Hot Pressing of Uranium Nitride
and Mixed Uranium Plutonium Nitride

Ji Young Chang

Experimental Work Was Performed At
Oak Ridge National Laboratory*
Oak Ridge Tennessee  37830
Currently employed at
Westinghouse Electric Corporation,
Advanced Reactors Division
P. O. Box 158
Madison, Penna.  15663

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SUMMARY

The hot pressing characteristics of mixed (U,Pu)N for advanced reactor fuel was studied in order to obtain a better insight into the densification process and thus improve the fuel fabrication technique.

Mixed (U,Pu)N of the density of 99% and 94% were fabricated by hot pressing at 1450°C and under pressures of 4000 psi and 3000 psi respectively. A digital computer program for the densification process was also developed to analyze and predict the density of the pellet at any given time or at applied pressures different from actual experimental conditions.

The time dependence of the temperature in the proposed equation to simulate the experimental heating period of the die was first introduced to improve the interpretation of experimental data in order to correlate with the equation:

\[
\frac{dp}{dt} = f(t, \rho) = \frac{A}{T(t)} (1-\rho) \left\{ \frac{1}{1-(1-\rho)^{2/3}} + B \ln(1-\rho) \right\}
\]

The best values of the hot pressing coefficient, defined as:

\[
A = \frac{3000 \rho}{k R^2}, \quad B = \frac{\sqrt{2\pi}}{P}
\]

were determined by curve fitting the equation with experimental data. The values were:

\[A = 1.296 \quad \text{and} \quad B = 0.352\]

for a mixed (U,Pu)N of the starting density of 63% that was fabricated by hot pressing under the pressure of 3000 psi at 1450°C ± 10°C.
ABSTRACT

The hot pressing characteristics of Uranium Nitride and Mixed Uranium Plutonium Nitride were studied. The utilization of computer programs together with the experimental technique developed in the present study may serve as a useful purpose of prediction and fabrication of advanced reactor fuel and other high temperature ceramic materials for the future. The densification of Nitrides follow closely with a plastic flow theory expressed as:

$$\frac{da}{dt} = \frac{A}{T(t)(1-p)} \left\{ \frac{1}{1-(1-p)^2/3} + B\ln(1-p) \right\}$$

The coefficients, A and B, were obtained from experiment and computer curve fitting.

INTRODUCTION

A densification study of a mixed uranium-plutonium nitride hot pressing technique has been undertaken, since the mixed nitride of uranium and plutonium has high potential for use as fuel in Advanced Reactors. In the past the densification mechanism has been studied by many investigators in the hope of obtaining a simple functional description of densification as a function of time, pressure, and temperature. More recently, the hot-pressing theory has been reviewed by Thummler et al and Ramquist. Densification during hot pressing can be described by three general mechanisms: (a) plastic flow; (b) particle rearrangement, sliding, and fragmentation; and (c) stress-enhanced diffusion. At present, even though the assumptions and mechanisms proposed are not perfectly applicable to all cases, each of the theoretical or phenomenological equations has in many cases proved very useful.

Systematic analysis of densification during hot pressing would reduce operational costs of fuel fabrication since a minimum number of experiments are required to establish desired fabrication conditions for the various batches of a starting material.
EXPERIMENTAL PROCEDURE

Hot Press

A high-frequency induction hot-press was designed to fit a glovebox (32 x 43 x 32 inch) with emphasis on a number of aspects such as safety and compactness. The hot-pressing capability was 10,000 psi in a 1/2 inch die at 1600°C. However, the size of the pellets produced were 0.372 inch in diameter and 0.25 ~ 0.39 inch in height. The densification of the pellets were measured continuously by a linear transducer attached near the loading shaft as shown in Figure 1. A recorder and all pressure controller are located outside of the glovebox.

Numerical Analysis

It is proposed in the present study that the model described in Equation (1) below be fitted to the densification data obtained from a hot-pressing experiment to obtain the best values of the hot-pressing coefficients and that the model be then employed with the hot-pressing coefficients to predict densification characteristics at different pressures. The possibility of predicting the densification for a new temperature profile is also considered.

