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High temperature steady-state creep of polycrystalline rutile, pure and doped with tantalum

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The steady state creep of polycrystalline (5–60 μm) rutile, which is doped with 1 cation % tantalum, is controlled by a Nabarro–Herring lattice diffusion process at 1100 to 1200° C. Doping with tantalum significantly depresses the steady state creep rate by lowering the concentrations of titanium interstitials and oxygen vacancies. The concentrations of these defects, and hence the steady state creep rate of doped rutile, can be increased by decreasing the oxygen partial pressure below 10^{-7} to 10^{-8} atm at 1200° C. Tentative evidence is presented in support of the hypothesis that the steady state creep of polycrystalline, undoped rutile at 950 to 1100° C is controlled by interfacial defect creation and/or annihilation at grain boundaries. Interfacial controlled deformation rates are probably due to the large concentrations (and perhaps high mobilities) of cation and anion lattice defects which are present in pure rutile equilibrated in both oxidizing and reducing atmospheres. The steady state creep rate was a very weak inverse function of the grain size and essentially independent of the oxygen partial pressure.

1. Introduction

Titanium dioxide is an intermediate band gap material with interesting electrical properties, particularly when it is doped with substitutional impurities such as Ta_2O_5, Nb_2O_5 or Al_2O_3 [1]. "p"-type material can be produced by doping with trivalent aluminium ions, whereas doping with pentavalent ions, such as tantalum and niobium, leads to "n"-type semiconduction. Since the concentration of both electronic and lattice defects can be readily controlled by the presence of these dopants, the rutile structure is an ideal candidate for the study of high temperature creep and/or sintering phenomena which will depend on the concentration and mobility of defects on either the cation or anion sublattice. For example, some evidence exists which indicates that the optimum sintering temperature in air is significantly increased by the addition of small amounts of tantalum [1].

Other than work on the creep of "pure" rutile single crystals [2, 3], no work has been reported on the creep of polycrystalline rutile. In this paper, the results of creep studies at low stresses (under 15 MPa) will be reported on both pure and tantalum-doped polycrystalline (5–60 μm) rutile. The objective will be to understand what diffusion processes are important in polycrystalline deformation and, perhaps, sintering and how they are affected by the presence of aliovalent dopants such as Ta^{5+}.

2. Experimental procedures

Undoped anatase TiO_2 powder‡ was converted to rutile crystallographic form by heating at 1100° C. Prior to hot-pressing in graphite dies, the calcined

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‡Pigment grade powders from National Lead Industries.

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powder was ball-milled. Undoped specimens with densities over 99% of theoretical were obtained with grain sizes of 5 and 25 μm after hot-pressing at 1100 and 1350° C, respectively.

Tantalum-doped (1 cation % Ta) polycrystalline TiO_2 specimens were prepared by sintering isostatically pressed discs at 1400° C for several hours in air. The doped powder was prepared by mixing an aqueous oxalic acid solution of tantalum oxalate with an aqueous slurry of TiO_2 powders. Upon slow addition of NH_4OH at room temperature, tantalic acid was precipitated on to the TiO_2 particles. After drying, the powder was calcined at 1100° C to convert the tantalic acid to Ta_2O_5. Prior to sintering, the powder was milled and then binder was added. Disc-shaped specimens were prepared by uniaxial pressing (138 MPa) followed by isostatic pressing at approximately 200 MPa. Sintered densities over 95% of theoretical were achieved in specimens with an average grain size of 5 μm.

Annealing specimens, which were embedded in powders of the same composition, at various temperatures in air yielded a distribution of grain sizes up to a maximum of about 60 μm. Grain sizes are standard linear intercept averages multiplied by 1.5. Grain sizes were measured before and after creep testing to confirm that no grain growth was occurring at temperatures $\leqslant 1200°$ C.

Dead-load, four-point-bending creep tests were conducted on machined, ground, and polished rectangular bar specimens with a cross-section of 2 mm x 5 mm. The experimental test apparatus has been described elsewhere [4]. Stresses and strains were calculated from standard viscoelastic relations [5]. Various oxygen partial pressures down to 10^{-15} atm measured with a zirconia galvanic cell were achieved using air, nitrogen and CO/CO_2 gas mixtures. All data in this paper represent steady state creep conditions which were easily achieved at the test temperatures (950 to 1200° C). In order to achieve steady state creep rates in undoped specimens, oxidizing anneals (several days) at temperatures greater than or equal to the test temperature were required. After hot-pressing, the colour of the undoped material was a dark blue (similar to the tantalum-doped specimens). After annealing or testing in oxidizing atmospheres, the colour of the undoped specimens was a straw yellow.

3. Experimental results

The major variables of stress, temperature, oxygen partial pressure, and grain size were systematically studied for the creep of "pure" and tantalum-doped polycrystalline rutile. Stress, temperature and oxygen partial pressure dependencies were determined by conducting single-specimen tests in which the variable to be studied was changed in step-wise fashion (e.g. stress) while holding constant all other variables (e.g. temperature, oxygen partial pressure).

