Thermochimica Acta, 103 (1986) 193–199
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

OXIDATION OF CHROMIUM CARBIDE

JEREMY N. CLARK[1], DOUGLAS R. GLASSON[1] and S. AMARASIRI A. JAYAWEERA[2]

[1]John Graymore Chemistry Laboratories, Department of Environmental Sciences, Plymouth Polytechnic, Plymouth, PL4 8AA, Devon, England, U.K.

[2]Department of Chemistry, Teesside Polytechnic, Middlesbrough, TS1 3BA, Cleveland, England, U.K.

ABSTRACT

The oxidation of chromium carbide has been studied gravimetrically. Products of reaction have been examined by gas sorption analysis and X-ray diffraction. Changes in phase composition, crystallinity and crystallite size are correlated with the reaction conditions.

Chromium carbide, Cr_3C_2, differs from most of the transitional metal carbides in that it forms stable films of metal oxide (Cr_2O_3) around the remaining carbide particles, inhibiting further oxidation. Thus chromium carbide additive inhibits oxidation of interstitial zirconium carbide, ZrC, by forming some chromic oxide which stabilises the zirconia (ZrO_2) layer around the remaining carbide crystallites.

INTRODUCTION

Transitional metal carbides (ref.1) are generally refractory materials in which high melting points (above 3000 °C) is accompanied by high degree of hardness (Mohs scale 8-9). Many of them are interstitial compounds, MC, (M = metal) with cubic (NaCl-type) structures analogous to the corresponding refractory hard metal nitrides (ref. 2), MN. Metals with up to 5 electrons in the d-shell form less stable d° and more stable d^5 configurations. Where the d° and d^5 stable configurations can vary widely, as in TiC or ZrC, there is only one carbide and it has a wide range of homogeneity. Larger numbers of carbide phases with narrower homogeneity ranges are formed as d^5 becomes the more probable configuration. Thus chromium forms 3 phases with high metal content, $Cr_{23}C_6$, Cr_7C_3 and Cr_3C_2.

Both transitional metal nitrides and carbides suffer from the disadvantage of atmospheric oxidation becoming appreciable at low temperatures (above about 500-700 °C) compared with their melting points. Earlier research on the oxidation of titanium and zirconium nitrides (ref. 3) has shown that the titanium and zirconium dioxide coatings are incompatible with the remaining nitrides and break away in finely-divided form. The oxidation of titanium carbide (ref. 4) suggests a similar behaviour.

In the present research, oxidation of chromium carbide has been studied

0040-6031/86/$03.50

gravimetrically. The surface area and porosity of the products have been examined by gravimetric nitrogen gas sorption, using a vacuum microbalance. Further information on changes in phase composition, crystallinity and particle size has been obtained by X-ray diffraction, so that the compatibility and stability of the chromium oxide coating can be ascertained. The behaviour of zirconium carbide on oxidation has been determined similarly and the possibility has been examined of chromium carbide additive forming oxide to stabilise the zirconia layer and thus inhibit oxidation.

EXPERIMENTAL

Thermogravimetric studies of the atmospheric oxidation of chromium carbide, Cr_3C_2, and zirconium carbide, ZrC, were made using a Stanton-Redcroft STA 781 thermal analyser. Larger samples (1 g) of the carbides were oxidised for various times at each of a number of fixed temperatures in air in a furnace.

The specific surface areas, S, of the cooled samples were determined by a gravimetric BET method (ref. 6) with nitrogen at -196 °C as the adsorbate on a CI Electronics mark 2C vacuum microbalance with µg to mg sensitivity, using samples of 0.2 g. The adsorption isotherms also indicated any porosity present (from hysteresis) and pore size ranges. Average crystallite sizes were deduced from the specific surfaces of the less porous materials. The metal oxides formed were identified by X-ray diffractometry.

