Journal of Nuclear Materials 384 (2009) 190–193

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Letter to the Editor

A new process based agglomeration parameter to characterize ceramic powders

Palanki Balakrishna *, B. Narasimha Murty, M. Anuradha

Nuclear Fuel Complex, 17-1-391/44 Subrahmanya Nagar, Saidabad, Hyderabad 500 059, Andhra Pradesh, India

ARTICLE INFO

Article history:
Received 9 May 2008
Accepted 12 November 2008

ABSTRACT

Uranium dioxide powders are made through aqueous chemical route involving precipitation, drying, calcination and reduction. The presence of agglomerates causes powder packing difficulties in the compaction die, and non-uniform and incomplete densification on sintering. To quantify the degree of agglomeration, several authors have proposed 'Agglomeration Parameters'. The change in BET specific surface area of calcined U_3O_8 upon reduction to UO_2 per unit temperature difference is a simple new measure of agglomeration in uranium dioxide powders.

1. Introduction

1.1. Agglomerates

The driving force for sintering being reduction in surface energy, it is essential to have as fine a starting powder as possible, with abundance of specific surface area. Fine powders, however, tend to agglomerate into larger entities and achieve some reduction in surface energy. 'Agglomerates' are particle clusters of irregular shape and uncontrolled size, which hinder flow properties and cause packing problems during die filling for compaction. The poor packing of powders containing agglomerates results in several types of defects in the green and sintered compacts [1,2].

1.2. Agglomerate types

In weak (soft) agglomerates, the primary particles are held together by short-range surface forces. Van der Waals forces arise from electron motion within the atoms and protrude beyond the surface of the particle [3]. In strong (hard) agglomerates, the constituent particles are held by solid bridges, which are formed as a result of sintering, fusion, chemical reaction or setting of a binder [4]. The most common type of agglomerate in a ceramic powder is one bonded by a diffusion bond formed during calcination. Such agglomerates are strong enough to retain their identity during green shaping.

The undesirable effects of agglomerates in ceramic processing have been reviewed [5]. The green density and the sintered density of zirconia decreased as the agglomeration increased [6,7]. The sintered density of cold pressed and sintered yttria-stabilized zirconia decreased as the agglomerate size was increased, whereas centrifugally cast material, which was free from agglomerates, sintered to near theoretical density [8]. Agglomerates in alumina powder were found to limit densification [9,10].

In the case of uranium dioxide too, defects in sintering have been attributed to the presence of agglomerates in the powder [11]. Early remedial measures included milling [12]. Ball milling, jet milling and attritor milling [13] have all been used. However, difficulties in containment of air radioactivity led to process innovations that give agglomerate free fine powders without the need for milling [14–16].

1.3. Agglomeration parameter

Several attempts have been made to quantify the extent of agglomeration in ceramic powders. Balek [17] defined an agglomeration parameter as:

$$AP_1 = \text{avg. aggl. Dia.(Coulter counter)} / \text{equiv. spherical dia. of crystallites(BET)}.$$

Roosen and Hausner [18] defined agglomeration parameter as the ratio of the median agglomerate size to the corresponding particle size. The particle size may be measured from a scanning electron micrograph.

Tremper and Gordon [19] pointed out that it is the coarse fraction of the powder that limits its ability to be sintered to theoretical density, and defined an agglomeration parameter:

$$AP_2 = \text{dia. that 10\% of aggl. are larger than(Coulter counter)} / \text{equiv. spherical dia. of crystallites(BET)}.$$

Adair et al. [20] stated that it is physically more realistic to use the mean volumes than diameters and defined an agglomeration number as:

* Corresponding author. Tel.: +91 40 24075616.
E-mail address: bpalanki@rediffmail.com (P. Balakrishna).

0022-3115/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2008.11.002

$AP_3 = V_{N,V}/V_S$,

where $V_{N,V}$ is the mean volume of the agglomerate (calculated from determined diameter) and is V_S the mean volume of the primary particle.

German [21] defined an agglomeration number,

$AP_4 = (D_{AM}\rho s)^3/2620$,

where D_{AM} is the agglomerate median size (D_{50} on the cumulative particle size distribution) in μm as reported on a mass basis from laser light scattering, sedimentation, sieving, or time of flight measurements. The BET specific surface area s is in m^2/g and the pycnometer density ρ is in g/cm^3. In this form the conversion factors cancel, giving the number of particles in a typical agglomerate as directly calculated from the BET adsorption surface area, pycnometer density, and median particle size.

As per the National Institute of Standards and Technology [22],

$AP_5 = (D_{50}\rho s/6)^3$,

where D_{50} is in μm, ρ is the particle density in g/cm^3, s is the BET specific surface area in m^2/g.

