

A REACTION RATE STUDY IN HYDROFLUORIC ACID OF THE DISSOLUTION OF TITANIUM AND THE ALPHA SOLID SOLUTION OF OXYGEN IN TITANIUM

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SUMMARY

Studies were conducted into the mechanism of dissolution in hydrofluoric-hydrochloric acid mixtures of titanium and of alpha solid solution specimens of oxygen in titanium. Special precautions were taken to preserve the trivalent state of titanium. For titanium a rate order of 0.76 and an activation energy of 6.9 ± 0.5 kcal was found and for titanium in TiO_x a rate order of 0.83 and an activation energy of 6.6 ± 0.5 kcal. Furthermore, the oxygen content of TiO_x , within the range studied, had no effect on the rate of hydrogen evolution; all specimens evolved hydrogen at the same fixed rate per unit area for a given temperature. It is concluded that a diffusionally controlled reaction can best explain the results.

INTRODUCTION

A review of the literature¹⁻³ involving the dissolution of titanium in hydrofluoric acid suggested that a further investigation into the subject might provide a better understanding of the mechanism. Accordingly, rate studies were carried out on the dissolution in hydrofluoric-hydrochloric acid mixtures of titanium and solid solutions of oxygen in titanium to determine whether the kinetics of the latter were vastly different from those of the metal.

The TiO_x specimens to be studied lay in the alpha solid solution region of the Ti-rich portion of the constitution diagram for Ti-O⁴. From previous work⁵ it was concluded that TiO_x was a solid solution of Ti and Ti_2O_3 . This suggested that only free titanium, *i.e.*, that not bonded with oxygen evolved hydrogen



the Ti_2O_3 dissolving with no hydrogen evolution. From these facts one might expect the kinetics for Ti in TiO_x and titanium sheet in HF to be the same, thus affording an insight into the probable mechanism for titanium dissolution.

EXPERIMENTAL

Material and apparatus

A specimen of commercial grade titanium metal was cut from a sheet of cold rolled metal (stress-relieved by annealing) and mounted in clear lucite plastic attached

to a stirrer so as to expose 1 cm² of surface to the acid. Prior to dissolution all samples were ground, polished, and etched in 3 *N* HF.

The apparatus used is described in the literature². To preserve the trivalent state of titanium, all oxygen in the system prior to each experiment was eliminated by flushing the apparatus with pure hydrogen gas. This was necessary since any oxygen remaining would tend to enter into an oxidation reaction which might alter the volume of H₂ collected per dissolution experiment. A volume of 300 ml of acid was used in all experiments and the temperature was controlled within $\pm 0.1^\circ\text{C}$.

The Ti-O alloys were prepared by thoroughly mixing calculated amounts of titanium powder (65 mesh, 98.27% pure, the balance being mainly oxygen) and titanium dioxide (reagent grade, 99.9% pure), and compacting the mixture in a 1-in. diam. die under a pressure of 7 t.s.i. The powder specimens were transferred to an alundum crucible and sintered in a vacuum resistance furnace for a period of 4 h at 1400°C (vacuum 2-3 microns). At the end of the reaction period the reaction tube was sealed off, air-quenched and allowed to stand overnight. The thoroughly sintered specimen was removed from the furnace, the higher oxide layer scraped from the surface, and the sample examined microscopically to determine homogeneity. The samples were then cut to size, polished and mounted in the same manner as described for titanium metal.

Analyses of the Ti-O samples were made using the hydrogen evolution method⁵. Four specimens were prepared within the alpha solid solution region (4.50 to 14.0% oxygen at 1400°C) corresponding to 4.97, 7.02, 7.98, and 10.8% oxygen b.w.

RESULTS

Rates with Ti metal

Since the velocity of the liquid across the sample surface affects the rate of dissolution, the influence of stirrer speed was observed for titanium dissolving in 0.10 *N* HF–1.0 *N* HCl at 25.0°C. The rate of hydrogen evolution for the range 0–460 rev/min is given by the plot of V versus s (Fig. 1), where V is the rate in units of mm³cm⁻² min⁻¹ (eqn. 2) and s is the stirrer speed in rev/min. A stirrer speed of 200 rev/min was maintained throughout all experiments. The maximum rates observed in each experiment are shown in Fig. 1.

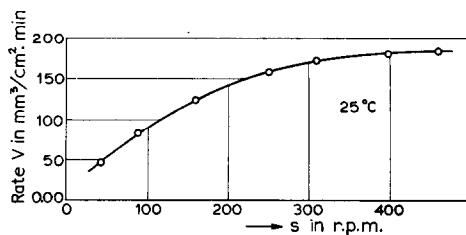


Fig. 1. Rate of hydrogen evolution V as a function of stirrer speed in rev/min. Titanium dissolving in 0.1 *N* HF, 1 *N* HCl.