RESULTS AND DISCUSSION

Chromium carbide oxidation

TG and X-ray diffraction data indicate that the initial carbide was Cr_3C_2 which oxidised to Cr_2O_3. The specific surface, S, of the initial chromium carbide was 0.42 m^2g^{-1}, (average crystallite size 2.1 µm). The chromium carbide slowly oxidised in air at 600 °C, being 22 % oxidised in 79 h, but there was no increase in the specific surface (cf. Fig. 1), so that the oxide did not scale off the remaining carbide. The final specific surface was only 0.39 m^2g^{-1}. After allowing for the 5.9 % weight increase on oxidiation, the initial 1 g sample had only changed its total surface area, S', from 0.42 m^2 to $0.39 \times 1.059 = 0.41$ m^2.

Theoretically the change in volume on oxidation of 1 g Cr_3C_2 (X-ray density, $D_x = 6.68$) to 1.267 g Cr_2O_3 ($D_x = 5.23$) should be from 0.150 to 0.242 cm^2, representing a 0.615-fold increase. Thus if the oxide forms a stable layer around each carbide crystallite, the surface area change should be given by $S'/S = (1 + 0.615x)^{2/3}$, where x = fraction of carbide oxidised (ref. 7). For 22 % oxidation, the surface area of the initial Cr_3C_2 of 0.42 m^2 should increase to 0.46 m^2. Since the experimental result of 0.41 m^2 is slightly less, a small amount of oxide sintering must have occurred, coalescing some of the particles.

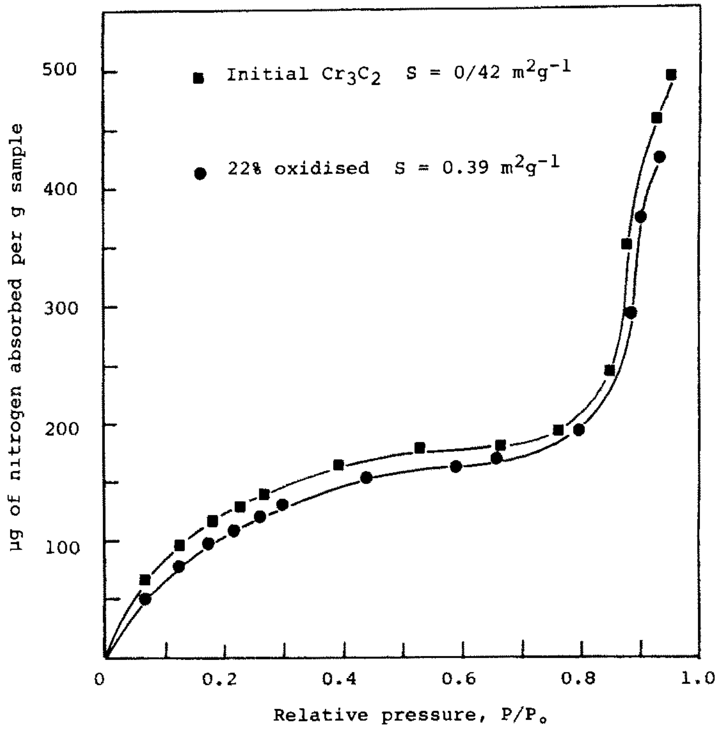

Fig. 1. Nitrogen adsorption isotherms at -196 °C on chromium carbide.

A limited amount of sintering of Cr_2O_3 by surface diffusion is possible, since 600 °C (873 K) is about one third of the melting point of Cr_2O_3 (2400 °C, 2673 K) in K. Sintering by crystal lattice diffusion also becomes appreciable above half the melting point in K (1064 °C, 1337 K). Therefore at higher temperatures, where oxidation to Cr_2O_3 is complete, the oxide product sinters more extensively and consolidates. There is certainly no scaling off (or spalling) of the oxide from the carbide surface even at 600 °C, in sharp contrast to the behaviour of zirconium carbide on oxidation.

