Thermochimica Acta, 84 (1985) 357–365
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE REACTION OF OXYGEN AND ZIRCONIUM

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(Received 22 August 1984)

ABSTRACT

The oxidation of zirconium powder was studied under isobaric conditions in oxygen at 146 Torr and at temperatures of 500, 550, 600, 650 and 700°C. The kinetic results indicated that the reaction is controlled by a combined diffusion–nuclei reaction mechanism. It is proposed that the diffusion is dominated by anion vacancies in the zirconium oxide. By ESR it was shown that these were oxygen vacancies of the substoichiometric ZrO_{2-x}.

INTRODUCTION

The oxidation of zirconium has been extensively studied because: (1) zirconium alloys are important for atomic reactors; (2) the system $Zr{-}O_2$ is rather simple compared to other metal–oxygen systems because usually only the dioxide is obtained

$$Zr_{(s)} + O_{2(g)} = ZrO_{2(s)} \tag{1}$$

so that this oxidation reaction can serve as model to other reactions. The greater part of these studies were performed on metal plates, spheres or sheets [1]. However, only few studies are reported on the oxidation of powders [2].

In the present communication the study of the oxidation of zirconium powder is reported. Results from such a study may shed light on the reactions of metal powders and oxygen, bearing in mind the controlled preparation of oxidic catalysts.

EXPERIMENTAL

Procedure

The kinetic experiments were carried out in a static system using a Cahn vacuum microbalance apparatus following the procedure previously de-

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scribed [5]. Perforated quartz buckets were used to enable maximum contact of the particles with the oxygen. The samples used weighed around 30 mg so that weight gain was around 10 mg.

Electron spin resonance (ESR)

These experiments were performed in situ by the procedure previously described [3].

Chemicals

All the reagents were of analytical grade. Zirconium powder (80 mesh) was supplied by Goodfellow, and was of 99.9% purity.

RESULTS

A series of metallic samples was oxidized at temperatures of 500, 550, 600, 650 and 700°C (Fig. 1). The oxidation took place in oxygen at a pressure of 146 Torr. At this pressure the oxygen did not change its pressure during the reaction, because part of the oxygen was liquified in the liquid nitrogen-cooled traps. Preliminary runs at low oxygen pressures (~ 1 Torr) gave irreproducible results.

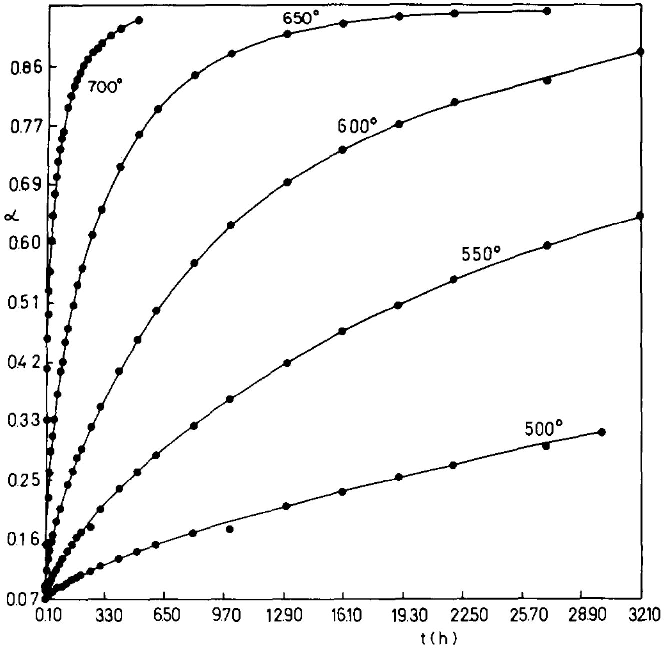


Fig. 1. Oxidation of zirconium at 500, 550, 650 and 700°C, and at 146 Torr oxygen.

Reactions without preoxidation

The reaction became violent at 400°C and results could not be recorded.

