Admixed binders and lubricants in ceramic powder pressing—A study of zinc behenate additive

Palanki Balakrishna*, B Narasimha Murty, R B Yadav, M Anuradha, P S A Narayanan & R Pramanik
Nuclear Fuel Complex, Hyderabad 500 062, India
and
S Majumdar
Radiometallurgy Division, Bhabha Atomic Research Centre, Bombay 400 085, India
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Admixed lubricants are used to bring down compaction and ejection pressures, and to increase packing efficiency in ceramic powder pressing. Admixed binders are used for increasing green strength of the compact. The stronger and denser green compacts so obtained, sinter to high densities without defects and with minimal shrinkage, leading to very high acceptance rates in large scale production. Zinc behenate powder has been used as a lubricant cum binder for uranium dioxide with very good results. Green density versus compaction pressure has been obtained. Weight loss with temperature of free and admixed zinc behenate and carbon and zinc loss in admixed compact and other data are presented. On the other hand, the use of zinc behenate could lead to bloating and high nitrogen values in sintered uranium dioxide under some conditions of processing, which have been identified.

Defects which appear after sintering have their origin in the arrangement of particles established by the shaping process. Green strength is important for handling of powder compacts. A tensile strength of 5 MPa is sufficient for powder metal bodies. Most ceramic green bodies are weaker than this, 1 or 2 MPa being typical. Green strength can be enhanced by using a binder in the powder.

When the die-wall lubricant is too thin, it tends to flow down the die-wall and collect on the bottom punch. Excess lubricant on the bottom punch is a known cause of bottom endcapping in the compact (Swaminathan N, personal communication). On the other hand, insufficient lubricant on the die-wall leads to friction cracks in the compact. Uniform availability of lubricant becomes more difficult as the number of punches in the press increases. Green density varies significantly from region to region in the same compact due to inter particle friction. Problems associated with die-wall lubricant and variations in green density within the compact can be minimized by an additive uniformly dispersed in the powder.

In the pressing of small diameter compacts, it is not practicable to have automatic die-wall lubrication, as the punch does not have sufficient space for a lubricant channel in it. In such cases also, the powders are admixed with the lubricant.

The goals of dry pressing ceramics are uniform compact size and green density, consistent part to part green density and a strong and defect-free compact. These may be achieved by using admixed lubricants or binders.

The common lubricants used in ceramic powder compaction are paraffin wax, aluminium stearate, butyl stearate, lithium stearate, magnesium stearate, sodium stearate, stearic acid, zinc stearate, oleic acid, poly glycols, talc, graphite and boron nitride. Common binders are poly vinyl alcohol, clay, microcrystalline wax. Uranium dioxide powders have been pressed with or without additives. Zinc stearate and zinc behenate were found suitable. A mixture of 1% zinc behenate and 1% naphthalene was used in UC and (U, Pu)C compaction. Other stearates have been used for deliberately lowering the sintered densities. After heating to 500°C in air, a black tar-like residue remained in the case of poly vinyl alcohol and poly acryl amide; no residue was found in the case of poly ethylene glycol. In previous papers, it was stated that defect-free UO₂ compacts could be made on laboratory scale or production scale by using zinc behenate additive.
Subsequently, a detailed investigation was carried out, the results of which form the basis of this paper.

Green density as a function of compaction pressure with and without zinc behenate admixed in UO₂ powder is presented here. Weight loss and other data on zinc behenate, in free and admixed condition, are also presented. A possible mode of decomposition of zinc behenate in a reducing atmosphere has been suggested. A serious problem of impurity and bloating that could be faced under some circumstances has been described and preventive measures suggested.

**Experimental Procedure**

The UO₂ powder is prepared through the ammonium diuranate route. It has a Brauner Emmett Teller (BET) specific surface area of 3.0 - 3.5 m²/g and a Fisher Average Particle Size of 2 to 2.5 micrometres. The powder does not flow readily into pressing die cavities, unless precompacted and granulated.