Zirconium carbide oxidation

The initial specific surface area of the zirconium carbide was 0.59 m^2g^{-1} (average crystallite size 1.5 µm). Atmospheric oxidation became appreciable above 400 °C, (22 % oxidised in 1 h at 400 °C and complete in 1 h above 500 °C). Although there was no change in the surface area at 400 °C, there were considerable changes at the higher temperatures, as illustrated in Fig. 2 for the samples oxidised isothermally for 1 h. The maximum increase in surface area is given at 500 °C, i.e., from 0.6 to 15.2 m^2g^{-1}. The smaller increases in the

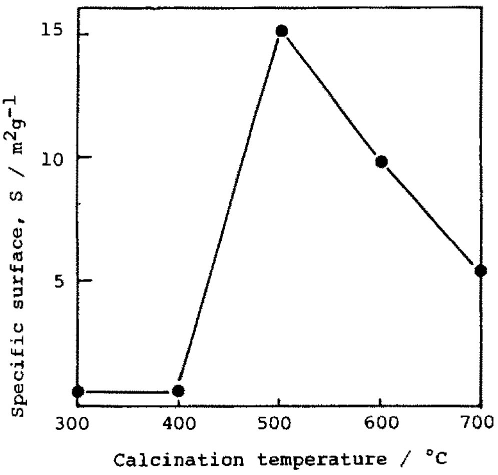

Fig. 2. Oxidation of zirconium carbide in air at different temperatures for 1 h.

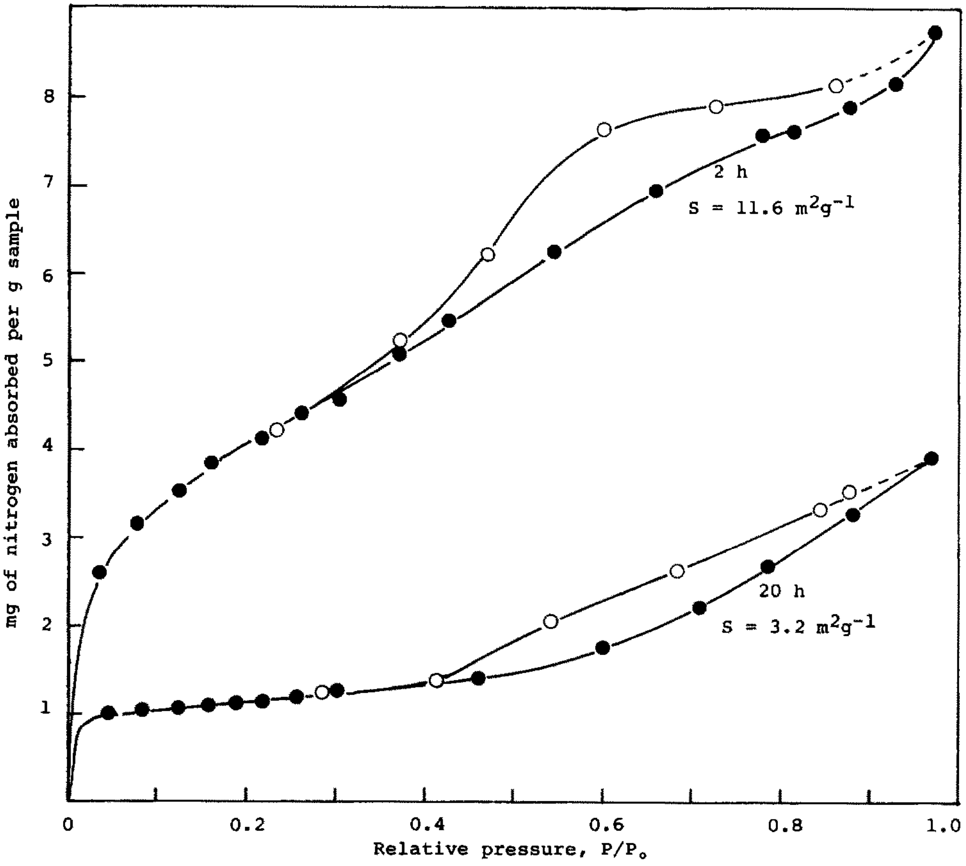

Fig. 3.a. Nitrogen adsorption isotherms at -196 °C on ZrC oxidised at 500 °C.

