Unsteady State Transfer Effects in the Oxidation of Graphite

by

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The effect of mass transport in limiting the rate of oxidation of large specimens of graphite in air under steady state conditions has been the subject of much study in our laboratories. The latest results are presented at this conference in the paper by Hawtin et al. More recently, the effect of unsteady state mass and heat transfer on the initial rate of oxidation of large graphite specimens has also been examined. The experimental results have been compared with values calculated using a mathematical model based, in part, on the model used previously by Hawtin and Murdoch in connexion with the steady state experiments. Because the pores in the graphite used are large Knudsen diffusion can be neglected and a free gas diffusion mechanism applied.

The graphite specimen is constructed in the form of a hollow cylinder 11-in long, 1.2-in I.D. and 6.5-in O.D. It contains internal electrical heaters and is suspended in a constant temperature vessel. By this means the specimen can be initially heated to a uniform temperature a few degrees above the surrounding vessel. Before starting an experiment the specimen is heated to a given temperature in a controlled flow of nitrogen. Air, or a suitable reactant gas, is substituted for the nitrogen and it is assumed that at this juncture there is a simultaneous replacement of the nitrogen at the external surface of the graphite by a reactant gas of uniform composition. This assumption has been shown by experiment to be justified. The rates of evolution of CO and CO_2 from the specimen are followed by the use of infra-red gas analysers. Temperature changes in the specimen arising from the heat of reaction are measured by means of several thermocouples located at various positions in it.

In calculating the effect of unsteady state diffusion the problem reduces to a calculation of transfer in the radial and axial directions of the cylinder. This is, in fact, particularly appropriate to extruded nuclear type graphite because there is some degree of anisotropy between properties in the axial, or extrusion, direction and in the radial or perpendicular direction. The calculation consists, essentially, of the solution of the partial differential equations describing simultaneous heat and mass transfer in the presence of a chemical reaction. It is carried out by calculating the varying, time dependent, oxygen concentration profiles inside the graphite pore structure. From these profiles corresponding reaction rate and product distribution profiles are constructed. The local reaction rates lead to corresponding heat releases which are calculated assuming a constant CO/CO_2 ratio and, therefore, a constant heat of reaction. These localised heat releases are used in turn to calculate a temperature profile. If this is large then the local reaction rates are modified, and hence the local oxygen concentrations.

The observed local temperature changes and the overall product concentration transients have been found to be in reasonable accord with the values predicted both as regard the magnitude of the effects and their time scale.

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