The sintering and morphology of interconnected porosity in UO₂ powder compacts

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Uranium dioxide powder compacts of ~ 46% green density were sintered in flowing hydrogen at temperatures between 1500 and 1700°C. On annealing, the compacts readily formed an interconnected system of pores stabilized by grain boundaries. The volume of open porosity decreased with an activation energy of 4.6 J mol⁻¹ at a rate controlled by grain growth. The grain-boundary migration removed the restraint on the porosity allowing shrinkage to commence. The compact surface area decreased with a higher activation energy of 6.0 J mol⁻¹. The mechanism proposed for the diminishing area was the smoothing of the faceted powder grains. Nucleation of atomic layers on the facets was shown to account for the high activation energy. The equilibrium shapes that may be adopted by interconnected porosity were calculated using a model in which simpler geometry was substituted for the real anticlastic surface curvature. The model demonstrated the stabilizing effect of increasing grain-boundary energy and the formation of closed pores.

1. Introduction
The sintering of UO₂ powder compacts may be usefully divided into three regimes comprising the formation of necks between particles, the diminution of interconnected porosity and the subsequent densification of isolated pores. The first regime has frequently been studied using dilatometry. Sintering occurs rapidly and may be measured at temperatures as low as 600°C [1, 2]. The final densification of isolated pores still situated on grain boundaries is much slower and necessitates temperatures above 1500°C to observe sintering [3].

The intermediate stage of sintering is characterized by interconnecting pores of complex geometrical shape. The sintering kinetics are further complicated by the green density of the original compact [4]. Compacts with green densities below ~ 50% sinter with a significant fraction of intragranular cavitation. Conversely, when the green density is greater than ~ 50%, the sintered microstructure consists entirely of intergranular cavitation at triple points.

The present paper investigates the sintering kinetics of UO₂ powder compacts of ~ 46% green density and demonstrates the relationship between grain growth and densification. The surface area of the interconnected pore system was measured by nitrogen adsorbtometry [5].

The morphology of the interconnected porosity was investigated by considering the energy of different possible configurations. Computer calculations of the configurational energy demonstrated the stable shapes. Reducing the cavity volume was shown to eventually result in the formation of a closed neck isolating the pore from the interconnecting system.

The morphology of porosity is important not only to an understanding of sintering but also in gas release from nuclear fuels. During gas release, inert gas accumulates on grain boundaries and along grain edges. The gas escapes to the surface by forming interconnected porosity. The formation of interconnected porosity is believed to be similar to the elimination of porosity during sintering.
2. Experimental

Cylindrical powder compacts 18 mm long and 8 mm diameter were made by compressing UO₂ powder to a load of 500 kg in a metal die lightly lubricated with a solution of stearic acid in ether. Sintering was carried out in a vertical alumina tube furnace at temperatures between 1500 and 1700°C in an atmosphere of flowing hydrogen. The furnace was continually run at temperature and specimens were inserted and withdrawn automatically to give a heating and cooling rate of ~ 1°C sec⁻¹. Sintering was repeatedly interrupted to measure the density and surface area of the compact.

Total porosity was calculated from the weight and from micrometer measurements of the compact size. The closed porosity was found by a hydrostatic comparative technique [6]. The method consists of comparing the compact weight with that of a single crystal of UO₂ in air and after vacuum impregnation of methanol. Comparison with the fully dense material makes it unnecessary to know the densities of air and methanol. The absolute density of the UO₂ single crystal was checked to be certain that it contained no porosity.

The compact surface area was measured by nitrogen adsorption in a Perkin Elmer adsorbтомeter by passing a mixture of nitrogen and helium over the compact at liquid nitrogen temperatures. The volume of adsorbed nitrogen was found for nitrogen partial pressures ranging between 0.08 and 0.63. The results were interpreted according to the BET Theory [7], by plotting $P/V_a (P_0 - P)$ against $P/P_0$, Fig. 1, where $P$ is the nitrogen partial pressure, $P_0$ is atmospheric pressure, $V_a$ is the absolute volume of adsorbed nitrogen and the surface area is proportional to the reciprocal of the slope. Since the plot passed through the origin of the graph it was possible to find the surface area from a single measurement and all subsequent readings were taken at a nitrogen partial pressure of 0.177.

3. Results and discussion

The surface area, open, closed and total porosity are given in Table I for three specimens annealed at 1500, 1600 and 1700°C. The amount of open porosity was calculated by subtracting the closed porosity from the total porosity. The porosity and surface area during sintering at 1500°C are shown in Fig. 2. The surface area diminished rapidly with sintering and accurate readings could not be taken below 0.04 m³ g⁻¹.

The initial stage of sintering occurred very rapidly and was probably complete by the time the specimen had reached temperature. A further powder compact was annealed at 1450°C for 1 h and fractured. The scanning electron micrograph of the surface, Fig. 3a, shows the compact...