Zinc behenate Zn(C₂₇H₄₅COO)₂ powder was so fine that it could reveal finger prints readily. The powder was hygroscopic. On drying at 80°C at 0.1 mm Hg pressure for 30 min, the moisture evolved was 0.18% by weight. BET specific surface area was found to be 7.12 m²/g. Fisher Average Particle Size could not be determined. The weight loss of the zinc behenate powder in free state as well as admixed in UO₂ compact was studied using a thermal analyzer.

When the zinc behenate content is 1% or more, a separate dewaxing furnace is required before sintering. When it is 0.3% or less, the compacts may be directly sintered, without dewaxing. It may be added to the virgin powder or to granulated powder. With virgin powder, 1% of the additive was the minimum required without the use of a die-wall lubricant. At 0.5%, screeching noise could be heard during compact ejection without die-wall lubricant. Compacts thus made showed axial striations on sintering and finish grinding. However, when the additive was used as a coating after granulation, 0.3% was found to be sufficient, without needing die-wall lubrication against 1% required before granulation. The tumbling operation required for adding zinc behenate has an additional benefit of homogenizing the granules with respect to coarse and fine fractions (Katiyar, NPS, personal communication). This is necessary for achieving uniform die fill in all the die holes of the press.

**Results**

Fig 1 shows the green density of UO₂ compact as a function of compaction pressure with and without zinc behenate. The weight loss of zinc behenate with increasing temperature is shown in Fig. 2 for free behenate and 1% behenate admixed in UO₂ pellet. The atmosphere was argon - 8% hydrogen mixture. In the case of oxide pellet, the weight loss begins at about 500°C and is complete at about 1000°C.

The retained carbon and zinc contents in the oxide pellet in the same atmosphere are shown in Fig. 3. Table 1 gives carbon and zinc contents of dewaxed pellets initially with 1 weight percent zinc behenate in different atmospheres at 500°C.
Table 1—Carbon, zinc and total gas in dewaxed pellets

<table>
<thead>
<tr>
<th>Condition</th>
<th>Carbon ppm</th>
<th>Zinc ppm</th>
<th>Total gas cc/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>No dewaxing</td>
<td>7410</td>
<td>850</td>
<td></td>
</tr>
<tr>
<td>Ar + 8% H₂</td>
<td>2900</td>
<td>800</td>
<td>2.417</td>
</tr>
<tr>
<td>vacuum</td>
<td>2697</td>
<td>930</td>
<td>2.777</td>
</tr>
<tr>
<td>argon</td>
<td>3800</td>
<td>535</td>
<td>1.607</td>
</tr>
<tr>
<td>CO₂</td>
<td>2752</td>
<td>810</td>
<td></td>
</tr>
<tr>
<td>No additive</td>
<td>50-150</td>
<td>&lt;200</td>
<td></td>
</tr>
</tbody>
</table>

Discussion

Decomposition of binder—In a reducing atmosphere, zinc behenate decomposes into behenic acid and zinc,
\[ \text{Zn(C}_{21}\text{H}_{43}\text{COO)}_{2} + \text{H}_2 \rightarrow 2 \text{C}_{21}\text{H}_{43}\text{COOH} + \text{Zn} \]

Behenic acid, in turn, is likely to get reduced to behenic alcohol,
\[ \text{C}_{21}\text{H}_{43}\text{COOH} + 2 \text{H}_2 \rightarrow \text{C}_{21}\text{H}_{43}\text{CH}_2\text{OH} + \text{H}_2\text{O} \]

Behenic alcohol on pyrolysis gives lower chain alcohols and alkanes. The carbon escapes in the form of methane, carbon monoxide or carbon dioxide.

Endcapping—There may be some problems associated with the use of binder or lubricant. According to Thompson\(^\text{13}\), the use of admixed lubricant increased the tendency to form a defect called endcapping. In the present case, the use of zinc behenate greatly reduced endcapping, indicating its binding property.

