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IN VACUUM-REDUCED AND HYDROGEN-REDUCED RUTILE

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Publication Date

1964-04-06

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(as Letter to the Editor)

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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Robert D. Shannon

April 6, 1964

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DIFFERENT DEFECT MECHANISMS IN VACUUM-REDUCED
AND HYDROGEN-REDUCED RUTILE*

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April 6, 1964

Considerable controversy over the defect structure of TiO_2 has arisen in the last few years. The formation of either titanium interstitials or oxygen vacancies has been suggested as the mechanism through which nonstoichiometric rutile is formed. Weight loss data as a function of oxygen pressure have been used to confirm the presence of oxygen vacancies^{1,2} while certain studies of the oxidation of titanium have led to the suggestion of a defect structure involving interstitial titanium ions.³ Chester⁴ found lines in the electron spin resonance spectrum obtained from hydrogen-reduced rutile that he attributed to: (a) a Ti^{+3} interstitial, (b) an oxygen vacancy, or (c) the presence of hydrogen ions. Studies of internal friction in nonstoichiometric rutile have favored the interstitial mechanism.^{5,6} Electrical resistivity data have provided evidence for both the interstitial and vacancy mechanism.⁷⁻¹¹

An important factor seems to be the atmosphere in which the defects are formed. Both Chester⁴ and Carnahan and Brittain⁵ noted that vacuum-reduced and hydrogen-reduced rutile behaved differently. For rutile reduced in vacuum at 600° to 1150°C Chester found an absence of the line that had been assigned to the interstitial, the vacancy or the presence of hydrogen. Carnahan and Brittain did not obtain relaxation peaks which

should have occurred for interstitials on a sample reduced in H_2-H_2O atmospheres at $720^\circ C$. Tannhauser¹⁰ found evidence for interstitials in TiO_2 which had been reduced in $CO-CO_2$ mixtures, and Yahia¹¹ indicated that interstitials are present at low pressures of O_2 (< 10 mm Hg) and vacancies at higher pressures. In summary, it appears that:

- (a) in hydrogen at all pressures and oxygen pressures greater than 10 mm Hg oxygen vacancies are predominant,
- (b) at oxygen pressures less than 10 mm Hg and in $CO-CO_2$ mixtures titanium interstitials form.

In this note I would like to show that studies of the anatase-rutile (TiO_2) transformation confirm the differences in behavior of vacuum- and hydrogen-reduced TiO_2 . The anatase-rutile transformation involves a collapse of the relatively open anatase structure from a cell volume of $\frac{136.0}{2} \text{ \AA}^3$ to 62.4 \AA^3 , a volume change of about 8%. This collapse takes place by a distortion of the oxygen framework and shifting of the majority of the Ti^{+4} ions by rupturing two of the six Ti-O bonds to form new bonds.¹² One would expect the removal of oxygen ions to facilitate this collapse and consequently to accelerate the transformation. Conversely the introduction of interstitial titanium ions might be expected to inhibit the transformation.

It is assumed at the outset that the defect mechanisms in anatase are essentially the same as those in rutile. Although there does not appear to be any data in the literature concerning different defect mechanisms in allotropic forms of a compound, the best justification for the assumption might be the similarity in bond strengths and identical cation-anion coordination.

The rate of transformation of anatase to rutile was measured in air, in vacuum (3×10^{-4} mm Hg obtained by an oil diffusion pump in conjunction with a liquid nitrogen cold trap), and in hydrogen-nitrogen mixtures.¹² The material used was reagent TiO_2 , supplied by Baker and Adamson Co., lot R163, and was composed of 99% anatase. Two types of data were obtained: (1) the samples run in air and $\text{H}_2\text{-N}_2$ were heated for constant time (30 min) at various temperatures and then quenched, and (2) samples run in vacuum and in air were heated isothermally for various times and then quenched. The analysis of the mixtures was performed by a standard x-ray diffraction method¹³ using integrated peak heights to determine the amount of anatase remaining. A rotating sample holder was used to minimize preferred orientation effects. The effect of 1% CuO , added as a solution of cupric nitrate, was also investigated by making constant time measurements.