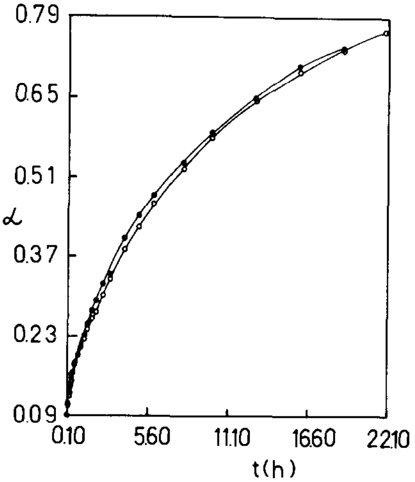
Preoxidation and reaction

The samples were evacuated overnight at 10^{-5} Torr, at room temperature. Subsequently, the temperature was raised to 600°C for annealing and desorption, and kept at this temperature for 1 h. Then the temperature was lowered to 200°C and oxygen bled in until an equilibrium pressure of 146 Torr was attained. The temperature was raised very slowly (5°C min^{-1}) to 500°C for preoxidation, with a simultaneous increase in weight. The preoxidation reaction was terminated after 6.5% of the metal had reacted. The oxygen was pumped off quickly to 10^{-5} Torr in 5 min. The sample's temperature was raised to one of the reaction temperatures (Fig. 1) and the pressure in the reaction chamber was equilibrated in a short time with the pressure in the region of 146 Torr. It is obvious that this treatment diffuses results of the initial stage of the reaction. The fraction α was calculated taking into account the preoxidation.

The reaction was repeated twice at each temperature. The reproducibility was $\pm 5\%$. The reactions at low temperatures were slow and did not reach $\alpha = 1$ even at the extended reaction periods (Fig. 1).

The effect of mass and dispersion on the reaction

Lower weights of zirconium were used (2.5 mg). The metal particles were spread on the bottom of the weighing bucket and contact between them was



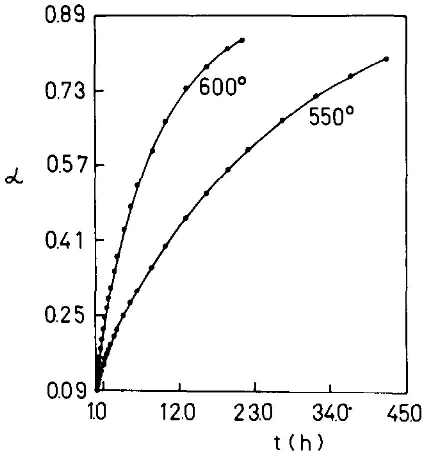


Fig. 2. Influence of zirconium metal weight on the reaction: (●) 25 mg; (○) 2.5 mg at 600°C.

Fig. 3. Influence of particle size and smoothness at 550 and 600°C.

minimized. The reaction was carried out at 600°C. From Fig. 2 it can be seen that the reaction is nearly identical to that of larger samples.

Particles size and texture

From microscopic observations it was realized that the particles were nearly spherical, however, their faces were not smooth. The particles were chemically polished with a solution of 5% HF/45% HNO_3/50% H_2O and rinsed with water (triply distilled) and ethanol. The particles obtained were smaller and spherical. The oxidation reactions were carried out on the polished, smaller particles, under identical conditions as described above for the "off-the-shelf" specimens. As shown in Fig. 3 there was no change in the reaction development.

Oxygen pressure

A reaction was performed at 550°C at a lower pressure of oxygen (13 Torr). The results are presented in Table 1. It may be realized that the reaction is not affected by the oxygen pressure in the region 13–146 Torr.

X-ray

The reaction products both at lower and higher temperatures showed that the product obtained was monoclinic zirconium oxide.

Heating above the transition temperature of zirconia

The sample was heated at 550°C. When 50% had reacted, the oxygen was rapidly pumped to 10^{-5} Torr. When this low pressure was reached, the sample's temperature was raised to 1200°C and kept there for 30 min. Subsequently, the temperature was lowered to 550°C and oxygen applied. The weight increased in a matter of seconds. After this oxidation, the reaction proceeded at a measurable rate; although it was higher than the usual rate for this temperature.