For mixed (U,Pu)N hot-pressing, the main portion of densification is assumed to be due to the plastic flow mechanism. The densification function, \( p \), is defined to be the ratio of the density of the compact to the theoretical density. During this period of densification the densification function, \( p \), satisfies approximately the differential Equation (1).

\[
\frac{dp}{dt} = \frac{A}{T(t)} \left(1-p \right) \left[\frac{1}{1-(1-p)^{2/3}} + B \ln(1-p)\right] \tag{1}
\]

where

\[
A = \frac{30 DP}{kR^2} \quad , \quad B = \sqrt{\frac{2\pi}{P}}
\]

and

\( T = \text{temperature, } \circ K \)
FIGURE 1. Induction Hot Press Designed for Glove Box
\[ D = \text{diffusion coefficient, cm}^2/\text{sec} \]
\[ \omega_0 = \text{original vacancy volume, cm}^3 \]
\[ P = \text{pressure, dyne/cm}^2 \]
\[ k = \text{Boltzmann constant, } 1.38 \times 10^{-16} \text{ ergs/°K} \]
\[ R = \text{grain radius, cm or powder particle radius, cm} \]
\[ \tau = \text{critical shear stress, dyne/cm}^2 \]
\[ t = \text{time, sec} \]

The time dependence of the temperature in (1) is introduced to simulate the experimental heating period of the die in the hot press while the temperature is raised to the desired level. Equation (1) is based on the work of McClelland, Murray et al., and Mackenzie and Shuttleworth.

**Results and Discussion**

Densification of Mixed (U,Pu)N and UN

Hot pressing test conditions and the end point density of UN and mixed (U,Pu)N are shown in Table 1. Referring to Test No. Pu-1 and Pu-2, the difference between the densities is due to the hot pressing pressure of 3.0 and 4.0 ksi which significantly affects the end point density at this temperature (1450°C). Even though the pressure is further increased to 5.0 ksi for Test No. Pu-3, the pellet density does not increase due to the lower temperature (1200°C). By employing a slightly higher temperature (1300°C) and a higher pressure (6.7 ksi) a higher density of 98% resulted in Test No. Pu-4. This combination of test conditions resulted in an end point density that is nearly the same as that obtained in Test No. Pu-2 which involved 4.0 ksi and 1450°C. In this case, the fabrication conditions of Test No. Pu-2 are considered to be more effective in extending the life of the hot pressing die.

To study the effect of pressure in detail, the pellets from Test No. Pu-5 were hot pressed under the pressure of 3000 psi as shown in Table 1, while the remaining hot-pressing conditions were the same as in Test No. Pu-2, except that the green density was 3% lower than that of the pellets in Test No. Pu-5. An end point density of 94% was obtained.
TABLE 1. Hot Pressing Test Conditions and Pellet Density of UN and Mixed (U,Pu)N

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Material</th>
<th>Cold Press</th>
<th>Hot Press</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pressure KSI</td>
<td>Green Density %T.D.</td>
</tr>
<tr>
<td>CH-1</td>
<td>UN</td>
<td>35</td>
<td>48</td>
</tr>
<tr>
<td>UT-1</td>
<td>UN</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>UN-1</td>
<td>UN</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>UN-2</td>
<td>UN</td>
<td>28</td>
<td>56</td>
</tr>
<tr>
<td>PU-1</td>
<td>UN-45%PuN</td>
<td>40</td>
<td>62</td>
</tr>
<tr>
<td>PU-2</td>
<td>UN-20%PuN</td>
<td>40</td>
<td>66</td>
</tr>
<tr>
<td>PU-3</td>
<td>UN-20%PuN</td>
<td>40</td>
<td>52</td>
</tr>
<tr>
<td>PU-4</td>
<td>UN-20%PuN</td>
<td>60</td>
<td>67</td>
</tr>
<tr>
<td>PU-5</td>
<td>UN-20%PuN</td>
<td>50</td>
<td>63</td>
</tr>
</tbody>
</table>
The result indicated that at 1450°C, one can achieve and control end point densities between 95% and 99% by appropriately increasing hot pressing pressure from 3000 psi to 4000 psi with starting green densities between 62% and 66%. As can be ascertained from Table 1, Test No. Pu-1 and Pu-5 involved nearly identical test conditions except for the higher plutonium nitride content in Test No. Pu-1, and yet the same density resulted. Also as shown in Figure 2, the reproducibility of the test method was good. The densification history of these two materials as shown in Figure 3 and Figure 4 indicates that even though the loading history and the rate of density increase is different, the density of both mixed uranium nitrides reached almost the same point (93%) after 75 minutes, starting from the initiation of significant deformation. This suggests that the study of temperature-pressure combinations be performed to obtain the pellets of maximum density in the future.

Open circles in Figure 2 indicate calculated end point densities based on Pu-5 for the upper bound and on Pu-3 for the lower bound with Equation (3). As can be seen, the UN in Test No. UT-1 had a very low hot pressing pressure of 2.4 ksi at 1425°C (detailed densification history of this sample is shown in Figure 5) while Test No. UN-2 shows a very low density due to the low hot pressing pressure of 3.1 ksi even though the temperature was 1600°C. This result again suggests that the optimal temperature-pressure combination should be found in order to fabricate the best pellets. The microstructure of the above sample indicates that large grain size pores make these pellets extremely brittle. Thus, higher pressures and low temperatures were recommended to control the pellet microstructure.

