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THE CORROSION INDUCED CHANGE OF PORE SIZE DISTRIBUTION AND SURFACE AREA OF A FUEL ELEMENT GRAPHITE

E. Hoinkis,
Hahn-Meitner-Institut für Kernforschung Berlin GmbH

H. Behret, D. Hartmann, A. Köhling, E. Robens
Battelle-Institut e.V., Frankfurt am Main, Germany

ABSTRACT

The transport behaviour of fission products in HTGR-fuel element graphite may be altered by changes of the pore structure of the graphite due to corrosion. The corrosion rate was measured at temperatures between 850 and 900 °C in a CO_2 atmosphere by a thermogravimetric method. Surface area and pore size distribution were determined before and after corrosion by measuring nitrogen adsorption isotherms at 77 K. The corrosion rate remained constant regardless of the pronounced increase in the specific surface area.

1. INTRODUCTION

The corrosion of graphite in a CO_2 atmosphere at temperatures between 1120 and 1170 K results in the development of volatile species. Therefore the mass decreases, the bulk becomes porous and the specific surface area increases.

The gravimetric method is well suited to the investigation of the corrosion behaviour of materials. All parameters of interest can be determined in the same apparatus, since the weight loss during degassing, the weight loss during corrosion and the corrosion rate can be observed. In addition, the specific surface area and the pore radius distribution in the micropore and mesopore range can be determined by measuring the sorption isotherm at low temperature before and after corrosion.

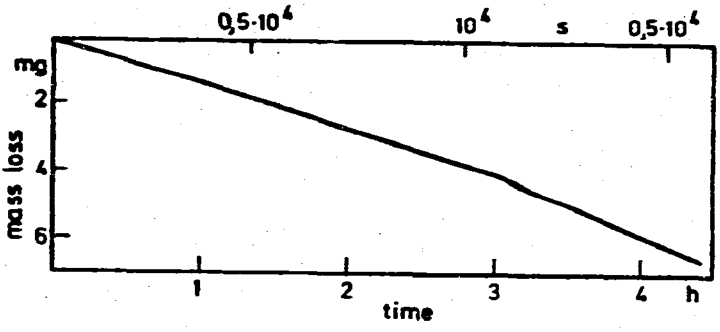

Fig. 1. Corrosion of graphite in CO_2 of 1.3 kPa at 1170 K. The sample mass is 1.3 g.

2. EXPERIMENTAL

The graphite investigated was in the form of compact cylindrical pellets 10 mm in diameter with a weight of about 1.3 g and a density of about 1.7 g cm^{-3}. The apparatus used has been described elswhere[1]. It consists of a vacuum microbalance after Gast[2], a vacuum aggregate comprising a turbomolecular pump, nitrogen pressure control and a thermostat with ovens or liquid nitrogen.

After degassing the samples at 1300 K in high vacuum the nitrogen adsorption and desorption isotherm was measured stepwise at 77 K. The specific surface area was determined using the simple BET equation[4], and the cumulative specific surface area was derived from the pore radius distribution (which was calculated according to Cranston and Inkley[3-5]). The samples were oxidized at temperatures between 1120 and 1170 K in high-grade (99.995 %) CO_2 at 1.3 kPa (= 13 mbar).

3. RESULTS

A typical weight loss curve is shown in Fig. 1. The mass of the sample decreases linearly with time, i.e. the corrosion rate remained constant despite the increasing surface area and the change in the pore structure. The corrosion rate was about 0.5 $\mu g\ s^{-1}$ at 1170 K. A weight loss of only 0.55 % resulted in an increase of the specific BET-surface area from 0.7 to 5.3 m^2g^{-1}.

