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Studies of Layered Uranium (VI) Compounds. V. Mechanisms of Densification of Hydrogen Uranyl Phosphate Tetrahydrate (HUP): Pressure-Induced Planar Glide and Solution Phase Sintering

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The good proton conductor $HUO_2PO_4 \cdot 4H_2O$ (HUP) can be easily fabricated into disks or films suitable for use in electrochromic displays, fuel cells, or batteries. Kinetic studies of the room-temperature densification reveal the presence of two mechanisms. At applied pressures of 20 MN m^{-2} the observed rapid densification was attributed to the gliding of the structural layers over each other to achieve essentially 100% of the theoretical density. When the powder had been wettened by solution, slow sintering occurred even in the absence of applied pressure, and we attribute this to a solution-phase sintering mechanism. The study is one of the few to be reported on platelet-shaped crystals rather than the usual spherical-shaped particles. This fact, together with the ease of cleavage of the layers, largely accounts for the excellent fabrication properties. The optimum conditions for pressing large clear robust disks are described.

Introduction

The layered uranyl compounds hydrogen uranyl phosphate tetrahydrate (*1, 2*) $HUO_2PO_4 \cdot 4H_2O$ (HUP) and hydrogen uranyl arsenate tetrahydrate (*3*) $HUO_2AsO_4 \cdot 4H_2O$ (HUAs) have recently been shown to have unusually high proton conductivities, of 0.4 ohm^{-1} m^{-1} at 290°K (*1, 2*) and 0.6 ohm^{-1} m^{-1} at 310°K, respectively. The ease with which these materials can be pressed into robust clear disks, and the essentially fixed stoichiometry of the tetrahydrate phases (*4*) are attractive features for their use as solid electrolytes in a range of applications such as solid-state hydrogen batteries (*5*), miniature fuel cells, and electrochromic displays (*6*). In this paper we describe our investigation into the reasons for the good fabrication properties, and propose a novel densification mechanism, which may also be applicable to other layer-type solids. The bulk nature of the conductivity has been previously explored using single crystal conductivity measurements (*3*) and pulse NMR techniques (*7*). An ordered hydrogen bond arrangement has been proposed for the orthorhombic forms of HUP and HUAs found below 274 and 301°K, respectively (*8*).

Experimental

Particle Size Control

The precipitation of HUP from solution produces platelets of square or irregular-octagon shape of a size which depends on the concentration, pH, and temperature of the solution, and the duration of the reac-

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tion and extent of digestion. In this study HUP was consistently prepared by adding 10 g $UO_2(NO_3)_2 \cdot 6H_2O$ (AR grade) dissolved in 50 ml distilled water to 8.4 ml of 2.4 *M* phosphoric acid so as to give equimolar proportions. The precipitation showed a pronounced induction period, as can be seen from the delayed changes in the pH, conductance, and temperature of the solution, plotted in Fig. 1. Precipitation was visually apparent after 7 min. During the exothermic formation, the pH dropped and the conductance rose due to replacement of the partly dissociated phosphoric acid by nitric acid. The final yield of 82% reflects the degree of insolubility of HUP at this pH (*2*). After 20 min, microscopic examination showed the particle size to be spread around the micrometer region. Filtration produced thixotropic slurries from which the starting materials for fabrication were obtained. To prevent particle size enlargement due to storage, a new batch of HUP was prepared as above prior to each fabrication run. (HUP is available from Alfa Chemicals, but although the conductivity is high, the material appears to be a mixture of the various forms of HUP, as previously described (*2*)).

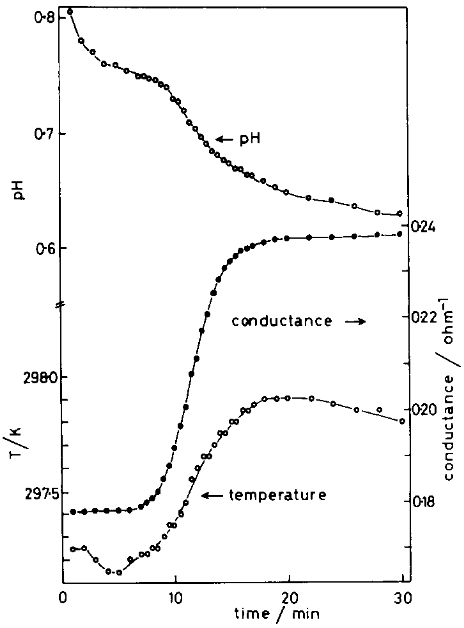

FIG. 1. The induction effect during the precipitation of HUP, as revealed by changes in the pH, conductance, and temperature of the solution.