3.1. Stress dependence

In Fig. 1 data are presented for tantalum-doped material which indicate the dominance of viscous creep (i.e. linear dependence between strain rate and stress) in an oxidizing atmosphere for stresses up to 13 MPa with no apparent threshold stress.

In Fig. 2 strain rate–stress data are presented for the steady state creep of undoped rutile at 964° C in an oxidizing atmosphere. Again nearly viscous behaviour is observed. The data in Fig. 2 were taken from specimens with grain sizes of 5 and 45 μm. The difference in creep rates was only a factor of three, indicating a very weak inverse grain-size dependence in undoped material.

A linear plot is presented in Fig. 3 in the low stress region for undoped rutile at two different grain sizes (5 and 25 μm). The data suggest linear creep at 1000° C in air with a threshold stress which increases as the grain size decreases. Increasing the grain size by a factor of five depressed the threshold stress by about a factor of 3.

In summary, the strain rate–stress data indicate that creep deformation in undoped and Ta-doped polycrystalline rutile is viscous at stresses below about 15 MPa. In the case of undoped material, viscous creep deformation appears to have a threshold stress associated with it.

3.2. Activation energy for creep deformation

The results of temperature change experiments in air for undoped and Ta-doped rutile specimens are shown in Fig. 4. From these data activation energies of approximately 264 and 510 kJ mol^{-1} were obtained, respectively. Furthermore, the data in Fig. 4 clearly indicate that small amounts of the tantalum dopant significantly decrease the steady state creep rate of polycrystalline rutile. For comparable grain sizes and stresses, creep rates are suppressed at 1100° C over two orders of magnitude by the tantalum dopant present at the 1% level.

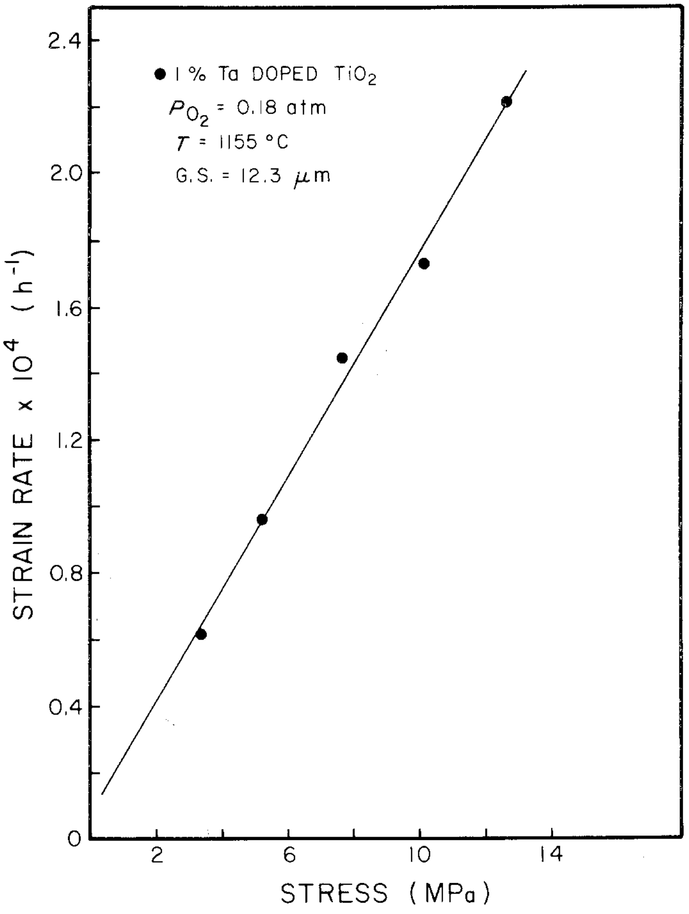

Figure 1 Viscous creep of tantalum-doped polycrystalline rutile.

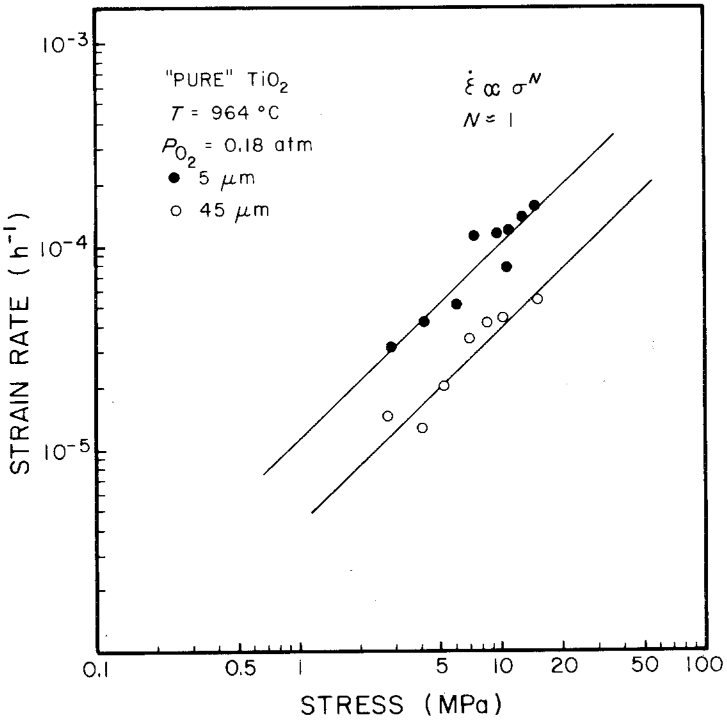

Figure 2 Viscous creep of undoped polycrystalline rutile.