1.4. A new agglomeration parameter

All the agglomeration parameters have been so far defined using only the physical characteristics of the agglomerate, some of which need sophisticated equipment to determine. The present work makes use of routinely available specific surface areas and thermal treatment temperatures to define a new agglomeration parameter.

Highly sinterable fine ceramic oxide powders are usually made through the aqueous chemical route. The precursor precipitate is dried and calcined to get the oxide powder. The specific surface area decreases on calcination. We define a new agglomeration parameter for a ceramic powder as the decrease in surface area per unit increase of thermal treatment temperature.

Aggl. parameter $AP_7 = \Delta s/\Delta T = (s_{T1} - s_{T2})/(T_1 - T_2)$,

where s_{T1} is the BET specific surface area of the powder when calcined at temperature T_1 and s_{T2} is that when calcined at temperature T_2.

In order to make the parameter dimensionless, it may be redefined as:

Aggl. parameter $AP_8 = (\Delta s/s)/(\Delta T/T)$
$= \{(s_{T1} - s_{T2})/s_{T1}\}/\{(T_1 - T_2)/T_1\}$.

This dimensionless parameter reflects the ratio of the fractional reduction in surface area to the fractional difference in calcination and reduction temperatures.

In the case of preparation of uranium dioxide powder, there are three thermal treatments in succession for the precursor ammonium diuranate [$(NH_4)_2U_2O_7$], namely, drying in air, calcination in air and finally, reduction in hydrogen. The product of calcination in air is U_3O_8 and the product of hydrogen reduction is UO_2. Here, the agglomeration parameter may be defined as:

Aggl. parameter $AP_7 = (s_{T\ \mathrm{calcin}} - s_{T\ \mathrm{reduction}})/(T_{\mathrm{calcin}} - T_{\mathrm{reduction}})$.

2. Experimental

The agglomeration parameter as defined above, has been evaluated for powders supplied by two different vendors using the data furnished by the vendors and correlated with the sintered density. About 10 tons of powder from each vendor has been taken into account. The powder consists of lots of each about 500 kg, for which a set of process parameters such as calcination temperature and reduction temperature, and characteristics such as U_3O_8 and UO_2 specific surface areas are recorded in a lot travel card. Both calcination and reduction are carried out in a rotary tubular furnace. The calcination and reduction temperatures are reached in 30 min while the soaking time at the final temperature is for 60 min. The pressing pressure was variable between 200 and 250 MPa, in order to achieve a green density of 5.5–5.6 g cm^{-3} in a compact of diameter and height of 18 mm each. Sintering is carried out in a pusher type sintering furnace with 1 h pushing interval. The sintering furnace profile corresponded to a heating rate of 200 °C h^{-1} to reach 1750 °C and a soaking time of 6 h at 1750 °C. A characteristic mean sintered density of the lot is also recorded. The travel cards of the material were scrutinized for values of different parameters. Typical samples of powder from the vendors were examined under the scanning electron microscope.

3. Results

The process parameters, namely calcination and reduction temperatures, the corresponding specific surface areas of U_3O_8 and UO_2,

Table 1
Process parameters of Vendor '**A**' and calculated agglomeration parameter.

Lot no.	Calcination temperature (°C)	Surface area U_3O_8 ($cm^2\ g^{-1}$)	Reduction temperature (°C)	Surface area UO_2 ($cm^2\ g^{-1}$)	Sintered density (g cm^{-3})	Aggl. parameter AP_7 ($cm^2\ g^{-1}$) (°C)
A-01	720	37600	590	32400	10.66	40
A-02	720	36500	590	32100	10.68	34
A-03	730	34100	580	26900	10.71	48
A-04	730	34200	580	26600	10.72	50.7
A-05	730	35000	580	27300	10.69	51.3
A-06	735	35600	580	28100	10.69	48
A-07	730	33000	570	25600	10.67	46
A-08	730	32600	570	26300	10.71	39
A-09	730	34200	580	27800	10.71	43
A-10	730	33300	560	28000	10.71	31
A-11	730	34100	570	27300	10.69	43
A-12	730	30800	530	26500	10.7	22
A-13	730	33300	560	30100	10.68	19
A-14	730	33700	570	27900	10.67	36
A-15	745	36400	580	32100	10.68	26
A-16	730	30900	530	27500	10.67	17
A-17	730	33100	560	27700	10.69	32
A-18	730	36400	580	29700	10.69	45
A-19	730	34300	580	27800	10.68	43
A-20	730	32000	560	26700	10.70	31.2

Table 2
Process parameters of Vendor '**B**' and calculated agglomeration parameter.