Pressing Procedure for Dry Powder

HUP slurries, some of which were washed to pH 2, were squeezed between filter papers to remove extraneous water, spread out on a watch glass, and left to dry to constant weight in air to produce the discrete tetrahydrate phase, the stability limits of which have been previously reported (*4*). The small dried lumps or sheet were very gently broken up, and the aggregate particles were loaded into the hole, 1 cm^2 in area, of a Perspex die, and leveled off. The assembly is shown in Fig. 2. The snugly fitting stainless-steel plungers were lightly palladium-blacked on the pressing surfaces to facilitate the conductivity measurements (*2*). The length was continually monitored using an accurate sliding vernier set between the jaws of the hydraulic press. No distortion of a blank setup was found under the maximum pressures applied of 20 MN m^{-2} (2 ton cm^{-2}).

Conductivities (AC) were measured over a range of frequencies using a Wayne-Kerr B221 bridge as previously descirbed (*2*). The values in the region of 10 kHz were essentially frequency independent, and this frequency was therefore used throughout. The conductance values were corrected by the relevant $1/A$ factor to give absolute conductivities. Previous measurements (*2*) have shown that clear disks have a density of 99.5 ± 0.5% that of the theoretical value derived from the unit cell dimensions, of 3.43 g cm^{-3} (*2*). For the purposes of this study, we have taken the relative densities of the final clear disks to be 100%. The relative densities are given by the final sample lengths divided by the lengths at a given time.

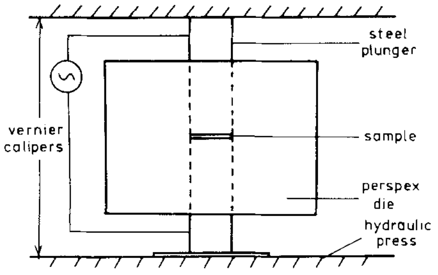

FIG. 2. Pressure assembly, consisting of a Perspex die and stainless-steel plungers, which was used for the simultaneous measurement of shrinkage and conductance.

Pressing Procedure for Wet Powder

HUP slurries were squeezed between filter papers, which lowered the extraneous water content to about 25–30%, and loaded directly into the cavities of Perspex dies. The plungers were inserted under pressures of less than 1 MN m^{-2} until the slurry layer was uniform. The pressure was then suddenly increased to 20 MN m^{-2} to begin the run. The presence of solution removed the necessity of blacking the plunger faces, and frequency-independent values of the conductivity could be obtained around 1592 Hz, the frequency thus used for wet samples. The relative densities calculated as above still relate to those for the HUP aggregate, and do not pertain to the average density of HUP plus liquid.

Results

In order first to identify operative densification mechanisms the following wide range of experiments were performed and compared. Figure 3 compares the rates of densification for wet and dry samples at various pressures. The data are representative of many different runs performed. No substantial differences in the behavior were found whether the samples were initially washed to pH 2, or left unwashed. In all cases 100% relative density of most of the sample was achieved eventually: the wet samples became clear all over whilst the dry samples only clarified in large patches, leaving opaque regions where the initial sample thickness was a minimum. Printed letters were sharply visible through the clear disks, which were typically 0.5 to 1 mm thick. A clear disk approximately 1 mm thick transmitted 36 to 50% of light from 530 to 850 nm, respectively. Below 630 nm the strong absorption of the uranyl ion is evidence, which imparts the lemon color to the material.

The data shows two rather striking features. First, under the sample pressure of 20 MN m^{-2}, the dry samples densified much faster than the wet samples. The presence of the solution might have been thought to allow liquid-phase sintering to occur. In fact, the presence of the solution has greatly retarded densificiation, from about 25 min when dry to many hours when wet in order to achieve clarity. Second, the effect of varying the pressure, using dry samples, was very pronounced. At 10 MN m^{-2} slow densification occurred to what appeared to be a limiting relative density of about 85%. In contrast, at 20 MN m^{-2} rapid densification occurred to 100% density.