These rates were calculated using the expression

$$V = \frac{1000 \Delta v}{A \Delta t} \text{ mm}^3 \text{ cm}^{-2} \text{ min}^{-1} \quad (2)$$

where Δv is the volume of H₂ in ml at STP evolved in Δt minutes and A is the area of the sample in cm².

From the stoichiometry of eqn. 1 the rate may be expressed in mg of Ti cm⁻²mm⁻¹ by multiplying eqn. 2 by the factor

$$\frac{2 \times 47.9}{3 \times 22,414} = 0.001425$$

The dissolution of titanium at four concentrations of HF, 0.050, 0.075, 0.10, and 0.50 *N*, all 1.00 *N* with respect to HCl, and at temperatures of 15°–45°C was investigated. Hydrochloric acid was added to control the equilibrium concentration of fluoride complexes. The concentration of the un-ionized HF was therefore essentially the same as the stoichiometric concentration of the acid. From plots of $\ln(\text{rate})$ versus $\ln(\text{acid})$ concentration an order of 0.76 was obtained. Hence, the rate of dissolution obeys the equation

$$V = kC^{0.76} \quad (3)$$

where k is the reaction rate constant in mm³cm⁻²mm⁻¹ liters equiv.⁻¹, and C the equiv. liter⁻¹ of the acid.

Similar results ($V = kC^{0.81}$) were obtained within error limits for the order of dissolution of titanium in HF in the absence of HCl. The rates of hydrogen evolution were higher, however, in the HF–HCl mixtures owing to the shift in equilibrium toward higher concentrations of un-ionized HF, although the increase could not be entirely accounted for by the equilibrium constant⁶. The rates were therefore dependent upon un-ionized HF as observed in experiments with other metals dissolving in HF^{7,8}.

Rates with TiO_x solid solutions

The dissolution of the four solid solution specimens was conducted at 25.0°C and in four hydrofluoric acid concentrations of 0.050, 0.075, 0.10 and 0.50 *N* all 1.00 *N* with respect to HCl. From a plot of $\ln(\text{rate})$ vs. $\ln(\text{concentration})$ the rate equation obtained for the dissolution of the Ti not bonded with oxygen in TiO_x is

$$V = kC^{0.83} \quad (4)$$

Table I summarizes the results for the four samples of TiO_x.

An examination of Table I reveals that the rate of hydrogen evolution for all of the specimens at a given acid concentration is nearly constant. Attempts to prepare specimens of lower oxygen content were not successful. The scatter from one specimen to another suggests no real differences. On this basis the average rate of hydrogen evolution was calculated for each acid concentration and is shown in Table I.

The total rate of dissolution of TiO_x in mg cm⁻² min⁻¹ was then determined from the established stoichiometry of eqn. 5,

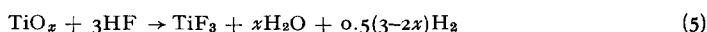


TABLE I
SUMMARY OF DISSOLUTION RATES OF THE Ti-O ALPHA SOLID SOLUTION IN HF-HCl
MIXTURES AT 25.0°C
(Conc. of HCl, 1 N throughout)

Sample	Rates of H_2 evolution* ($mm^3cm^{-2}min^{-1}$) in HF			
	HF Normality			
	0.05	0.075	0.1	0.5
TiO _{0.157}	102	164	248	924
TiO _{0.228}	89	157	210	715
TiO _{0.280}	118	175	193	618
TiO _{0.365}	100	204	246	775
Average	102	175	224	758

* Each rate value an average of two runs.

and is summarized in Table II.

TABLE II
TOTAL RATES OF DISSOLUTION ($mgcm^{-2}min^{-1}$) OF TiO_x ALLOYS IN
VARYING HF CONCENTRATIONS AT 25.0°C

Sample	HF Normality			
	0.050	0.075	0.10	0.50
TiO _{0.157}	0.171	0.293	0.375	1.27
TiO _{0.228}	0.184	0.316	0.404	1.37
TiO _{0.280}	0.191	0.328	0.420	1.42
TiO _{0.365}	0.216	0.370	0.474	1.60