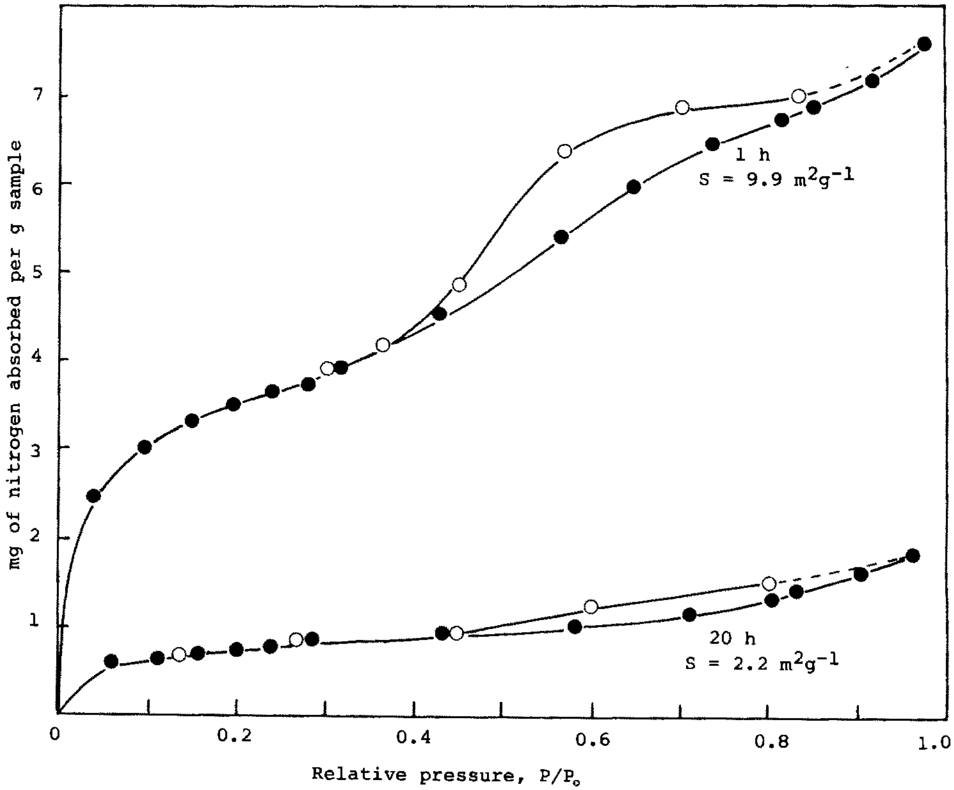

Fig. 3.b. Nitrogen adsorption isotherms at -196 °C on ZrC oxidised at 600 °C.

surface area at 600 and 700 °C are ascribed to more sintering of the newly-formed zirconia. This is evidenced further by comparing the surface areas and porosity of the zirconia products on further calcination at 500 and 600 °C in Fig. 3.a. and b. The surface areas and porosity both decrease on heating for 20 h. The hysteresis loops indicate full ranges of mesoporosity (2-50 nm pore diameters, corresponding to relative pressure ranges of 0.38-0.96 in the Kelvin equation) with some loss of the smallest pores and general diminution in the pore volume (from decreasing size of the hysteresis loops) after 20 h.

