Journal of Thermal Analysis, Vol. 35 (1989) 1405–1412

CHARACTERIZATION OF SINTERING OF GELLED UO_3 MICROSPHERES

*A. F. Bishay, A. S. Abdel-Halim, F. H. Hammad, M. F. Abadir**
and *A. M. Elaslaby*

METALLURGY DEPARTMENT, ATOMIC ENERGY AUTHORITY,
*FACULTY OF ENGINEERING, CAIRO UNIVERSITY, CAIRO, EGYPT

(Received April 14, 1988; in revised form January 30, 1989)

UO_3 microspheres, prepared using an internal gelation process, were reduced and sintered. Hydrogen and argon atmospheres were used at temperatures ranging from 1100 °C to 1400 °C for different durations.

It was found that the sintered density is higher for spheres reduced at 700 °C than at any other reduction temperature. Lower densities were achieved in argon atmosphere than in hydrogen for the same sintering and reduction temperature. More than 98% Th.D. could be obtained by calcining the UO_3-spheres at 400 °C for 1 hr, reducing at 700 °C and then sintering at 1400 °C for 2 hrs in hydrogen atmosphere.

Several processes have been developed for the fabrication of UO_3 microspheres [1, 2] which can be used as fuel material in different types of nuclear reactors. Fuel pins containing vibro-compacted microspheres (sphere-pac) are suitable for light water reactors (LWR) [3] as well as for fast breeder reactors (FBR) [4]. Fuel kernels in coated particle fuel have been used for high-temperature gas-cooled reactors (HTGR) [5]. Spherical kernels can be fabricated by dry [6] and wet chemical processes [7, 8].

The wet chemical processes for the fabrication of fuel microspheres differ considerably from each other. They are generally termed sol-gel [9, 10] and gelation processes [11]. Sol-gel processes utilize tetravalent uranium colloid solutions that can be transformed into a stable gel by external or internal gelation [5].

The objective of this study was to investigate the effects of hydrogen and argon atmospheres on the sintering of the reduced microspheres for different durations to obtain high-density UO_2 spheres.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Experimental technique

The UO_3 gel microspheres were prepared as described earlier [12]. The microspheres were reduced in hydrogen or ammonia at different temperatures and were sintered in hydrogen atmosphere.

The pellets fabricated from the spheres with a forming pressure of 36.9×10^7 N/m^2 were sintered in hydrogen or argon atmosphere at temperatures ranging from 1100° to 1400°.

Results and discussion

Effect of calcination on sintering of UO_2 microspheres

Figure 1 shows the relation between the calcination temperature and the percentage increase in density. It is seen from this Figure that in both ammonia and hydrogen the density of the spheres calcined at 400° was higher than the density of the spheres calcined at 200°, 600° or 800°. It is to be expected that a relatively high percentage increase in density will be obtained for spheres calcined at 200°, owing to the presence of the UO_3 phase. This value was about 107% for a 2-hr

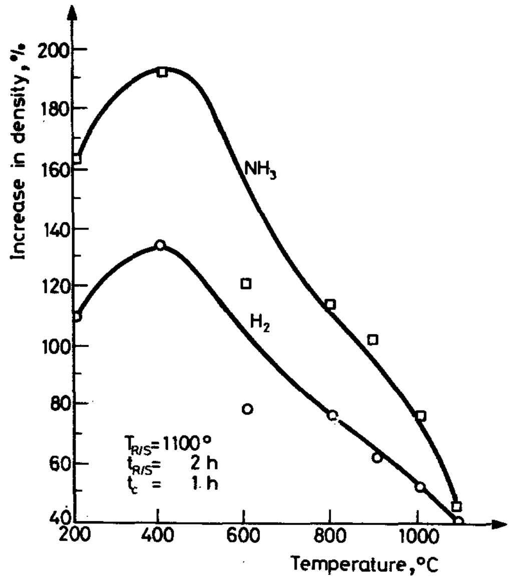

Fig. 1 Effect of calcination temperature on percentage increase in density of spheres during reduction sintering

reduction/sintering run in hydrogen. This increases to 135% for spheres calcined at 400°, because of the evolved impurities. The evolved impurities increase the specific surface area from 5.78 m^2/g at 200° to 8.34 m^2/g at 400°. At higher calcination temperatures, the percentage increase in density drops from 78 to 61%, owing to the formation of U_3O_8 on calcination and to the decreasing surface area, as found by Belle [13]. The evolution of oxygen at these temperatures creates a porous structure which is not readily sinterable in the 2-hr run. In addition, the transformation of UO_2 is not accompanied by a spectacular change in density. At calcination temperatures of 1000° and 1100° sintering was initiated during calcination and the corresponding change in density on reduction/sintering is less pronounced, particularly since the reduction/sintering period is only 2 hrs. It is also seen from Fig. 1 that the reduction/sintering density of spheres at 1100° in ammonia was higher in hydrogen. This is in good agreement with the results obtained by Radford et al. [14], who found that ammonia aids the sintering of UO_2. It can promote densification even at lower temperatures. The densification enhancement can be obtained either by sintering in ammonia or by calcining ammonium diuranate in ammonia. This enhancement in densification can be attributed to the fact that uranium is a catalyst for the decomposition of ammonia [15]. It is known that the gas (and product) are chemisorbed onto the surface, where the decomposition occurs [14]. The decomposition is exothermic and localized energy can lead to an enhancement of surface or grain boundary properties such as grain growth, surface diffusion and sintering [14].