At 1110°C there is a reversible phase transition from a monoclinic to a tetragonal phase which is accompanied by a large volume change (~ 6%),

TABLE 1

The influence of oxygen pressure on the reaction rate of the oxidation of zirconium by oxygen

Time (h)	0.5	1.0	2.0	3.0	8.0	16.0	27.0
α (146 Torr)	0.046	0.07	0.1096	0.1414	0.263	0.411	0.55
α (13 Torr)	0.0395	0.066	0.105	0.138	0.263	0.4046	0.533

which causes zirconia to crack under thermal cycling [4]. Sometimes there is a hysteresis in the phase transition. In the present study under the conditions of the reaction, the lag was not longer than the reaction times.

ESR

The evacuated zirconium metal did not show a signal at room temperature. The adsorption of oxygen at room temperature and 40°C resulted in a similar spectrum to that observed in vacuum. Heating the sample in vacuum and under ambient oxygen at 300°C did not produce a signal. A broad signal (Fig. 4) appeared when the sample was heated in oxygen at the reaction conditions at 550, 600 and 690°C. Evacuation at this temperature after the reaction took place did not result in the disappearance of the signal.

DISCUSSION

The oxidation of powdered zirconium was carried out under isobaric conditions (pressure of oxygen at 146 Torr) and the temperatures of 500,

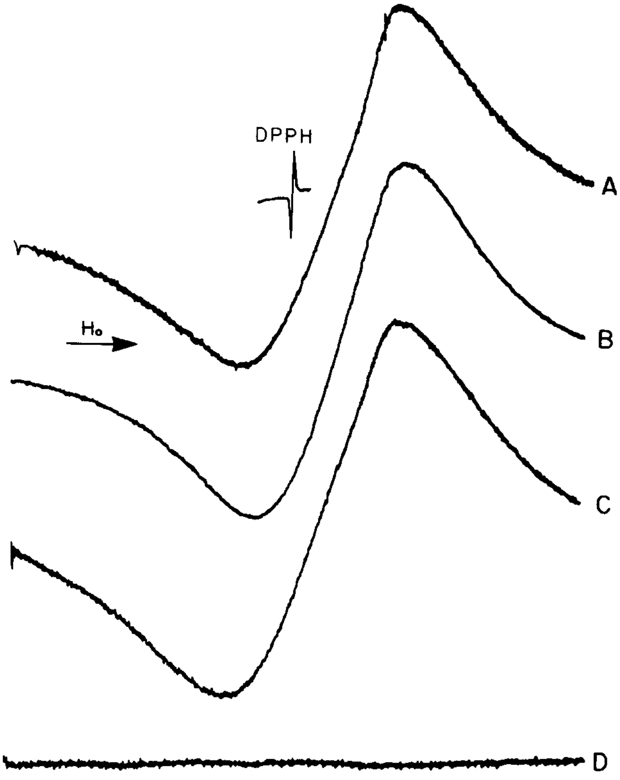


Fig. 4. ESR of oxidized zirconium: (A) 550°C; (B) 600°C; (C) 690°C; (D) metal prior to reaction.

550, 600, 650 and 700°C after a preoxidation (Fig. 1). By this preoxidation an oxidic layer of substoichiometric zirconium (ZrO_{2-x}) was formed, which very probably separates the metal and the oxygen. The solid product of the reaction was monoclinic zirconium oxide (eqn. 1). The ESR recordings indicate that the zirconia obtained is a deficient compound having a composition which may be described by ZrO_{2-x}. These deficiencies may enhance the rate of phase transition, thus minimizing a hysteresis in the reactions where heating was at 1200°C.