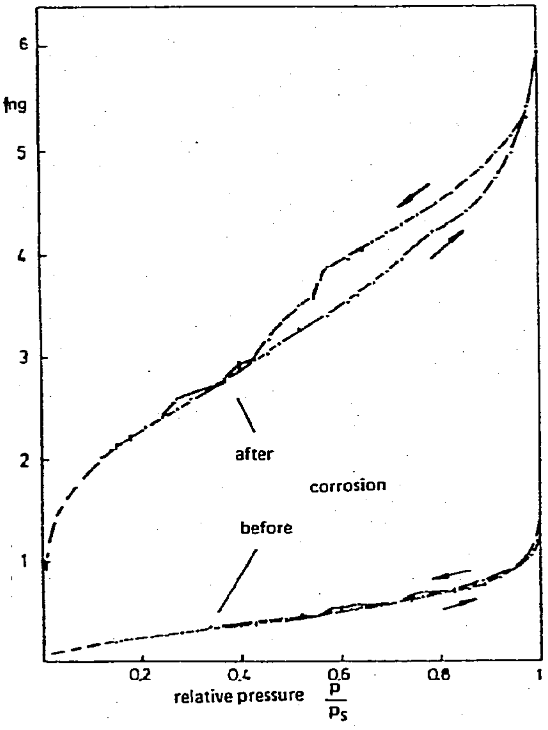

Fig. 2 Nitrogen isotherms of a graphite sample at 77 K before and after corrosion in CO_2 of 13 mbar at 1170 K

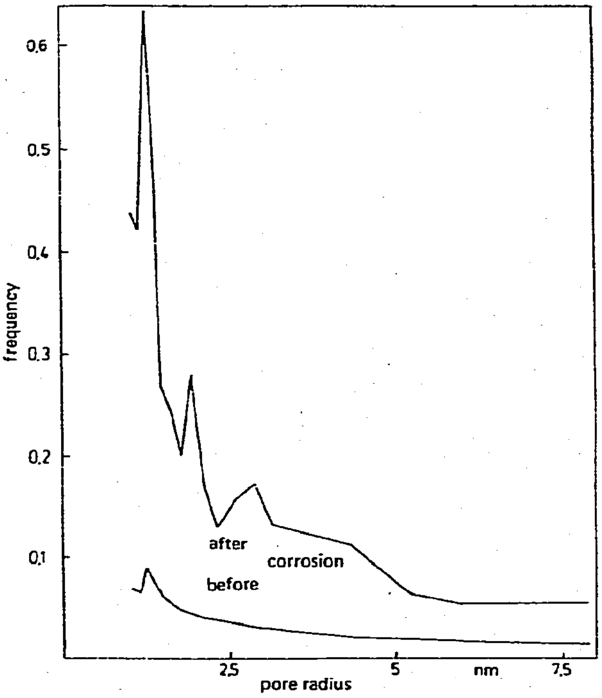

Fig. 3 Pore radius frequency derived from the adsorption isotherm using a cylindrical pore shape model

The isotherm before and after corrosion is shown in Fig. 2. All isotherms obtained are of the type B shape according to the deBoer classification[6]. The hysteresis loop was markedly extended by the corrosion and in some cases extended to very low relative pressures. The pore width frequency is shown in Fig. 3 as a function of the pore radius. The most frequent radius is located at the lower limit of the mesopore range, which is the only range in which the calculation is valid. This means that the pore system consists mainly of micropores and small mesopores. Pores of the same size are generated in great numbers by the corrosion process.

4. CONCLUSIONS

In the mesopore range the comparison of the cumulative specific surface area with the BET value shows discrepancies. This is due to the high micropore content: the amount of N_2 adsorbed in micropores is not included in the cumulative calculation.

The extension of the hysteresis loop may be caused by other factors, i.e. by a pore blocking effect, as suggested by Doe and Haynes[7]: the depletion of the inner pore volume may be hindered by micropores in the outer region. In addition, swelling of the structure may occur.

The generation of micropores due to oxidation seems to be the reason for the almost constant corrosion rate which occurs despite the increasing surface area. The narrow pore necks hinder exchange of the reacting species (CO_2, CO) during the corrosion process.

A more detailed discussion will be published elsewhere.

ACKNOWLEDGEMENT

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