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Note

THE OXIDATION REACTION OF POWDERED ZIRCONIUM AND CARBON DIOXIDE

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The oxidation of zirconium metal powder was found to be controlled by inward diffusion of oxygen through the substoichiometric zirconium oxide, ZrO_{2-x} [1]. The oxidation of the powdered metal was independent of the oxygen pressure. The apparent activation energy calculated was ~ 154 kJ mol^{-1}.

In the present note we report on the oxidation of zirconium metal powder by carbon dioxide. In variance to the reaction of zirconium with oxygen where only one product was obtained, i.e., monoclinic zirconium dioxide [1], here there is a possibility of the production of several products such as carbon, zirconium dioxide, zirconium carbide and carbon monoxide. Guerlet and Lehr [2] reported that for the reaction of carbon monoxide and zirconium strips at temperatures lower than 850°C only two species were formed: carbon and monoclinic zirconium dioxide.

The experimental procedure followed in the present work was the same as that reported previously [1]. The carbon dioxide pressure was 150 Torr and the traps were cooled by immersion in carbon dioxide–acetone. At this pressure the work is not carried out under isobaric conditions. However, with the sample masses used (~ 26 mg) a 100% reaction decreased the pressure only by ~ 1 Torr. The temperature range was 600–800°C. At temperatures lower than 600°C the reaction rate was rather slow.

No preoxidation reaction [1] was needed here, since no deflagration took place at the above-mentioned temperature range when oxidizing with carbon dioxide. The samples were conditioned by evacuating overnight at pressures lower than 10^{-5} Torr at room temperature and subsequently the temperature of the sample was raised to 500°C and kept at this temperature for 1 h at 10^{-5} Torr. Then the temperature was set to the reaction temperature and carbon dioxide bled in.

A preliminary reaction was carried out at 700°C on a sample weighing 26 mg. The sample reached a constant weight of 35.1 mg showing that the

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reaction went nearly to completion to form zirconium dioxide. The calculated weight was 35.12 mg. The coolant in the traps was then substituted with liquid nitrogen and the condensation of the unreacted carbon dioxide was very slow. After 36 h the pressure dropped to 1965 μm, however, it did not reach a plateau. Assuming the reaction

$$\mathrm{Zr} + 2\mathrm{CO}_2 = \mathrm{ZrO}_2 + 2\mathrm{CO} \qquad (1)$$

the pressure of carbon monoxide expected would be 1145 μm. X-ray diffraction of the solid product showed that it is monoclinic zirconia. The effect of carbon monoxide was surveyed by exposing zirconium metal to carbon monoxide at a pressure of 100 Torr and 700°C. No change in the weight was recorded after heating for 1 h.

The reactions of carbon dioxide and zirconium were carried out at temperatures of 600, 650, 700, 750 and 800°C (Fig. 1). The solid products were tested by X-ray diffraction after reactions at 600 and 800°C. At 600°C metallic zirconium and monoclinic zirconia were identified, and at 800°C monoclinic zirconia and small amounts of zirconium were present.

The analyzing of the results by the two programs [1] showed a good agreement (Fig. 2) to a phase boundary (PB) kinetic equation [3], and nuclei 1.2 equation (Fig. 3). The apparent activation energies calculated were: $E_{\mathrm{PB}} = 112.26$ kJ mol^{-1} and $E_{\mathrm{N1.2}} = 119.30$ kJ mol^{-1}.

Qualitative experiments were carried out to test the influence of carbon

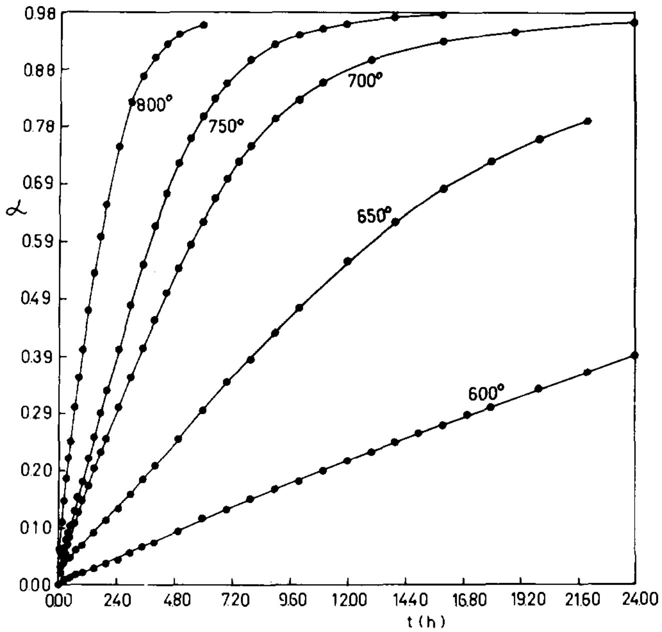


Fig. 1. Oxidation of zirconium by carbon dioxide at 600, 650, 700, 750 and 800°C at 150 Torr.