Kinetics

The experimental results (Fig. 1) were analyzed using a CDC computer [5]. The following general kinetic equation was applied

$$f(\alpha) = kt^n + C \tag{2}$$

where n and C are constants. The plotting of $f(\alpha)$ vs. t gave the rate, k. A program was prepared for fourteen equations summarized by Hulbert [6]. A second program was prepared which was identical to the first except that a nuclei analysis was performed where n varied from 0.2 to 4.0. It was found, using these programs, that the best fitting for the reaction was the Ginstling–Brounstein equation (Fig. 5) which was based on a Jander model

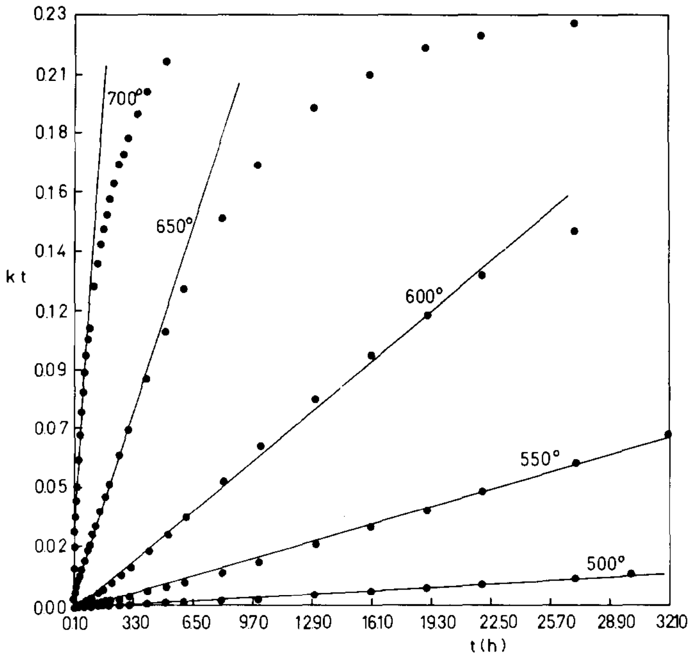


Fig. 5. A presentation of the results in Fig. 1 described by the equation of Ginstling and Brounstein.

[7]. Also, a nuclei 2/3 equation (Fig. 6) fitted the results. Above $\alpha = 0.8$ the reaction did not fit any of the equations. The apparent activation energies calculated for the Ginstling–Brounstein and nuclei 2/3 were: $E_{GB} = 154.37$ kJ mol^{-1} and $E_{N2/3} = 154.62$ kJ mol^{-1}. The size and surface smoothness of the granules did not have any effect on the rates measured at the two temperatures (Table 1, Figs. 2 and 7). The agreement of the results with the Ginstling–Brounstein equation, which is a Jander type equation, may indicate a diffusion-controlled reaction. On the other hand, following a nuclei-type equation could suggest that the reaction is controlled by a combined mechanism. A mathematical derivation is brought by Hulbert [6] showing an interconnection between these two proposed mechanisms. It is proposed that substoichiometric zirconia is obtained as a continuous and protective layer and serves as a diffusion medium of oxygen to the metal. The oxygen vacancies are formed as follows

$$Zr_{(s)} + (1 - x)O_2 = ZrO_{2-x} \tag{3}$$

where $x \ll 1$.

Oxygen was adsorbed onto the oxide layer prepared by the preoxidation (this protective layer may prevent the dissolution of oxygen in zirconium). Two reactions were possible: (i) a further oxidation of ZrO_{2-x}; (ii) a diffusion assisted by the oxygen vacancies. From the ESR results it may be