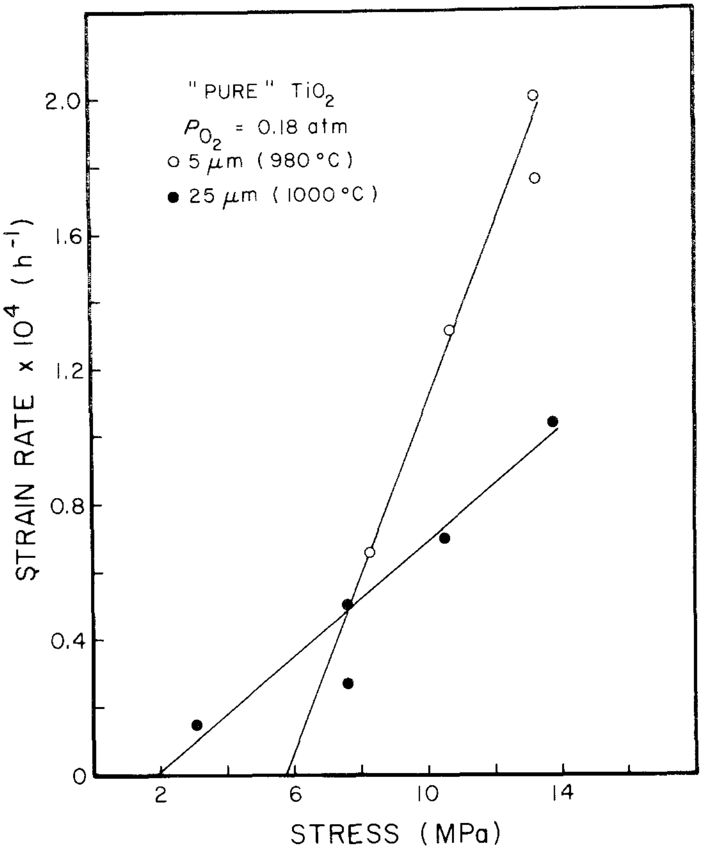

Figure 3 Viscous creep with a threshold stress – undoped, polycrystalline rutile.

3.3. Effect of oxygen partial pressure

In Fig. 5 the effect of oxygen partial pressure on the steady state creep of Ta-doped, polycrystalline rutile at 1200° C and 3.4 MPa is shown for two different grain sizes: 24 and 56 µm. At the lowest P_{O_2} values ($< 10^{-7}$ atm), tests were run at lower temperatures to minimize strain accumulation at the very fast creep rates. All data were corrected to 1200° C, using an activation energy of 510 kJ mol^{-1}. The data reveal a slight decrease in creep rate as the oxygen partial pressure is dropped from 0.18 atm to about 10^{-7} atm. Below 10^{-7} atm the creep rate is enhanced considerably by further decreases in pressure to 10^{-15} atm. Note also that the creep rate is a strong inverse function of the grain size.

In comparable tests at approximately 1000° C, the steady state creep rate of undoped rutile at low stresses (~3 MPa) was found to be essentially independent of oxygen partial pressure from about 0.17 to 10^{-15} atm.

3.4. Grain size effects

The effects of grain size on the steady state creep of Ta-doped rutile at 1200° C are shown in Fig. 6 for deformation tests in both oxidizing ($P_{O_2} \sim 0.18$ atm) and reducing atmospheres ($P_{O_2} \simeq 10^{-14}$ atm). The steady state creep rate varies with the inverse square of the grain size in both oxidizing and reducing environments over grain sizes between 5 and 60 µm. Note the significant enhancement (~ × 40) in the creep rate as the oxygen partial pressure is decreased from 0.18 to 10^{-14} atm.

In contrast to Ta-doped material, the creep rate of undoped, polycrystalline rutile was a very weak function of the grain size (e.g. Fig. 2). In the grain size range between 5 and 45 µm, the creep rate was decreased by less than a factor of 3 to 4. For Ta-doped material, the creep rate is suppressed by a factor of 81 for a comparable increase in grain size.