To prove this point, Test No. UN-1 was hot pressed under the pressure of 6.3 ksi at 1400°C, resulting in an end point density of 97%. The microstructure of this sample is shown in Figure 6. It exhibits about half the grain size of the earlier sample and the pores are smaller and more evenly distributed. As a result, these pellets were much stronger than those of Test No. UT-1.
FIGURE 2. End Point Density of UN and Mixed (U, Pu)N. Open Circles are Calculated Values.
FIGURE 3. Densification of UN-45%PuN. Hot Pressed Under the Pressure of 3000 psi at 1450°C (Test No. PU-1)
FIGURE 4. Densification of UN-20%PuN. Hot Pressed Under the Pressure of 3000 psi at 1450°C (Test No. Pu-5).
FIGURE 5. Densification of UN Hot Pressed Under the Pressure of 2400 psi at 1425°C (Test No. UT-1)

FIGURE 6. UN Hot Pressed Under the Pressure of 6300 psi at 1400°C for 1.5 Hours. Density 97% (Test No. UN-1) Etched in a Solution Consisting of 90 ml Lactic Acid, 30 ml HNO₃, and 3 ml HF for 45 Seconds.
Finally, high density mixed (U,Pu)N fuel pellets were fabricated using reasonable combinations of hot-pressing conditions as in Iest No. Pu-2. The pellets were formed in a 0.371 inch die under the pressure of 4.0 ksi yielding a green density of 66%. The detailed pressure and temperature rise during the hot pressing is shown in Figure 7. The green pellets were compressed with lower pressure (1400 psi) to prevent cracking of the green pellets at room temperature. Then the temperature of the furnace was raised at the rate of 5°C/minute. Densification began at 940°C ± 10°C and when the temperature reached 1245°C, the density of the pellets had increased from 56% to 72%; at this point, the pressure was raised gradually to 4000 psi. The temperature continued to increase during this period of time. A smooth density increase avoided gas trapping in the pellets. After 90 minutes of hot pressing, pellets of 99% theoretical density were obtained.

Digital Computer Simulation of Hot Pressing

A typical computer Calcomp plot for hot pressing of mixed (U,Pu)N is shown in Figure 8. The unbroken curve represents uranium-plutonium nitride fuel data obtained from a hot-pressing experiment run at 3000 psi with a steady state temperature of 1450°C beginning at the assigned time, t = 65 minutes. The dashed curve that approximates best the experimental curve was obtained using the model of Equation (1) with hot pressing coefficients, A = 1.296 and B = 0.352. The values of A and B were obtained by means of trial and error. The remaining curves were obtained by suitably modifying the pressure to predict the densification process at different hot pressing conditions. The numbers appearing at the ends of the dashed curves are the associated pressures. The dashed curves without an associated number corresponds to P = 12000 psi.
FIGURE 7. Densification of UN-20%PuN. Hot Pressed Under the Pressure of 4000 psi at 1450°C (Test No. Pu-2).
FIGURE 8. Calculated Densification of UN-20%PuN Fuel Pellets with Various Hot Pressing Pressure and Time at 1450°C. Simulated by Digital Computer. Unbroken Curve Representing Data Obtained from Hot-Pressing Experiment Under 3000 psi at 1450°C.
CONCLUSION

1. A theoretical green density of 62\%-67\% is preferable for fabrication of high density pellets. Mixed (U,Pu)N of the density of 99\% was fabricated under a pressure of 4000 psi at 1450°C, and 94\% pellet density was achieved under the pressure of 3000 psi at 1450°C.

2. As shown in Test No. CH-1, hot pressing under high pressure is a very effective means of obtaining pellets of high density at a given temperature. As can be shown in Test No. Pu-4, however, the pressure is not so effective as the temperature, when the temperature is low and the viscosity of the material is high. Thus, increasing the temperature of the pellets under low pressure (1400 psi) and then applying pressure to higher levels after the temperature of the pellets exceeds 1250°C is highly recommended for obtaining mixed (U,Pu)N of high density. Such an example is shown in Figure 7.

For hot pressing of mixed uranium-plutonium nitride at 1450°C and under the pressure of 3000 psi, the values for the hot press coefficients were determined to be

\[ A = 1.296 \quad B = 0.352 \]

3. Measuring and analyzing techniques developed for continuous densification of hot pressing were proven to be very useful both for the determination of the best fabrication conditions and for the evaluation of fuel pellets.

However, care must be exercised in the application of the results. Additional experimental data are required to obtain reliable "A" and "B" values for each hot pressing temperature and especially for different starting materials and different testing parameters such as powder characteristics, green density of starting material or heating rate of hot press die and loading sequence during hot pressing.
At present, it appears that the hot pressing characteristics of mixed (U,Pu)N follow very closely the viscid flow mechanism above 85% theoretical density under the test conditions described for Test No. Pu-5.

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