In Fig. 1 the percent transformation is plotted vs temperature for samples heated in air, in $\text{H}_2\text{-N}_2$, and with 1% CuO additions. The rate is seen to be accelerated by both hydrogen atmospheres and the CuO addition. The assumption of an anion vacancy model offers an explanation of the accelerating effect of the hydrogen atmosphere by either reducing the number of Ti-O bonds which must be broken and/or by reducing the energy which must be overcome in deforming the structure. The presence of titanium interstitials would almost certainly make the collapse of the structure more difficult and lead to a reduced transformation rate. Straumanis¹³ has suggested that the acceleration may be caused by the formation of a Magnéli $\text{Ti}_n\text{O}_{2n-1}$ phase. Such a phase would tend to nucleate rutile crystallites and could account for the observed increase

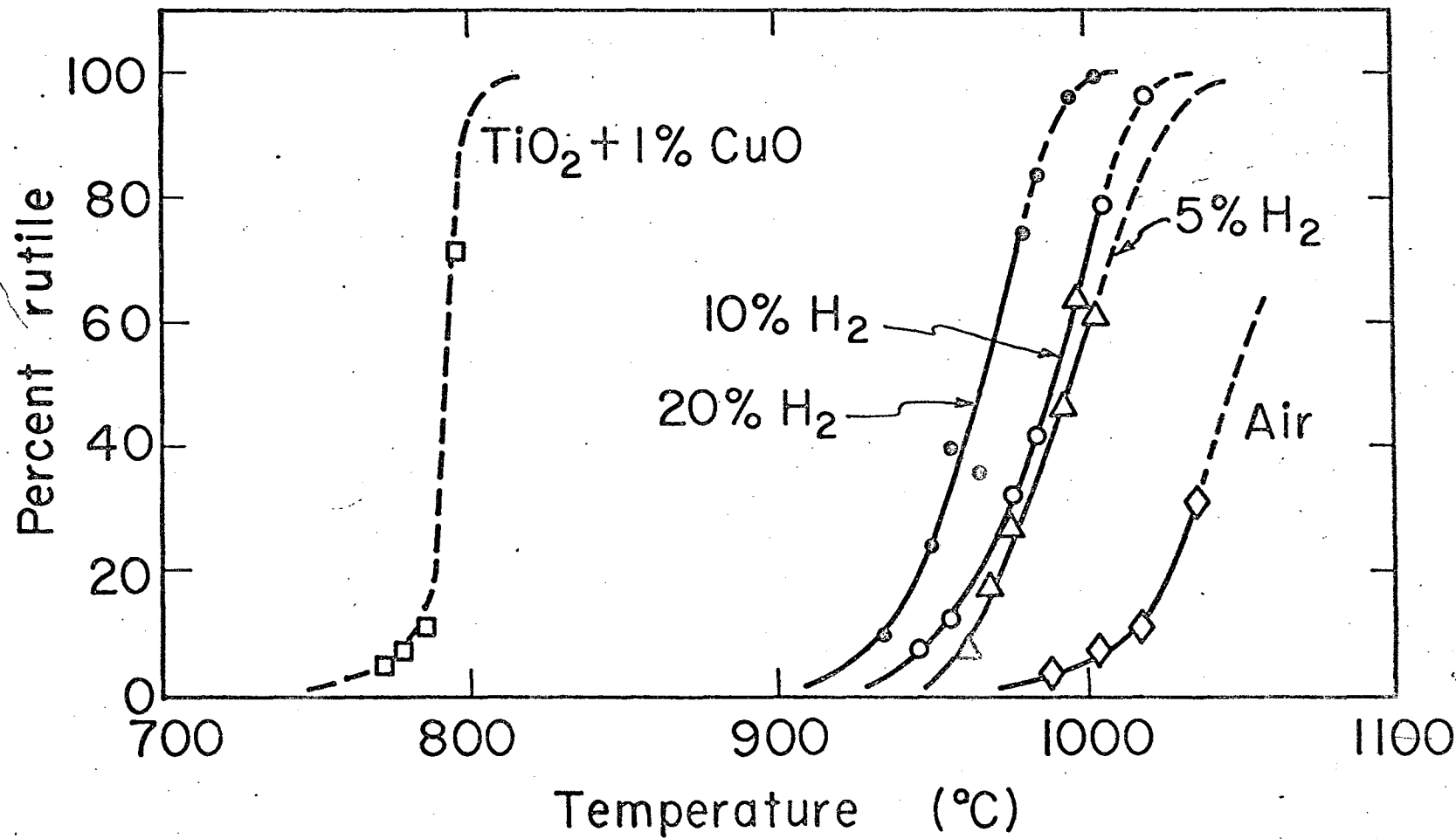


Fig. 1

MU-33753

in rate. The effect of CuO is similar to that of hydrogen and presumably acts through (1) the formation of a substitutional solid solution, thereby creating anion vacancies, and (2) diffusion of these vacancies into the crystal. In this case the extent of solid solution (0.35 mole %) was not great enough to allow formation of a second phase.¹⁴

Figure 2 shows the rate of transformation in air and vacuum at 1017°C. The kinetics obtained in vacuum are quite different from those obtained in hydrogen. The experimental rate of transformation in vacuum follows that in air up to about 30% transformation and then rapidly begins to decrease. Since the reduction process is probably also temperature activated, it might be postulated that the point at which the rate begins to decrease corresponds to the point at which the rate of formation of interstitials becomes measurable. If the defect mechanism in vacuum is the formation of titanium interstitials, these interstitials could effectively stuff the structure and hinder the transformation.

These data seem to indicate that different defect structures arise in hydrogen- and vacuum-reduced TiO₂ as both Chester and Carnahan and Brittain have observed. However, it is difficult to reconcile the interstitial mechanism for vacuum-reduced rutile with the work of Straumanis et al.¹⁵ They observed the following changes in lattice dimensions and density in rutile which was reduced in vacuum at 1400°C and then reoxidized under varying degrees of O₂ pressure.

Sample	Color	Density (20° C)	a (Å)	c	Δ_a
unreduced	white	4.2498	4.59373 ± .00005	2.95812	
reduced	blue-gray	4.2371	4.59352	2.95810	-.00021
reduced	blue-black	4.2361	4.59343	2.05824	-.00030