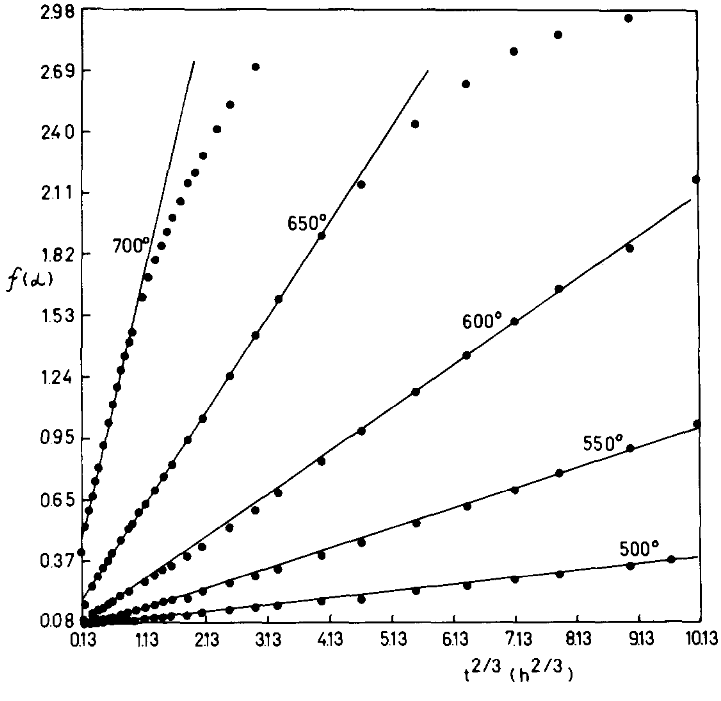


Fig. 6. A presentation of the kinetics in Fig. 1 described by a nuclei 2/3 equation.

concluded that up to 50% ZrO_{2-x} is present which excludes the possibility of the oxidation of zirconia. At the extended times above α-values of 0.8 the diffusion coefficient may change because of the layer's thickness. At this stage the kinetics may represent an oxidation reaction of substoichiometric zirconia to ZrO_2.

Ronson [8] found that the oxidation of powdered $ZrO_{1.975}$ fitted the equation proposed by Serin and Ellickson. In the present work the results did not fit this equation. It is possible that the value of x in ZrO_{2-x} is different. The possibility that the Zr/ZrO_{2-x} interface affects the reaction cannot be excluded. The diffusion of oxygen adsorbed on the oxide occurs through the oxygen anionic vacancies. Zirconium metal dissolves fairly high amounts of oxygen. However, here, because of the preoxidation, the metal is not exposed to gaseous oxygen. The oxygen adsorbed on the zirconia diffuses to the interfacial metal oxide [9] where nuclei of zirconium oxide are present. These nuclei grow further by diffusion until about 80% of the metal is oxidized.

Further support that the oxide layer is regular and separates the metal from the gaseous oxygen is provided by the cycle of heating and cooling of the sample at 1200 and 550°C. The cracks which were formed in the oxide layer exposed new faces of zirconium which resulted in a violent reaction. This fast reaction becomes slower because of the formation of a new oxide layer. The higher rate obtained after the heating-cooling cycle may be a result of the formation of a larger surface area. The independence of the reaction rate to oxygen pressure gives additional support to the idea that the reaction is controlled by bulk diffusion and not by surface reaction.

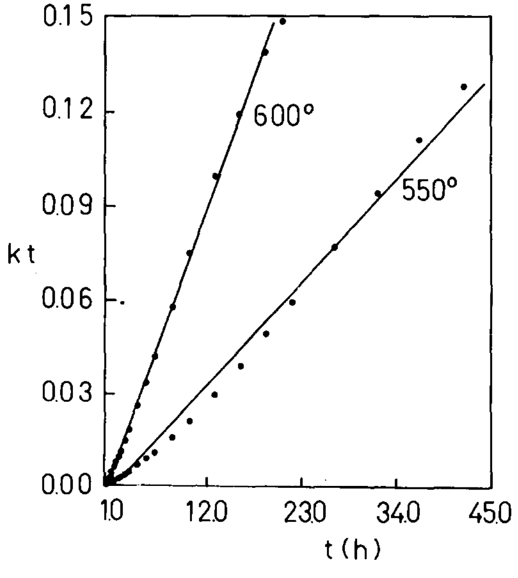


Fig. 7. A Ginstling and Brounstein presentation of the results from Fig. 3.

CONCLUSIONS

(1) The oxidation of powdered zirconium results in the formation of monoclinic zirconia.

(2) The reaction is diffusion controlled. The diffusion is assisted by the defects in the deficient substoichiometric ZrO_{2-x}.

(3) The reaction does not obey equations at α-values higher than 0.8, because at this stage nonstoichiometric ZrO_{2-x} oxidation may take place simultaneously with the metal oxidation.

(4) In order to obtain a zirconia preparation which has a smooth surface the oxidation must be carried out at a temperature lower than 1110°C.

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