES

Pressure (kbars)	*Temperature (°K)*	ΔH_{tr} *(kcal/mole)*
0.001	1183; 1223	−2.79; −2.89
3.8	1063	−2.51
10.0	958	−2.26
15.0	863	−2.04
20.0	773	−1.82
24.0	693	−1.64

$$\frac{dT}{dP} = \frac{T_{tr}\Delta V_{tr} c}{\Delta H_{tr}}; \quad \Delta V_{tr} = \frac{M}{d_{anat.}} - \frac{M}{d_{rut.}}; \quad \frac{dT}{dP} = -0.02°/bar$$

M = molecular weight of TiO_2
d = density of anatase and rutile
c = 0.02421 cal (conversion factor) to cm³ bar

TABLE III

SPECTROCHEMICAL ANALYSES OF TiO_2 (ANATASE AS-RECEIVED) AND AFTER HEATING AT VARIOUS PRESSURES (RUTILE)

Impurity (wt.%)	*Anatase powder*	*1000°C, 1 bar 1–64 h, air*	*1000°C, 20 kbars 20 min (quench)*	*1000°C (max.), 20 kbars (Resistance experiment)*
Si	0.012	0.012	0.020	0.025
Al	0.013	0.013	0.030	0.035
Fe	0.010	0.016	0.020	0.020
Ni	0.0005	0.0005	0.0008	0.0008
Cr	0.001	0.001	0.001	0.001
Mn	0.0003	0.0005	0.0008	0.0008
Ca	0.005	0.005	0.007	0.008
Mg	0.0045	0.005	0.005	0.006
B	0.0002	0.0002	0.018	0.120
Pt	—	0.005	0.008	0.006

3.4. Impurities and phase transition at various pressures

The experiments at 1 bar showed, with the exception of iron and platinum, no significant impurity pick-up compared to the as-received anatase powder. As mentioned earlier, iron (0.005–0.007%) was picked up from the steel dies during the preparation of the specimens. Platinum contamination of 0.003–0.005% was determined after heating specimens for 64 h at 1000°C (see Table III). The fast heating-rate experiments (100°C/min) using platinum cylinders around the specimens showed an increase in principal impurities up to: Si 0.015%, Al 0.020%, Fe 0.017%, Ni 0.0006%, Cr 0.001%, Mn 0.0006%, Ca 0.006%, Mg 0.005%, B 0.008%, Pt 0.006%. These data are average analyses of specimens subjected to 20 kbars at 1000°C for 20 min followed by quenching. The analysis of specimens subjected to a pressure of 20 kbars at 1000°C for 20 min (heating rate 200°C/h) showed a further increase in principal impurities after quenching (Table III). Finally, the largest impurity pick-up was noted from the analyses of the resistance experiments (200°C/h heating rate) with respect to B, Si, and Al. These impurities are due to the lava and boron nitride parts used in the high-pressure cells. The resistance and quenching experiments at various rates at high pressure showed an instantaneous rutile formation when cooling from above the anatase–rutile phase equilibrium line (see Fig. 7). Therefore, one might conclude—even though an increase of impurities was observed for the various high-pressure methods—that the impurities determined here have little effect on the transformation.

Anatase was doped with 0.2% boron nitride to check the influence of boron and nitrogen on the transition rate at 1 bar. The results of the transition experiments undertaken at 910°, 930°, and 950°C showed essentially no difference compared to the rates found on pure anatase (see Fig. 8).

3.5. Phase stability and stoichiometry

High-pressure resistance and quenching experiments were undertaken on rutile specimens to check the irreversible anatase–rutile transition known for low pressures and temperatures. Figure 9 shows the electrical resistance measurements on rutile at 3.8 and 15 kbars, respectively. X-ray analyses after cooling showed only the rutile phase present in these specimens. Quenching experiments on rutile specimens up to 15 kbars and from 1000°C to room temperature showed similar results.

Chemical analyses on rutile specimens received from the high-pressure phase transition study indicated a decrease in oxygen content with increasing temperature. A range in composition from $TiO_{1.98}$ (710°C; 20 kbars) to $TiO_{1.91}$ (950°C; 20 kbars) was noted. Chemical analyses on TiO_2 specimens received from the transition study at 1 bar resulted in essentially stoichiometric composition ($TiO_{1.99}$ after 64 h at 950°C). (The composition of the initial anatase powder was $TiO_{1.995}$.) It should be mentioned that according to ANDERSSON *et al.*[10] the homogeneity range for TiO_2 does not extend below $TiO_{1.90}$.

3.6. Microscopy study on TiO_2 specimens

Specimens received from the high-pressure experiments were polished and etched in the previously described manner prior to optical study. Figure 10 is a typical electron micrograph of a rutile specimen prepared at 10 kbars and heated up to 1000°C. Close to spherical grain shapes were observed on high-pressure samples prepared at 3.8–24 kbars and 1000°C. Uniform increase in grain size on passing from



Fig. 10. Electron micrograph (carbon replica) of a rutile specimen pressed at 10 kbars and heated to 1000°C showing spherical grains and etch pits.

the center of the specimen to the outer edge, earlier reported for ZrO_2 and HfO_2[11], was again found in TiO_2. The grain size near the center of specimens ranged from 1–3 μ and increased to 8–24 μ at the outer edge. These data were found on specimens subjected to 3.8–24 kbars at 1000°C; another interesting observation was a fairly uniform distribution of etch pits throughout the grains. These results indicate that a fairly

homogeneous pressure deviation exists throughout the specimens during the high-pressure–temperature experiments.

4. CONCLUSION

(1) Electrical resistance and quenching experiments at high pressure showed the anatase–rutile transition to be pressure-temperature dependent with a slope of $dT/dP = -0.02$ degrees bar^{-1}.

(2) The transition at 1 bar in contrast to high pressure was observed to be strongly dependent on time and temperature.

(3) The oxygen deficiency found in the high-pressure experiments might have caused an acceleration of the transition rate at higher temperatures.

(4) A pressure gradient indicated by grain size difference suggests that the transition starts at the center of the specimens and is followed by nucleation of rutile crystallites going to the outer edge.

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