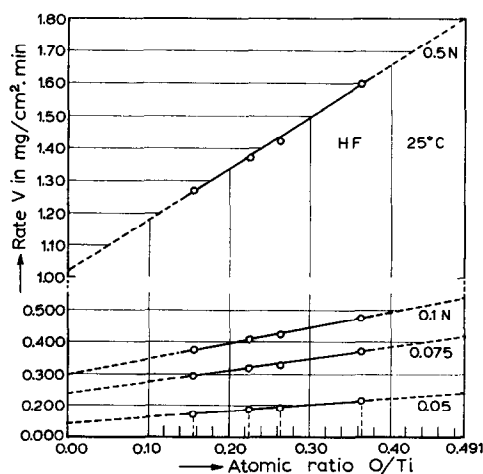


Fig. 2. Total rate of dissolution of TiO_x alloys (α -phase border at 14.0% b.w. of O) in a mixture of 0.10 N HF and 1.00 N HCl.

The variation of dissolution of the alpha solid solutions in 0.10 N HF–1.00 N HCl with respect to the atomic ratio (O/Ti) is shown in Fig. 2. The straight lines are extrapolated in both directions so as to cover the entire alpha solid solution region. The extrapolated values of the rate at 0.000 (O/Ti) are 0.140, 0.235, 0.296 and 1.019 as compared to respective values of 0.110, 0.157, 0.210 and 0.656 mgcm⁻²min⁻¹ for the commercial metal. The larger values for the powder metallurgy products are expected since the surface area on a micro scale is undoubtedly larger than for the solid metal. Nevertheless, the reaction order, calculated from the rate values extrapolated to zero oxygen, agrees within the limits of error with that obtained for the compact metal (0.77 vs. 0.76).

Effect of temperature on rates

Rate studies were made on both titanium metal and TiO_x alpha solid solutions dissolving in 0.10 N HF–1.00 N HCl over a range of temperatures that included 15, 25, 35 and 45°C. From the average maximum rates the reaction rate constants were obtained and graphs of $\ln k$ vs. $1/T$ were constructed. A straight line was obtained in each case as expressed by the following equations; and the activation energies E_a^* were calculated

$$\begin{aligned}\ln k &= -3.50 \cdot 10^3/T + 18.5 \text{ (Ti)} \\ E_a^* &= 6.93 \text{ kcal}\end{aligned}\tag{6}$$

$$\begin{aligned}\ln k &= -3.33 \cdot 10^3/T + 18.5 \text{ (Ti in TiO}_x\text{)} \\ E_a^* &= 6.63 \text{ kcal}\end{aligned}\tag{7}$$

DISCUSSION AND CONCLUSIONS

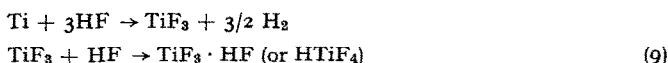
From the relatively low values of the temperature coefficient (E_a^*) and the stirring effect, the slow step is suggested to be physical rather than chemical. However, chemical activation steps cannot be excluded on the basis of energy magnitude alone, particularly if electrochemical processes are involved.

If the dissolution is controlled by a chemical activation step it is difficult to explain the experimental evidence establishing within error limits a fixed rate of hydrogen evolution per unit area of TiO_x specimens in the same acid concentrations. These results appear to favor the physical activation step since one would expect that the presence of varying amounts of Ti₂O₃ (incapable of producing hydrogen) as cathodic sites would have a decided effect on the rate of hydrogen evolution of titanium not bonded with oxygen, particularly if an electrochemical mechanism were rate-controlling. Furthermore, the reaction orders and activation energies for titanium sheet and Ti in TiO_x dissolving in HF are equal within experimental limits of error, indicating that varying amounts of the oxide cause no measurable difference in the kinetic properties of the two titanium samples. If the reaction is diffusionally controlled and obeys Fick's first law the rates should be proportional to the HF concentration, yielding an order of one as observed for other metals dissolving in HF⁶⁻⁹. The deviation of the value from unity cannot be attributed to experimental technique since run after run has resulted in values always close to 0.80 and the methods are the same as used for zirconium and hafnium studies^{8,9}.

It is known that a very slow reaction of TiF_3 with HF results in hydrogen evolution according to the equation



If one assumes that the process of dissolution of Ti involves competition of a product TiF_3 for the diffusing molecular HF according to the following equations



this may account, since reaction 8 is very slow, for the experimental order being less than unity¹⁰. Further experiments are in progress to account for the observed order.

From the foregoing it can be concluded that the slow step cannot be electrochemically controlled and that since the order and activation energy for the dissolution of titanium metal and Ti in TiO_x in HF are the same, the mechanism of dissolution is the same for both; the slow step is probably governed by the diffusion of molecular HF to the reacting surface.

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