Lot no.	Calcination temperature (°C)	Surface area U_3O_8 ($cm^2\ g^{-1}$)	Reduction temperature (°C)	Surface area UO_2 ($cm^2\ g^{-1}$)	Sintered density ($g\ cm^{-3}$)	Aggl. parameter AP_7 ($cm^2\ g^{-1}$) (°C)
B-01	660	37600	600	29000	10.62	143
B-02	680	38800	575	31600	10.62	68
B-03	675	41500	575	35000	10.51	65
B-04	675	44100	600	35900	10.64	109
B-05	665	41900	600	31400	10.64	161.5
B-06	670	39100	600	31100	10.59	114
B-07	665	33200	600	29300	10.61	60
B-08	660	36000	600	29300	10.6	112
B-09	660	37400	600	29700	10.58	128
B-10	665	41200	600	33400	10.6	120
B-11	665	36900	600	29900	10.6	108
B-12	680	40900	575	29800	10.56	106
B-13	660	38400	600	30700	10.59	128
B-14	660	35200	575	26800	10.67	99
B-15	660	38700	600	30200	10.61	142
B-16	665	38500	600	29500	10.6	138
B-17	680	36500	575	30600	10.52	56
B-18	665	40600	600	32200	10.6	129
B-19	680	35200	575	30300	10.69	47
B-20	670	41500	600	32100	10.59	134

Table 3
Relation between sintered density and agglomeration parameter.

Vendor	Avg. sintered density ($g\ cm^{-3}$)	Avg. agglomeration parameter ($cm^2\ g^{-1}$) (°C)
A	10.69	37
B	10.61	108

Table 4
Analysis of variance (ANOVA).

Source of variation	Sum of squares	d.f.	Mean square	F calculated	F (1%) (1.38) from table
Between samples	0.06425	1	0.06425	0.06425/ 0.000778947 or 82.48	7.36
Within samples	0.0296	38	0.000778947		
Total	0.09385	39	0.065028947		

the sintered densities and the calculated agglomeration parameters for Vendor **A** and Vendor **B** are given in Tables 1 and 2, respectively.

Sintered densities are measured at an accuracy of ±0.05 $g\ cm^{-3}$ at 95% confidence level. The theoretical density of uranium dioxide is 10.96 $g\ cm^{-3}$. The average sintered density and corresponding average agglomeration parameter are given in Table 3. The calculated actual variance ratio of sintered density distributions and the value from F-table are given in Table 4. The results show that powder samples from B, which exhibited higher agglomeration parameters, also yielded lower sintered densities than those of Vendor **A** at 1% level of significance.

4. Discussion

For a single sphere, whose geometry has the lowest surface area per unit volume among all possible shapes, there is no driving force for further reduction in surface area. However, for two spheres in contact, a driving force exists for surface area reduction. Here there are two possibilities. The first possibility of area reduction is through neck formation and growth (by surface diffusion), without particle centers approaching each other.

The second possibility of surface area reduction is through densification (by volume diffusion) with particle centers approaching each other. Surface diffusion is dominant at lower temperatures while volume diffusion is dominant at higher temperatures. In the course of sintering of a powder compact, necks form at the contact points and grow, and the particle centers move towards each other, causing densification of the compact. On the other hand, in the case of loose powder, there is no compaction pressure for maintaining particle contacts that are essential for neck formation. However, those particles which happen to be in local contact with each other, do develop necks, resulting in bonded particle clusters. The extent of contact between particles is given by the coordination number N_c which is 2–4 for loose powder [23,24] and 7–9 in a powder compact with green density 59% [25]. Neck formation, its growth and densification, all of which are essential in compact sintering are unwanted in powder calcination or reduction. In the case where the particles exist independent of each other without clustering together, on heating, there is only a small change in surface area, by way of particle rounding. There can be no neck growth due to absence of contact between the particles. On the other hand, if the particles are in contact, some reduction in surface area may be expected due to neck formation and growth and possibly densification, depending on the temperature regime of calcination. The magnitude of reduction in surface area on thermal treatment is then indicative of the extent of agglomeration.

The powder lots of vendor '**B**' exhibited a higher agglomeration parameter than those from vendor '**A**'. The mean sintered density of the powder lots from vendor '**B**' is also found to be less than that of vendor '**A**'.

There are a few differences in the process equipment of the two vendors. Vendor '**B**' used a turbo-drier that operated at 300 °C for drying the precursor ammonium diuranate, while Vendor '**A**' used a spray drier that operated at 120 °C. The spray drier seems to have given a less agglomerated ammonium diuratnate (ADU) precursor that finally resulted in a less agglomerated UO_2 powder.

The draw back of the present work is that the data from several presses and sintering furnaces have been analysed, with the possibility of variation from press to press and furnace to furnace. Moreover, all the compacts were subjected to the maximum sintering temperature of 1750 °C. Hence the correlation between agglomeration parameter and sintered density is not striking. A better correlation may be expected when a lower sintering temperature is used, and when the same compacting press and the same sintering furnace are used under identical conditions.