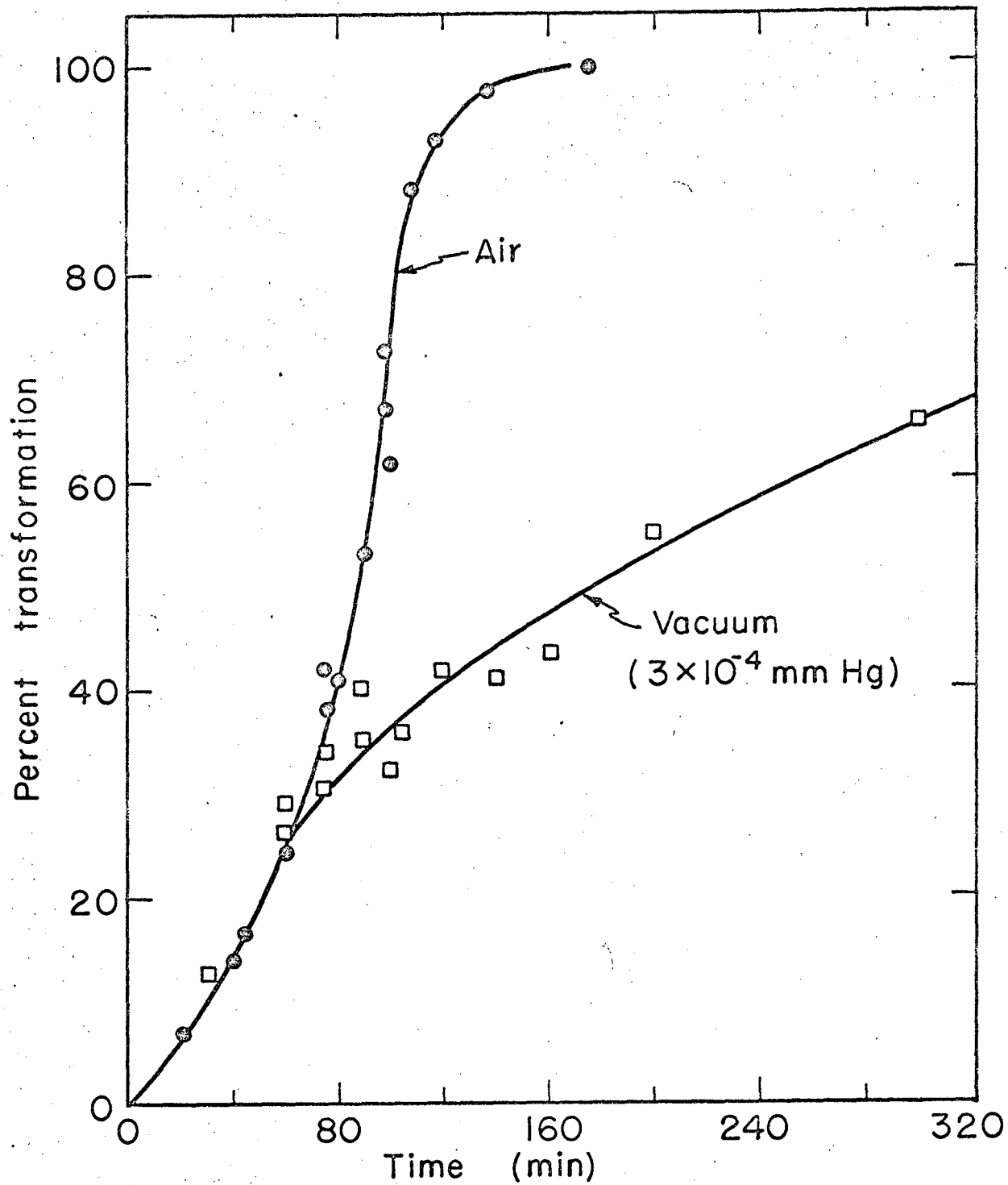


Fig. 2

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The shrinkage in the unit cell dimensions and decrease in density are strong arguments against an interstitial mechanism.

Straumanis' samples were reduced at pressures of $1-4 \times 10^{-3}$ mm Hg in a closed-end porcelain tube heated by a Pt resistance winding. The tube was closed by a water-cooled plate with a standard "O" ring seal.¹⁴ Under these conditions it is possible that the initial reduction occurred not by dissociation in vacuum but by reaction with organic vapors originating from vacuum grease present on the "O" rings.

An important question appears to be why the presence of hydrogen should favor the formation of oxygen vacancies. Von Hippel et al.¹⁶ found that quantities of hydrogen in the order of parts per million of hydrogen to oxygen easily enter the rutile structure and form hydroxyl ions. The presence of oxygen vacancies in rutile implies (1) the migration of these vacancies rather than titanium interstitials from the surface where the reduction occurs toward the interior of the crystal, and (2) the counter movement of oxygen ions from the interior to surface. Therefore, the presence of hydrogen must either increase the diffusivity of vacancies or reduce the diffusivity of titanium interstitials. Hydroxyl ions, because of their lower negative charge and almost identical ionic radius, should encounter less of an energy barrier than $O^{=}$ ions when jumping from an occupied site to a vacancy and would provide the required higher diffusivity. If the presence of hydroxyl ions is responsible for the presence of vacancies rather than interstitials, then small quantities of water vapor might have the same effect. Consequently, any reduction of TiO_2 performed in vacuum without trapping out the water vapor would tend to produce vacancies rather than interstitials. It appears that

specification of the reduction conditions for TiO_2 must include not only the partial pressure of oxygen but also the partial pressures of water vapor and hydrogen.

FOOTNOTE AND REFERENCES

* This work was done under the auspices of the U. S. Atomic Energy Commission.

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FIGURE CAPTIONS

Fig. 1. Percent transformation vs temperature

Reaction time = 30 min

Baker and Adamson Co., reagent grade TiO_2 , lot R163.

Fig. 2. Percent transformation vs time in air and vacuum

Temperature = $1017^\circ C$

Baker and Adamson Co., reagent grade TiO_2 , lot R163.

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