4. Discussion

To summarize, the steady state creep of Ta-doped rutile is Newtonian viscous with an activation energy of 510 kJ mol^{-1}. Creep rates can be significantly enhanced by decreases in the oxygen partial pressure. Furthermore, creep rates vary inversely

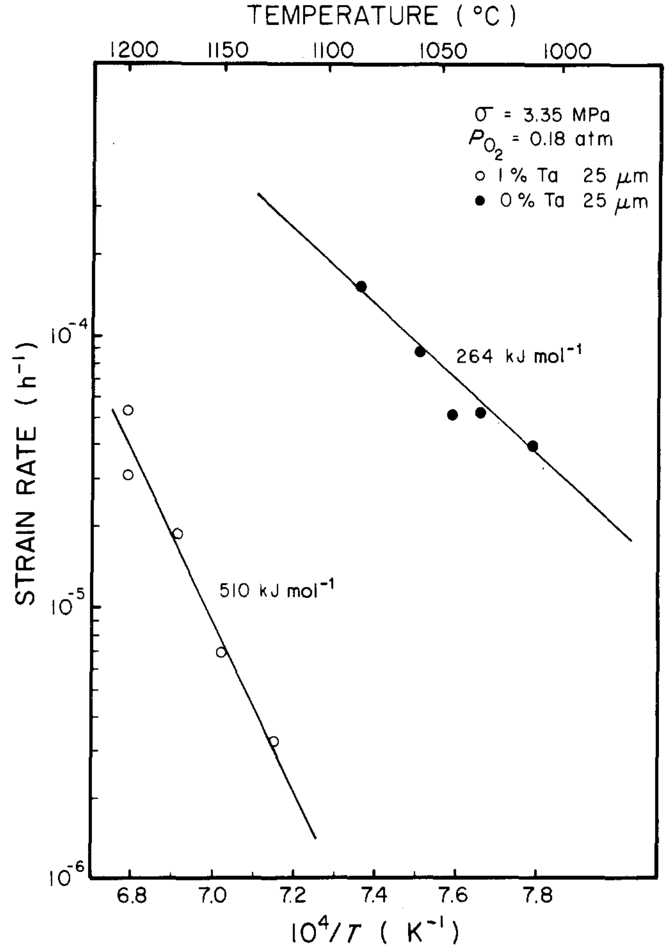

Figure 4 Effect of tantalum doping on the steady state creep of polycrystalline rutile.

with the square of the grain size. These characteristics are markedly different from those observed in undoped material. In the latter, viscous creep with a threshold stress is observed. The creep activation energy is a factor of 2 smaller (264 kJ mol^{-1}). Creep rates are insensitive to changes in oxygen partial pressure and they are a weak inverse function of the grain size. Finally, tantalum doping at the 1 cation % level significantly suppresses the viscous creep rate.

Taking into account the effects of grain size and stress, it is concluded that the steady state creep of polycrystalline rutile doped with tantalum is rate-limited by a volume (lattice) diffusion process. The reciprocal square grain-size dependence of the creep rate in both oxidizing and reducing atmosphere is consistent with Nabarro–Herring diffusional creep [6, 7]. Doping with tantalum significantly depresses the creep rate. Similar effects have been observed with respect to sintering kinetics [1]. In both cases, the temperature at which mass transport is sufficient for either diffusional creep or sintering is increased approximately 200° by doping with 1 cation % tantalum.

In the case of undoped TiO_2, the mechanism of creep deformation at low stress is apparently different from that of doped material. While the rate of deformation is very rapid, the creep rate is a very weak function of the grain size and essentially independent of changes in the oxygen partial pressure. Furthermore, some experimental evidence is present which suggests that the creep rate is linear with stress after a threshold or yield stress is exceeded. This threshold stress increases as the grain size is decreased. All of these effects strongly suggest that the creep mechanism involves mass transport kinetics which are kinetically limited by some interfacial (or grain boundary) process involving the creation and/or annihilation of point defects [8].

In order to compare mass transport processes in polycrystalline rutile with those measured by tracer diffusion in single crystals, diffusion coefficients were calculated from the Nabarro–Herring

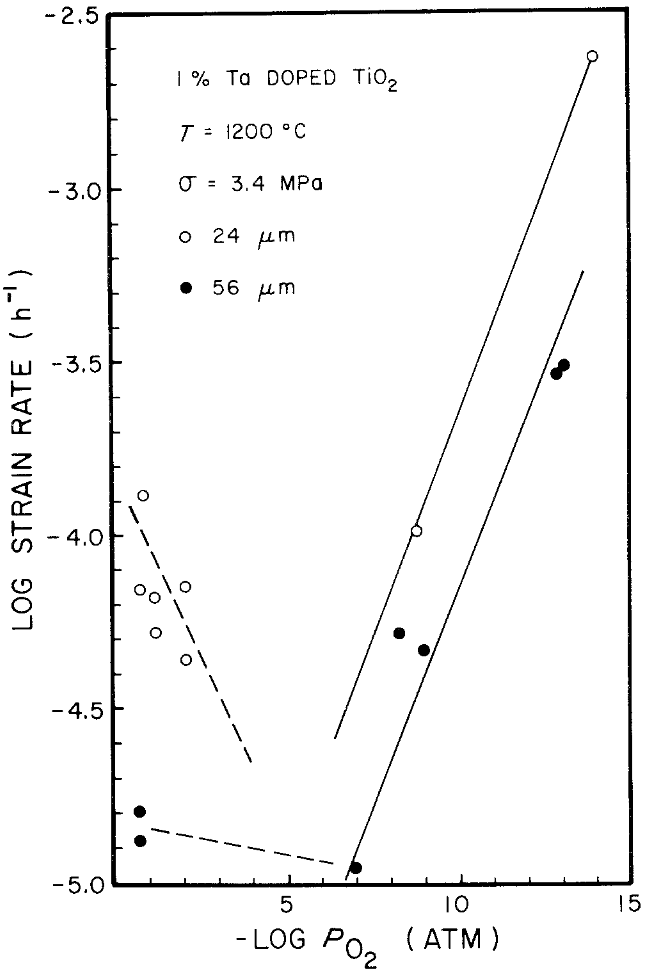

Figure 5 Effect of oxygen partial pressure on the creep of tantalum-doped polycrystalline rutile.

