

### Reduction of Zirconium and Hafnium Oxides

MANY attempts have been made to reduce zirconium dioxide with hydrogen. At temperatures up to 1,500° C. no positive results have been reported<sup>1-3</sup>. Newbury and Pring<sup>4</sup> reported that at 2,500° C. and a hydrogen pressure of 150 atm. no reduction took place. Mott<sup>5</sup> stated that in an electric arc at 6,000° C. and at a hydrogen pressure of 22 atm. reduction was difficult but that sometimes a small amount of "yellow Zr<sub>2</sub>O<sub>3</sub>" was produced. In the reduction of ZrO<sub>2</sub> with lithium or calcium hydride it has been suggested that the active reducing agent is atomic hydrogen. Simonenko<sup>6</sup>, using a d.c. arc between tungsten electrodes, in a hydrogen atmosphere, claimed to have produced metallic zirconium from ZrO<sub>2</sub> placed in the cathode cavity. He believed that the ions of molecular and atomic hydrogen were responsible for the reduction, their effectiveness being increased by the negative potential.

Atomic hydrogen produced by passing hydrogen at low pressure through an electromagnetic field of 29 Mc./s. or lower (Blackwood and McTaggart<sup>7</sup>) will reduce many oxides but not ZrO<sub>2</sub>. However, it was found that if the frequency of the exciting field was increased to 2,500 Mc./s. a surface layer was formed which was black or golden. This material had a specific resistivity of the order of 1 ohm-cm. although measurements were difficult for obvious reasons. It has not been possible so far to determine the Zr:O ratio, but X-ray diffraction indicated that no change of phase occurred, the pattern remaining that of the dioxide. During treatments the temperature of the samples varied from about 200° C. to 1,200° C. depending on the power supplied (50-400 watts input to the magnetron).

Hafnium oxide, when treated in the same way, also became black and conducting. Thorium oxide remained unchanged. It would appear that a reduction took place in the case of ZrO<sub>2</sub> and HfO<sub>2</sub> similar to that occurring when TiO<sub>2</sub> is reduced in hydrogen at red heat. In the 2,500 Mc./s. field the energy normally possessed by hydrogen atoms is presumably increased by further excitation and ionization, as visualized by Simonenko, to a value which permits reduction of the above oxides to proceed.

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<sup>1</sup> Friederich, E., and Sittig, L., *Z. anorg. Chem.*, **143**, 293 (1925).

<sup>2</sup> Grube, G., and Ratsch, K., *Z. Electroch.*, **45**, 838 (1939).

<sup>3</sup> Meister, G., *Metal Progr.*, **53**, 515 (1948).

<sup>4</sup> Newbury, E., and Pring, J. N., *Proc. Roy. Soc., A*, **92**, 276 (1916).

<sup>5</sup> Mott, W. R., *Trans. Amer. Electrochem. Soc.*, **31**, 365 (1917).

<sup>6</sup> Simonenko, D. L., *Doklady Akad. Nauk S.S.R.* (2), **51**, 303 (1946).

<sup>7</sup> Blackwood, J. D., and McTaggart, F. K., *Austral. J. Chem.*, **12**, 114 (1959).

### Irradiation Decomposition of Carbon Dioxide

DURING investigation of the reaction between carbon dioxide and graphite induced by radiation, we have examined the decomposition by irradiation of carbon dioxide in the absence of graphite. These irradiations have been carried out in transparent silica vessels into which the required amounts of carbon dioxide are condensed before sealing off.

Particular care was taken to exclude organic contaminants by cleaning the silica vessels, wool and rods in hot chromic acid, followed by three washings in hot distilled water and firing at 1,000° C. for 2 hr. in an atmosphere enriched with oxygen. Carbon dioxide was prepared from 'Cardice', distilling three times before use, with rejection of first and last fractions. Mercury vapour was eliminated by the use of a trap at -78° C. placed immediately before the vessels to be filled. Analysis of the gas after irradiation was carried out by a gas chromatographic method<sup>1</sup>. The samples received a thermal neutron dose of  $2.3 \times 10^{18}$  n.cm.<sup>-2</sup> in the core of the Harwell reactor *Bepo*. From the integrated dose of thermal neutrons as measured by cobalt wires, the energy dose received by the carbon dioxide was calculated using the calorimetric data of Anderson and Waite<sup>2</sup>.

Four general conclusions may be drawn from the results:

(1) The decomposition by irradiation of carbon dioxide in the absence of an oxygen acceptor is extremely small. (2) An increase in the surface area of the silica as effected by the introduction of silica wool into the vessels does not increase the efficiency of carbon monoxide production (the  $G_{CO}$  value). The higher  $G_{CO}$  values obtained using vessels packed with silica rods are inexplicable at present. (3) An increase in the carbon dioxide pressure up to 9.5 atmospheres at the operating temperature of 100° C. does not cause a major change in  $G_{CO}$ . (4) There is always a deficiency of oxygen compared with the carbon monoxide formed.

Table 1. RADIATION-INDUCED DECOMPOSITION OF CARBON DIOXIDE IN EMPTY AND PACKED SILICA VESSELS

Empty vessels, surface area ~ 50 cm. <sup>2</sup> filling pressure (at 0° C.) mm. mercury		Rod-packed vessels, surface area ~ 200 cm. <sup>2</sup> filling pressure (at 0° C.) mm. mercury		Wool-packed vessels surface area ~ 1,200 cm. <sup>2</sup> filling pressure (at 0° C.) mm. mercury	
	$G_{CO}$		$G_{CO}$		$G_{CO}$
42	<0.03	66	0.21	42	<0.007
81	<0.004	142	0.04	169	<0.002
158	<0.002	287	<0.009	307	<0.001
343	<0.001	596	<0.015	671	<0.001
629	<0.001				
807	<0.002				
1,761	<0.002				
2,130	<0.001				
3,237	<0.001				
3,967	<0.001				
5,327	<0.001				

The first of these conclusions is in agreement with the earlier work of Harteck and Dondes<sup>3</sup>, but the second and third conclusions are in direct contradiction to their work. The formation of ozone in the radiolysis of carbon dioxide as postulated by Harteck and Dondes would explain the oxygen deficiency in the present work. This would also agree with the recent work of Mahan<sup>4</sup> on the photochemical decomposition of carbon dioxide.

It is hoped to publish more details of this work at a later date. The support and irradiation facilities of the United Kingdom Atomic Energy Authority are gratefully acknowledged.

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<sup>2</sup> Anderson and Waite, *A.E.R.E.-C/R* 2253 (1960).

<sup>3</sup> Harteck and Dondes, *J. Chem. Phys.*, **23**, 902 (1955); **26**, 1727 (1957).

<sup>4</sup> Mahan, *J. Chem. Phys.*, **33** 959 (1960).