Bloating—In the course of sintering, evolved gases must be eliminated while the surface permeability of the compact is high. Additive burnout is very dependent on the composition and strength of the additive material, the composition of the gas surrounding and in the pores of the product, and the rates of diffusion of the decomposition product gases and furnace gas through the product, which is dependent on permeability of the green body\(^\text{5}\).

Low density—When zinc behenate is mixed in the powder before granulation, care should be taken to keep the precompaction pressure low, to avoid formation of hard granules with low apparent specific volume. The breaking strength of compacts made from granules decreases as the apparent specific volume of the granules is decreased\(^\text{14}\). Hard granules retain their identity in final compaction and in sintering. Instead of the final compact sintering as a whole and shrinking towards its centre, each granule shrinks towards its own centre, leaving an overall low density framework on sintering.

Increasing the final compaction pressure to overcome the low sintered densities leads to stress relief defects such as cracking and endcapping. In view of these problems, it is advisable to add zinc behenate after granulating the powder.

Nitrogen impurity—On the basis of a process for the preparation of uranium mononitride\(^\text{15}\), nitrogen impurity in sintered UO₂ appears to have been caused by the reaction of UO₂ with nitrogen from the sintering atmosphere cracked ammonia in the presence of trapped carbon. At 1400 — 1600°C,
\[ 2\text{UO}_2 + 5\text{C} + 3\text{N}_2 + 2\text{H}_2 \rightarrow 2\text{UN} + 4\text{CO} + \text{CH}_4 \]

This cannot happen when the furnace atmosphere is hydrogen or argon-hydrogen mixture, that is, when it is free from nitrogen. The carbon comes from binder or die-wall or powder admixed lubricant. Its burn-out depends on its quantity,
temperature and oxygen potential or moisture level in the sintering furnace atmosphere. The problem exists only when short length continuous sintering furnaces and short pushing intervals corresponding to fast heating rates are used and absent in other oxide ceramics sintered in air. To avoid nitride formation, the \( \text{U}_2 \) sintering furnace profile and pushing interval are so adjusted as to allow sufficient time for volatilizing of the binder before its decomposition and carbon burn out after decomposition at a low temperature when the compacts are still permeable and allow carbonaceous gases to diffuse out. This way subsequent nitride formation at 1400°C can be avoided. Admixed lubricants and binders may also be avoided altogether and minimal die-wall lubricant used. It has been found that poly ethylene glycol is superior to oleic acid as the die-wall lubricant in respect of nitride formation in \( \text{U}_2 \) sintered pellet. Care should be taken however, to adjust its viscosity to enable complete lubricant film formation over the die-wall. In a laboratory thermal analysis, evaporation of poly ethylene glycol was found to be complete by 423°C while oleic acid required a higher temperature 495°C (Balaji Rao Y, personal communication).

Compacts made from higher specific surface area powders tend to pick up more nitrogen as reactivity of a powder increases with increasing surface area. A high green density means finer interconnected porosity and more tortuous path for diffusion of organic materials out of the body. The mean pore size in a packed ceramic body is mainly a function of particle size and powder volume fraction. The porosity of a green compact can be increased by lowering the green density. A large size of the pore channels means easy diffusing out of organic materials and their decomposition products.

Zinc deposition—If zinc behenate is used in excessive quantity, a separate dewaxing furnace would be required. Otherwise, the decomposition product zinc in a reducing atmosphere, depositing in the cooler parts of the sintering furnace may cause problems.

Conclusion

Zinc behenate may be used in small concentrations (up to 0.3 % by weight without dewaxing or 1% with dewaxing) as a binder in \( \text{U}_2 \) (or mixed oxide) powder compaction, with the advantage of higher green strength, higher and uniform green and sintered density, uniform shrinkage and greater final acceptance levels. Care should be taken, however, in that the binder is homogeneously dispersed in the powder and the sintering furnace atmospheres and temperature-time profiles are such that bloating and nitriding in sintered \( \text{U}_2 \) are avoided.

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