creep data according to the following equation, taking into account coupled diffusion of both the cation and anion [9, 10]:

$$\dot{\epsilon} = \frac{14\Omega_{\mathrm{v}}\sigma}{kT(GS)^2} D_{\mathrm{complex}}$$

and

$$D_{\mathrm{complex}} = \frac{D^1_{\mathrm{Ti}} D^1_{\mathrm{O}}}{D^1_{\mathrm{O}} + 2D^1_{\mathrm{Ti}}}$$

D^1_{Ti} and D^1_{O} are the titanium and oxygen lattice diffusion coefficients, respectively, Ω_{v} is the molecular volume and k is Boltzmann's constant. In Fig. 7 calculated values of D_{complex}, which were computed from the steady state creep of undoped and tantalum-doped rutile, are compared with titanium [11, 12] and oxygen [13] tracer diffusion coefficients measured on undoped single crystals equilibrated in air atmosphere. Diffusion coefficients calculated from the creep of undoped polycrystalline rutile are underestimated because volume diffusion is so rapid that the kinetics are probably rate-limited by interfacial reactions at grain boundaries. Nevertheless, reasonable agreement exists between diffusion coefficients inferred from creep data and tracer measurements. It is noted that the diffusion coefficients calculated from the creep of doped rutile in a very reducing atmosphere are comparable to what might be expected for diffusion in undoped material equilibrated in an oxidizing atmosphere. Note also the significant depressing effect of tantalum doping on lattice diffusion.

Since tantalum substitutes for titanium on the cation lattice, it can be concluded that the concentration of both titanium interstitials ($\mathrm{Ti}_{\mathrm{I}}^{3\cdot}$, $\mathrm{Ti}_{\mathrm{I}}^{4\cdot}$)* and oxygen vacancies ($\mathrm{V}_{\mathrm{O}}^{2\cdot}$) will be depressed as the concentration of the tantalum dopant is increased. Owing to charge considerations, the interstitial concentration will be depressed by a

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*Partially or completely ionized.

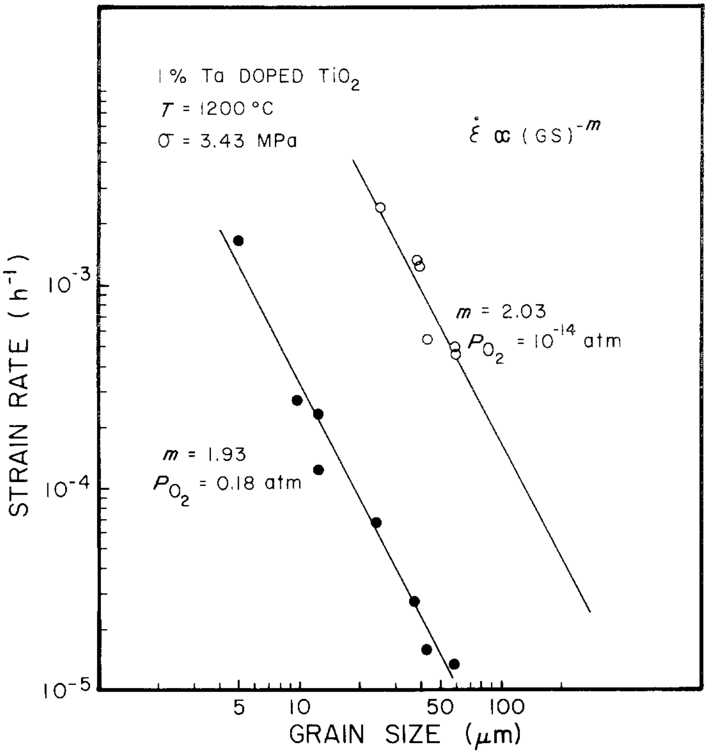

Figure 6 Grain-size effects on the diffusional creep of tantalum-doped polycrystalline rutile.