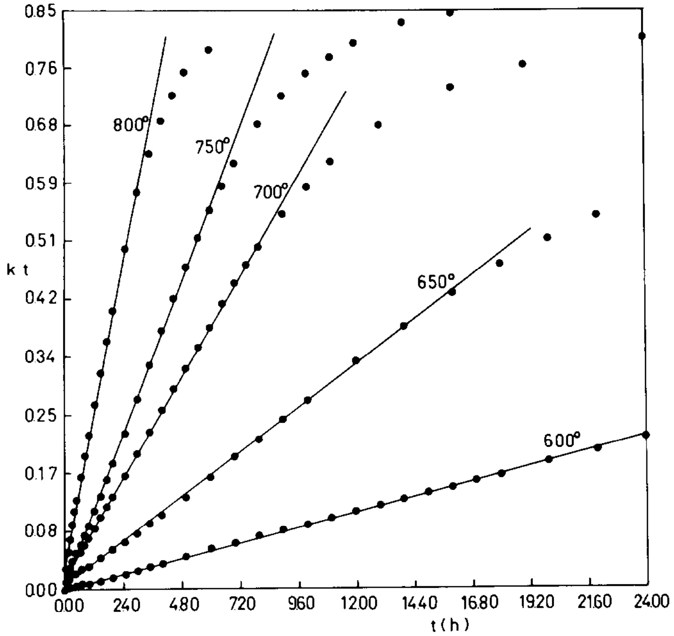
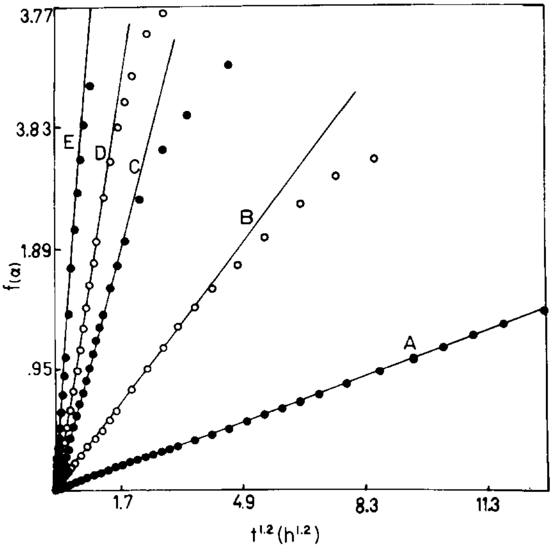


Fig. 2. A presentation of the results in Fig. 1 described by a phase-boundary equation.



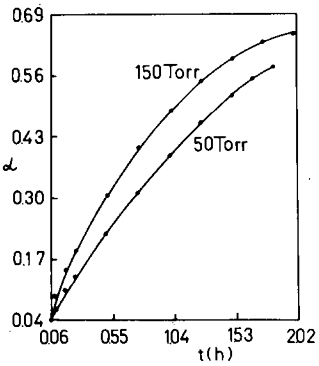


Fig. 3. A presentation of the results in Fig. 1 described by a nuclei 1.2 equation. (A) 600; (B) 650; (C) 700; (D) 750; (E) 800°C.

Fig. 4. The influence of carbon dioxide pressure on the reaction with zirconium.

dioxide pressure on the reaction rate. The results at pressures of 50 and 150 Torr at 800°C, which are presented in Fig. 4, show that the reaction rate is higher at 150 Torr. A preliminary run at 300 Torr and 800°C showed that the reaction rate was higher than that at 150 Torr.

It is proposed from the pressure dependency that the reaction is phase-boundary controlled. An additional support to this is the lower activation energy of the zirconium–carbon dioxide reaction compared to the system zirconium–oxygen (~ 154 kJ mol^{-1}) [1]. These results favor a surface-controlled mechanism.

REFERENCES

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