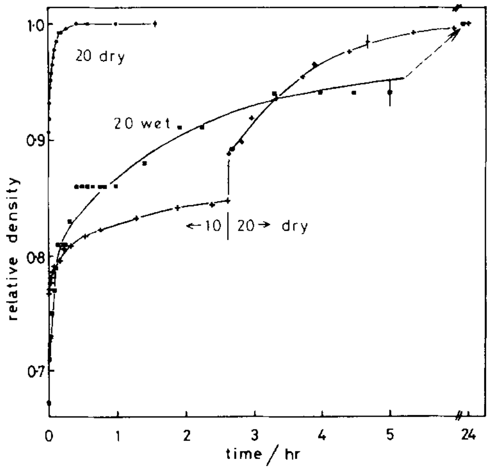

FIG. 3. Relative density vs time for wet and dry samples pressed at 10 or 20 MN m^{-2} (10 or 20). After approximately one day the wet sample became 100% dense, as indicated by the arrow.

We were able to obtain valuable information about the particle orientation as a function of time by following the conductivities of the disks, since the conductivity of the platelets is highly anisotropic (*3*), the preferred directions being in the platelet planes. Figure 4 shows the typical changes observed in the conductivity during pressing of wet and dry HUP samples. For the dry material the initial increase in the conductivity closely parallels the increase in the relative density. However, over extended times after 100% densification has been achieved, it is clear that the conductivity drops gradually but substantially. This reflects slow changes in the grain or grain boundary character not revealed by the data in Fig. 3.

If we compare the conductivity values obtained with that measured for single crystals parallel to the flat faces (0.6 ohm^{-1} m^{-1} at 290°K) (*3*), we can determine the average inclination of the platelets if we assume that the grain boundary regions have a conductivity similar to the bulk particles. This is certainly approximately the case since the parallel conductivity of clear disks (0.4 ohm^{-1} m^{-1} at 290°K) (*2*) is very close, considering experimental errors, to the parallel single crystal value given above. Using the single-crystal values appropriate to the temperature of the pressing experiment gave a final inclination from the flat direction of 6 ± 2°. The inclination at the point of maximum conductivity was 8 ± 2°. After allowing for the lower initial density, the inclination after 3 min pressing was also found to be 8 + 2°.

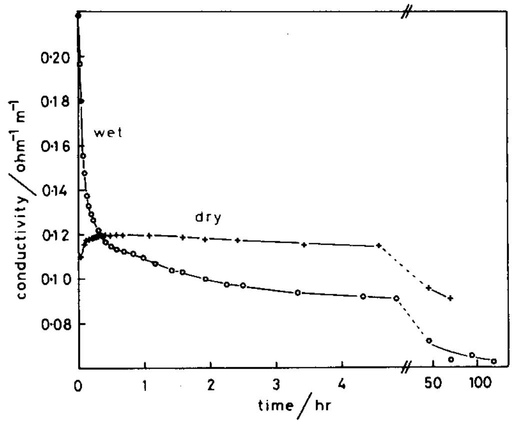

Fig. 4. Conductivities (ac) vs time for wet and dry samples pressed at 20 MN m^{-2}, measured at 299.2 and 297.2°K, respectively. For each point, the appropriate $1/A$ factor has been used to obtain the conductivities.

Figure 4 also shows the changes in the conductivity for a wet sample. In this case, the acidic solution, which alone had a conductivity of 17 ohm^{-1} m^{-1}, provided the major contribution to the conductivity in the initial stages. As densification proceeds, the conductivity of the wet sample becomes lower than that of the dry sample, despite the effect of residual acid solution. This is interpreted as indicating a more complete alignment of the platelets towards the flat direction than was achieved in the dry sample. After 5 days a value of 4 ± 2° tilt can be calculated, as done above, taking into account the actual temperature of the experiment. The smaller tilt achieved for the wet sample probably occurs because the platelets can more readily slide over each other, lubricated by the solution, to achieve a more uniform packing.

Another series of experiments were performed at lower pressures. It was found to be possible to press clear disks of HUP using 3–5 MN m^{-2} either from reasonably moist slurries, or from nearly dry HUP containing only 6% extraneous solution. Large clear thin sheets 6 cm in diameter and 100 μm thick could be pressed from HUP containing 10% extraneous solution, and the detailed preparation and use of such films for electrochromic displays has been previously described (*6*). However, clarification of the sheets at these low pressures took a day or more. Furthermore, in complete contrast to the speed of pressing of completely dry powders at 20 MN m^{-2}, dry powders were not observed to clarify at all at 5 MN m^{-2}.

In yet another series of experiments, clarification of wet samples was observed even with no applied pressure. If a thick slurry were sandwiched between two glass slides, and left with no pressure applied, the central portion of the film would begin to clarify after several days. Furthermore, if a thick smear of slurry were left to dry in a confined environment, the mass would become translucent and quite hard after many days. These experiments indicate the definite presence of a slow solution—phase sintering mechanism, of the type described by Kingery (*9*).