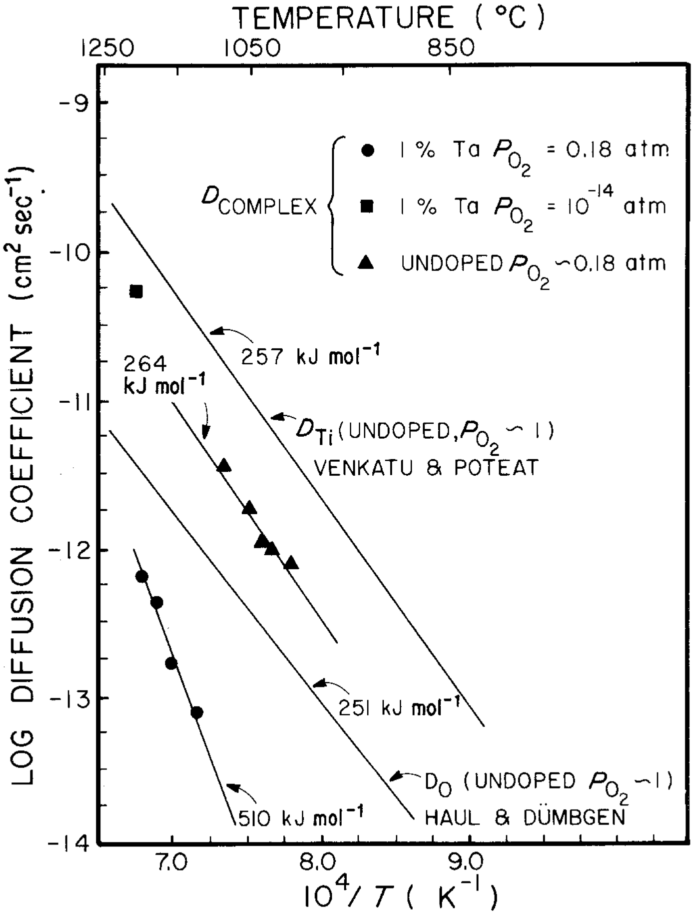

Figure 7 Comparison of diffusion coefficients obtained from tracer measurements and diffusional creep data.

greater degree than the oxygen vacancy concentration. In an oxidizing atmosphere, it is expected that the tantalum dopant will be compensated by both conduction band electrons and titanium vacancies ($V_{Ti}^{4'}$). At high dopant levels, the concentration of titanium vacancies will become significant and perhaps even dominant. With these simple considerations in mind, it is expected that, at small dopant concentrations, both titanium (via interstitials) and oxygen (via vacancies) lattice diffusion should proceed through a minimum since the concentration of titanium vacancies will increase as the tantalum concentration is increased. In this regime, creep rates will probably be cation diffusion controlled and proceed through a minimum as the concentration of cation vacancies becomes larger than the concentration of anion vacancies. At high dopants, the creep rate should again be depressed and controlled by oxygen lattice diffusion. In this study at a single dopant, insufficient data are available to distinguish between kinetics controlled by titanium (via interstitial or vacancy) and oxygen (via vacancy) lattice diffusion.

A schematic plot is made in Fig. 8 for the concentration of lattice defects in rutile at a fixed temperature (~ 1400° C) and oxygen partial pressure ($P_{O_2} \simeq 1$ atm) for different dopant levels. For purposes of illustration, the material in undoped form is assumed to be pure and not affected by the presence of any acceptors. Using this figure, which is based on simple mass action considerations† and defect concentrations inferred from conductivity data [14] as an approximate guide, mass transport by lattice diffusion in predicted to follow the solid dark line. At small dopant concentrations ($<10^{-3}$ cation fraction), lattice diffusion will be suppressed to some minimum. At this point, cation transport is predicted to increase due to the increasing concentration of titanium vacancies. At large dopant concentrations ($>10^{-2}$), mass transport is predicted to be dominated by anion

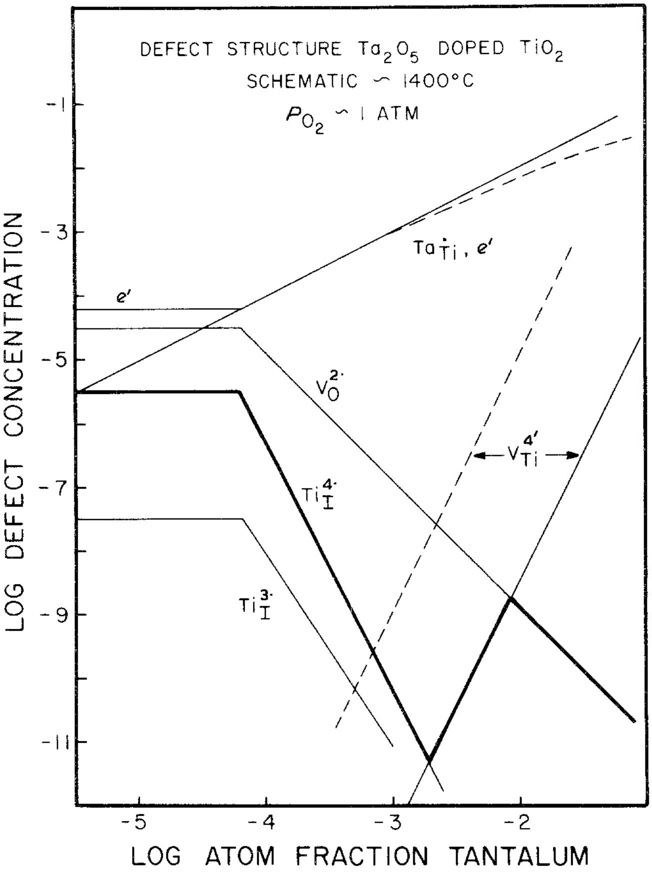

Figure 8 Schematic illustration of the effect of tantalum doping on defect concentrations in rutile.