5. Summary

A new agglomeration parameter to characterize ceramic powders, namely, change in specific surface area per unit temperature gradient in thermal processing, has been proposed. For UO_2, the change in BET specific surface area from U_3O_8 to UO_2, divided by the difference between the calcination and reduction temperatures is taken to be the agglomeration parameter. The UO_2 powder supplied by one vendor was found to exhibit a higher agglomeration parameter, which correlated with a lower sintered density relative to that of another vendor.

References

[1] P. Balakrishna, C.K. Asnani, R.M. Kartha, K. Ramachandran, K. Sarat Babu, V. Ravichandran, V.B. Narasimha Murty, C. Ganguly, J. Am. Nucl. Soc. 127 (1999) 375.
[2] Palanki Balakrishna, B. Narasimha Murty, M. Anuradha, R.B. Yadav, R.N. Jayaraj, J. Am. Nucl. Soc. 150 (2) (2005) 189.
[3] P.A. Hartley, G.D. Parfitt, L.B. Pol, Powder Technol. 42 (1) (1985) 35.
[4] G.Y. Onada, L.L. Hench, Physical characterization terminology, in: G.Y. Onada, L.L. Hench (Eds.), Ceramic Processing Before Firing, John Wiley, New York, 1970, p. 36.
[5] P. Balakrishna, Interceram 44 (1) (1995) 18.
[6] Dean-Mo Liu, Jiang-Tsair Lin, J. Mater. Sci. 34 (1999) 1959.
[7] Dean-Mo Liu, Jiang-Tsair Lin, W.H. Tuan, Ceram. Int. 25 (1999) 551.
[8] W.H. Rhodes, J. Am. Ceram. Soc. 64 (1) (1981) 19.
[9] D.E. Niesz, R.B. Bennet, in: G.Y. Onada, L.L. Hench (Eds.), Ceramic Processing before Firing, John Wiley, New York, 1970, pp. 61–73.
[10] J.W. Halloran, Agglomerates and agglomeration in ceramic processing, in: L.L. Hench, D.R. Ulrich (Eds.), Ultra Structure Processing of Ceramics, Glasses and Composites, John Wiley, New York, 1984, pp. 404–417.
[11] W.J.S. Craigon, Some Properties of Uranium Dioxide Powders and Sintered Pellets and Their Relationships to Conditions of Preparation, Eldorado Mining and Refining Ltd., Report No. T62-23.
[12] J. Belle (Ed.), Uranium Dioxide: Properties and Nuclear Applications, Naval Reactors, Division of reactor development, USAEC, Washington, 1961.
[13] Palanki Balakrishna, B. Narasimha Murty, D.V. Ratnam, M. Anuradha, C. Ganguly, Ceram. Int. 29 (1) (2003) 99.
[14] P. Balakrishna, A. Singh, U.C. Gupta, K.K. Sinha, Agglomerate-free fine ceramic UO_2 powders, in: Top Fuel'97 British Nuclear Energy Society, Thomas Telford, London, 1997 (republished Interceram 48 (2) (1999) 98–103).
[15] P. Balakrishna, B. Narasimha Murty, K.P. Chakraborthy, R.N. Jayaraj, C. Ganguly, Mater. Manuf. Processes 15 (5) (2000) 679.
[16] B. Narasimha Murty, Palanki Balakrishna, R.B. Yadav, C. Ganguly, Powder Technol. 115 (2001) 167.
[17] V. Balek, J. Mater. Sci. 5 (1970) 714.
[18] A. Roosen, H. Hausner, Adv. Ceram. 12 (1984) 714.
[19] R.T. Tremper, R.S. Gordon, Agglomeration effects on the sintering of alumina powders prepared by autoclaving aluminium metal, in: G.Y. Onada, L.L. Hench (Eds.), Ceramic Processing Before Firing, John Wiley, New York, 1970, p. 170.
[20] J.H. Adair, A.J. Roese, L.G. Mc Coy, Particle size analysis of ceramic powders, in: K.M. Nair (Ed.), Processing for Improved Productivity, vol. 11, American Ceramic Society, 1984, pp. 142–156.
[21] Randall M. German, Int. J. Powder Metall. 32 (4) (1996) 365.
[22] Vincent A. Hackley, Charia F. Ferraris, The Use of Nomenclature in dispersion Science and Technology: Recommended Practice Guide, National Institute of Standards and Technology, Special Publication 960-3, August 2001, p. 6.
[23] M.J. Vold, J. Phys. Chem. 64 (1960) 1616.
[24] M. Nakagaki, H. Sunada, J. Pharm. 83 (1) (1963) 73.
[25] T. Ikegami, Y. Moriyoshi, J. Am. Ceram. Soc. 67 (3) (1984) 174.