Discussion

The results show the presence of two densification mechanisms. First, solution-phase sintering occurs in the presence of solution. Transport of material occurs through the solution phase by virtue of the ionic concentration established by the solubility equilibrium. The solubility of HUP in phosphoric acid of pH 2 is $10^{-3}M$, and is more than this at higher acidities (*10*). These values would be quite adequate to account for the slow rate of solution phase sintering.

The second densification mechanism occurs for dry HUP. In the absence of solution-phase sintering, possible mechanisms which are usually considered are (*11*) (i) plastic flow in the crystallites by dislocation movement; (ii) viscous flow of a vitreous grain boundary phase; and (iii) grain deformation by lattice or grain boundary diffusion. Our data indicate the first mechanism.

A test of the data against plastic flow via dislocation movement was made by evaluating n in the equation for plastic flow (*12*)

$$\frac{1}{\rho}\frac{d\rho}{dt} = k\sigma^n, \qquad (1)$$

where ρ is the density and σ is the applied stress. For the same density, comparison of the densification rate for the two pressures used, 20 and 10 MN m^{-2}, will enable n to be evaluated. Although the density ranges for the two runs do not overlap precisely as can be seen from Fig. 3, a low estimate of n has been made by comparing the final densification rate at 10 MN m^{-2}, with the initial rate at 20 MN m^{-2}. The value of n obtained was 8, which is a minimum value. Normally, n for this mechanism is 2, ranging sometimes up to 7 (*12*).

Since mechanisms (ii) and (iii) above do not involve a pressure dependence which is more than linear, our data would be consistent with plastic flow, and the unusually large value of n may even indicate that, in addition, fracture is occurring. Plots of log (relative density) against time for the various runs did not give a straight-line relationship, as predicted from Eq.1, which may also suggest the presence of both creep and fracture. Creep in ionic crystals, such as the alkali halides, has been shown to be due to dislocation motion, and only occurs rapidly above the plastic limit corresponding to a threshold pressure (*13*). Similarly, fracture only occurs above a particular threshold pressure. In the case of HUP, the crystallites are reasonably soft, and whole layers may slide over each other via a plastic flow or fracture mechanism. A fracture mechanism is not normally found in pressure sintering of ceramic materials such as oxides (*14*), but might be expected in layered materials such as graphite and boron nitride, and in softer materials such as KCl, which can be pressed into clear disks for infrared studies within minutes at room temperature.

Concerning the retarding effect of solution upon densification at high pressure (Fig. 3), this may be explained by a slow expulsion of water between the platelets or between the plungers and the die. A further factor may be an increase in the fracture resistance of the platelets in the presence of solution, due to a reduced number of surface flaws.

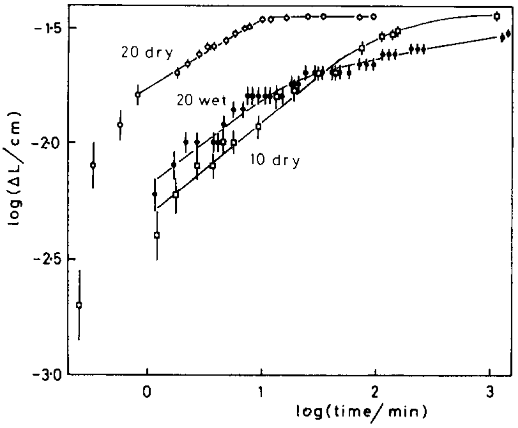

FIG. 5. Log (shrinkage) vs log (time) for the same runs as shown in Fig. 3.

Finally, it was of interest to plot the data according to the conventional densification relationship (*15*) $(\Delta L/L_0)\ \alpha\ t^m$ for sintering by normal diffusion processes (mechanism (iii) above). ΔL is the shrinkage, given by the change in length at time t, from the initial length L_0. The data is shown in Fig. 5. The data for the dry samples showed slopes of 0.3 to 0.4 before the final plateaus were reached. Data for the wet sample showed a similar initial slope, followed by a more gradual approach to the plateau. It is of interest to note that although these plots are quite typical for diffusion controlled processes, they should be interpreted in the light of the above discussion as indicating a lack of real discrimination between mechanisms, of this type of plot, perhaps as a result of the nature of the log–log axes. This point is becoming more widely accepted in the study of sintering mechanisms (*16*).

Acknowledgments

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