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†Actually because tantalum doped rutile can be a degenerate semi-conductor [1], Fermi–Dirac statistics should be used in some situations to calculate defect concentrations and not classical Boltzmann statistics which are implicitly assumed in a mass action treatment [1].

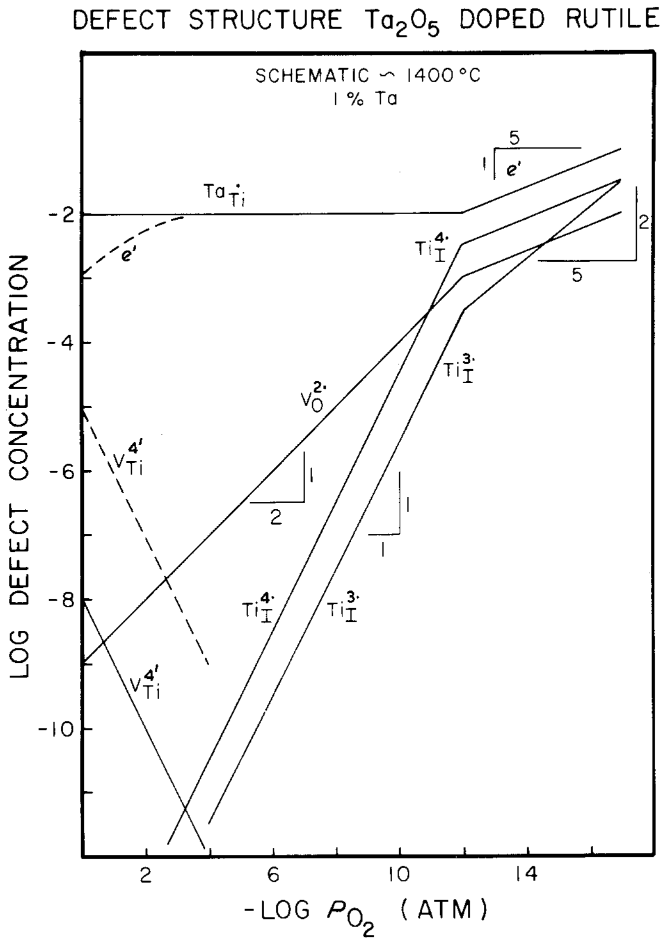

Figure 9 Schematic illustration of the effect of oxygen partial pressure on defect concentrations in rutile.

lattice diffusion and depressed again by the addition of more dopant.‡ This behaviour has been qualitatively confirmed in sintering studies at 1400° C [1]. Optimum densities are achieved at the 1% dopant concentration. At lower (~0.2%) and higher (>2%) dopant concentrations, sintering in air to high densities is very difficult. For the creep of tantalum-doped, polycrystalline rutile at 1200° C, it is clear that lattice diffusion is significantly suppressed; however, more data at different dopant concentrations are required before definitive conclusions can be made on the species (anion or cation) which is controlling lattice diffusion. At the 1% dopant concentration, it is suspected that the kinetics are controlled by oxygen lattice diffusion (via vacancy exchange).

The effects of oxygen partial pressure on the steady state creep of polycrystalline rutile doped with tantalum can also be understood qualitatively by examining simple mass action effects. In Fig. 9, the concentration of lattice defects at 1400° C and a dopant depresses both the concentration of titanium interstitials and oxygen vacancies at high oxygen partial pressures, it is predicted that the creep rate of doped material will be independent of the oxygen partial pressure until the pressure is reduced below about 10^{-7} to 10^{-8} atm§. At this point, the concentrations of both titanium interstitials and oxygen vacancies increase to enhance lattice diffusion. In the intermediate pressure regime (i.e. $>10^{-7}$ to 10^{-8} atm), the concentrations of all lattice defects are significantly depressed.

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‡The exact position of this maximum will, of course, depend on the position of the line describing the concentration of cation vacancies. Two positions have been shown for purposes of illustration. It is also possible, of course, that if anion grain-boundary transport is rapid, as might be the case [15], then the kinetics will be controlled by cation lattice diffusion via exchange with vacancies and no maximum will be observed with increasing dopant concentration.

§If oxygen grain-boundary transport is rapid, then creep will be controlled by cation diffusion and creep rates will drop to a minimum with a decrease in oxygen partial pressure from 1 to 10^{-7} atm.

At pressures under 10^{-12} to 10^{-16} atm, depending on the exact temperature, it is expected that the conduction band electrons will be compensated by titanium interstitials (intrinsic "n"-type semi-conduction).¶ Electrical conductivity measurements [17] on Ta-doped, polycrystalline rutile actually indicate a plateau (donor-controlled conduction) independent of P_{O_2} until the pressure drops below 10^{-14} atm at 1300° C (~ 10^{-12} atm at 1400° C and ~ 10^{-16} atm at 1200° C). However, in creep (and probably sintering) the concentrations of minority lattice defects ($\mathrm{Ti}_\mathrm{I}^{3\cdot}$, $\mathrm{Ti}_\mathrm{I}^{4\cdot}$ or $\mathrm{V}_\mathrm{O}^{2\cdot}$) increase with decreasing oxygen partial pressure and they become significant in mass transport at pressures well above the transition in electrical conductivity which is sensitive to the dominant charged defects (i.e. conduction band electrons).