Effect of chromium carbide on the oxidation of zirconium carbide

The zirconia formed at 700 °C from 1h oxidation of zirconium carbide still retains some mesoporosity, even though its surface area is only 5.3 m^2g^{-1} (Fig. 4). It is known that the addition of chromium carbide improves the oxidation resistance of TiC-Co hard metals (where the % Co may be up to 18 %). The scales formed are thinner, protective and tenaceously adhering; a parabolic oxidation rate is given in contrast to linear rates where the scales spall off (ref. 4 and

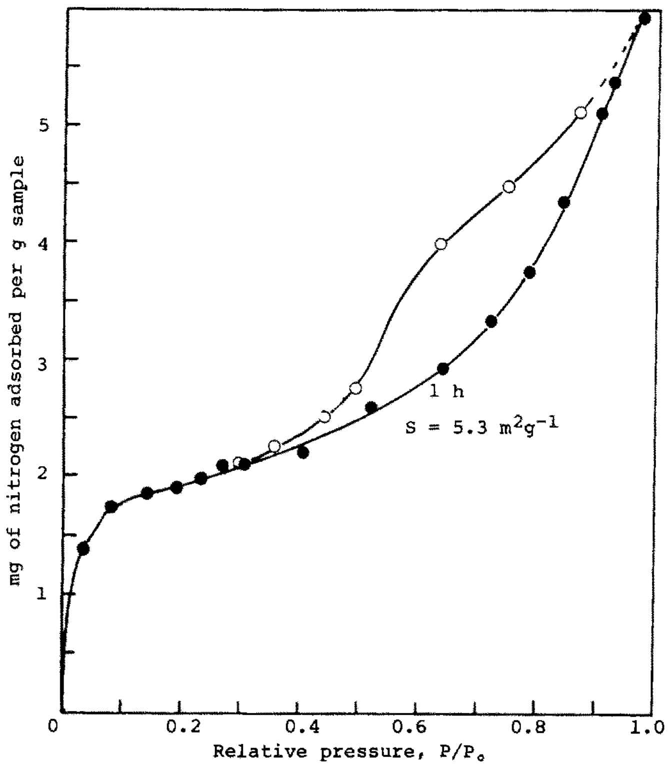

Fig. 4. Nitrogen adsorption isotherms at -196 °C on ZrC oxidised at 700 °C.

5). By analogy the oxidation of zirconium carbide was expected to be inhibited by the addition of chromium carbide. Thsi was investigated as follows.

An approximately 1:1 mixture (by weight) of ZrC and Cr_3C_2 was investigated by thermogravimetry. At 700 °C, isothermal TG in air showed that less than 84 % of the ZrC was oxidised in 1 h, compared with almost complete (94 %) oxidation of ZrC in ¼ h when Cr_3C_2 is absent. Comparison with the TG curves for the separate oxidations in air of the ZrC and Cr_3C_2 at a heating rate of 10 °C min^{-1} showed that ZrC oxidised mainly at 400 - 650 °C and Cr_3C_2 at 650 - 1200 °C. Thus the Cr_3C_2 inhibits oxidation of the ZrC even when only a small amount of it is oxidised to Cr_2O_3. The Cr_2O_3 evidently promotes the sintering of the newly-formed zirconia, giving a more stable oxide layer around the remaining ZrC and this is confirmed by the specific surface area of the 1 h oxidised product being only 1.8 m^2g^{-1} instead of 2.5 m^2g^{-1} if the chromium carbide had been ineffective.

ACKNOWLEDGEMENTS

The authors wish to thank Mr. R.R. Willmers of the British Steel Corporation (Teesside Laboratories) for his collaboration and the Science and Engineering

Research Council for research grants.

REFERENCES

1 D.R. Glasson and J.A. Jones, J. appl. Chem., 19 (1969) 125-37
2 D.R. Glasson and S.A.A. Jayaweera, J. appl. Chem., 18 (1968) 65-77
3 D.R. Glasson and S.A.A. Jayaweera, J. appl. Chem., 19 (1969) 182-4
4 O. Kubaschewski and B.E. Hopkins, Oxidation of metals and alloys, 2nd Edn., Butterworths, London, 1962, pp. 262-5
5 R. Kieffer and F. Kölbl, Z. anorg. Chem., 262 (1950) 229
6 D.R. Glasson, J. chem. Soc., (1956) 1506-10
7 D.R. Glasson, J. appl. Chem., 8 (1958) 798-803