Finally, a comment should be made that not only is lattice diffusion suppressed in Ta-doped rutile, but the activation energy for diffusion is significantly increased. This can be explained qualitatively in terms of doping which controls the concentration of conduction band electrons and increases the apparent defect formation energy for the minority lattice defects. The activation energy for the creep of undoped material is comparable to tracer diffusion coefficients of both titanium and oxygen. This apparent agreement may be fortuitous in that creep may not be controlled by any lattice diffusion process. It is believed that because of the high defect concentrations in undoped rutile, lattice diffusion is too fast to be accommodated by defect creation and/or annihilation processes at grain boundaries.

5. Conclusion

The diffusional creep of tantalum-doped polycrystalline rutile at 1100 to 1200° C is rate-controlled by a lattice diffusion process. At the 1 cation % dopant concentration, mass transport is probably limited by oxygen lattice diffusion via a vacancy exchange mechanism which is suppressed by the dopant in solid solution. In reducing atmospheres ($<10^{-1}$ atm), both cation and anion lattice diffusion, and hence diffusional creep rates, are enhanced by increased concentrations of both titanium interstitials and oxygen vacancies. Additional studies are needed at different dopant levels to identify possible transitions in mass transport kinetics which are dominated by (1) cation diffusion involving interstitial defects, (2) cation diffusion via vacancy exchange and (3) anion diffusion via vacancy exchange.

Tentative evidence was presented in support of the hypothesis that the creep of polycrystalline, undoped rutile at 950 to 1100° C is controlled by interfacial defect creation and/or annihilation at grain boundaries. Interfacial control of mass transport kinetics implies very rapid lattice diffusion processes caused by relatively large defect concentrations and/or mobilities on the cation and anion sublattices [18].

Acknowledgements

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References

1. G. R. MILLER and O. W. JOHNSON, The Sintering of Conductive Rutile: A Model System for Sintering Electronic Ceramics, in "Processing of Crystalline Ceramics", edited by Hayne Palmour III, R. E. Davis and T. M. Hare (Plenum, New York, 1978) pp. 181–91.
2. WALTER M. HIRTHE and JOHN O. BRITTAIN, *J. Amer. Ceram. Soc.* **46** (1963) 411.
3. N. E. FARB, O. W. JOHNSON and P. GIBBS, *J. Appl. Phys.* **36** (1965) 1746.
4. GLENN W. HOLLENBERG and RONALD S. GORDON, *J. Amer. Ceram. Soc.* **56** (1973) 140.
5. G. W. HOLLENBERG, G. R. TERWILLIGER and R. S. GORDON, *ibid.* **54** (1971) 196.
6. F. R. N. NABARRO, in "Report of a Conference on Strength of Solids", University of Bristol, H. Wills Physical Laboratory, Bristol, England, 1947 (Physical Society of London, 1948) pp. 75–80.
7. CONYERS HERRING, *J. Appl. Phys.* **21** (5) (1950) 437.
8. B. BURTON, "Diffusional Creep of Polycrystalline Materials" (Trans Technical Publications, Bay Village, Ohio, 1977) pp. 61–78.
9. RONALD S. GORDON, *J. Amer. Ceram. Soc.* **56** (1973) 147.
10. R. S. GORDON, Ambipolar Diffusion and its Application to Diffusion Creep, in "Mass Transport Phenomena in Ceramics", edited by A. R. Cooper and A. H. Heuer (Plenum, New York, 1975) pp. 445–64.
11. R. HAUL and G. DÜMBGEN, *Z. Elektrochemie* **66** (1962) 636.
12. *Idem, J. Phys. Chem. Solids* **26** (1965) 1.
13. D. L. VENKATU and L. E. POTEAT, *Mater. Eng. Sci. Eng.* **5** (1969/70) 258.
14. R. N. BLUMENTHAL, J. BAUKUS and W. M. HIRTHE, *J. Electrochem. Soc.* **114** (1967) 172.
15. O. W. JOHNSON and G. R. MILLER, private

¶For purposes of illustration we have assumed that completely ionized titanium interstitials are dominant [13]. Eventually, as the P_{O_2} is lowered even further, trivalent titanium interstitials will become dominant.

communication.
16. J. R. AKSE and H. B. WHITEHURST, *J. Phys. Chem. Solids* 39 (1978) 457.
17. L. FARR, Senior Thesis, University of Utah (1982).
18. Y. IKUMA and R. S. GORDON, Role of Interfacial Defect Creation-Annihilation Processes at Grain Boundaries on the Diffusional Creep of Polycrystalline Alumina, in "Surfaces and Interfaces in Ceramic and Ceramic Metal Systems", edited by J. Pask and A. Evans (Plenum, New York, (1981) pp. 283–94.

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