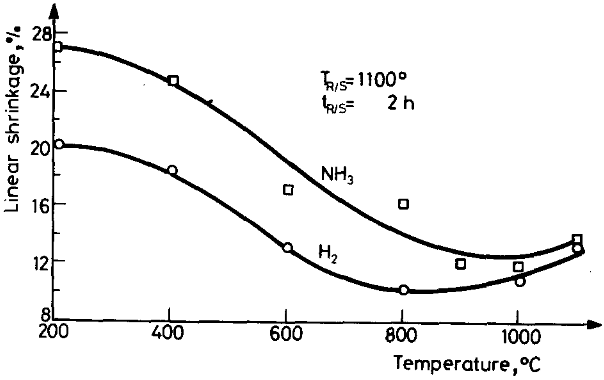

Fig. 2 Effect of calcination temperature on percentage shrinkage of spheres

Figure 2 shows that relation between the calcination temperature of UO_3 microspheres and their percentage linear shrinkage after reduction/sintering at 1100° for 2 hrs in either hydrogen or ammonia. It is clear from this Figure that the percentage linear shrinkage of UO_3 microspheres decreases as the calcination temperature increases, and above 800° the linear shrinkage tends to stabilize owing to the fact that presintering has taken place on calcination. This curve is expected to rise at temperatures above 1100° because of the completion of sintering which has not taken place on calcination.

Effects of reduction temperature and reducing gas on sintered sphere density

Figure 3 shows the relation between the reduction temperature and the density of sintered UO_2 spheres. It is seen from this Figure that the density of the sintered spheres which were reduced at 700° was higher than the density of sintered spheres which were reduced at 600°, 800° or 900°. This is probably because the reduction at 700° in hydrogen is unaccompanied by sintering, and there is therefore an increase in surface area due to the initiation of sintering. This is in accordance with the results of Belle [13]. Matthews et al. [16] found that the density of sintered pellets made from gel spheres decreased from 90 to 72% Th.D. on increase of the calcining temperature from 700° to 900° in Ar + 4% H_2 for 4 hrs. This trend followed the decreasing surface area and increasing crystallite size. The density of sintered spheres reduced at 600° was lower than that of sintered spheres reduced at 700° or 800°. This can be explained in light of the findings of Tiegs et al. [17], who stated that

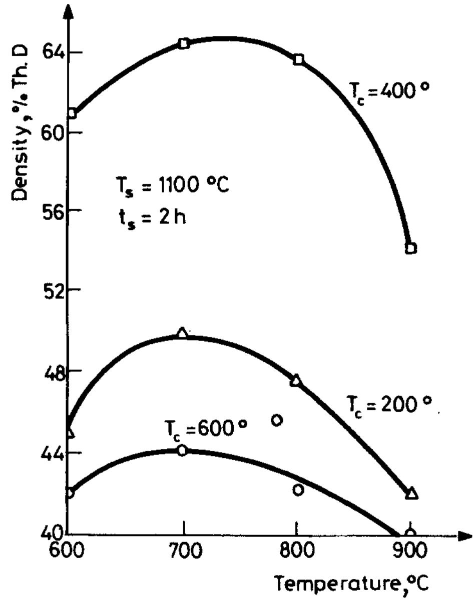

Fig. 3 Effect of reduction temperature on sintered sphere density (sintering atmosphere H_2)

the microspheres calcined at 600° in pure hydrogen appeared to be especially reactive and were oxidized completely to U_3O_8 upon exposure to room air, while those calcined at higher temperature did not undergo reoxidation on exposure to air.

Figure 4 shows the relation between the calcination temperature and the sintered sphere density in argon atmosphere. It is clear from the Figure that the sintered sphere density depends upon the calcination temperature, and the sintered density of spheres reduced in ammonia gas are higher than that of spheres reduced in hydrogen atmosphere. This is in good agreement with the results obtained by Radford et al. [14].

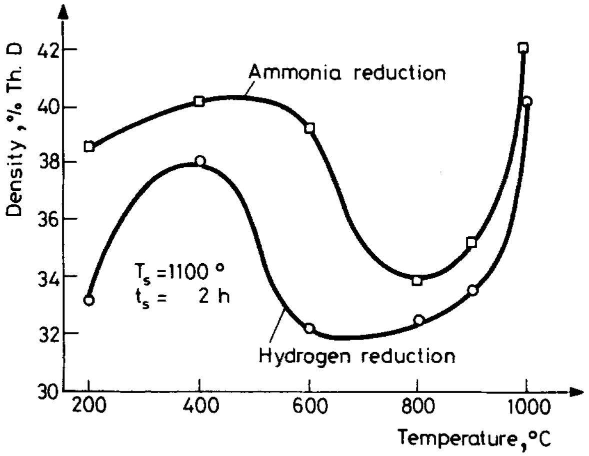

Fig. 4 Effect of reducing gas on sintered sphere density (sintering atmosphere Ar)

Figure 5 shows the relation between the calcination temperature of the spheres and the sintered pellet density. It is seen from this Figure that an increase in calcination temperature increases the sintered pellet density up to 600°; above this temperature, the sintered pellet density decreases again. Further, pellets fabricated from spheres reduced at 700° are denser than pellets fabricated from spheres reduced at 600°. The proper interpretation of these results is that an increase of calcination or reduction temperature increases the oxidation resistance (decreased O/U ratio) of UO_2 spheres and hence increases the integrity of the pellets. But for $T_c = 800°$, the activity of UO_2 decreases due to the decrease in surface area during calcination. From calcination studies on UO_3 spheres, Matthews et al. [16] found that an increase of the calcining time and/or reduction temperature reduced the rate of reoxidation in air and thereby permitted a longer storage time before pellet fabricaton. Previous studies established that the stoichiometry of UO_2 powders

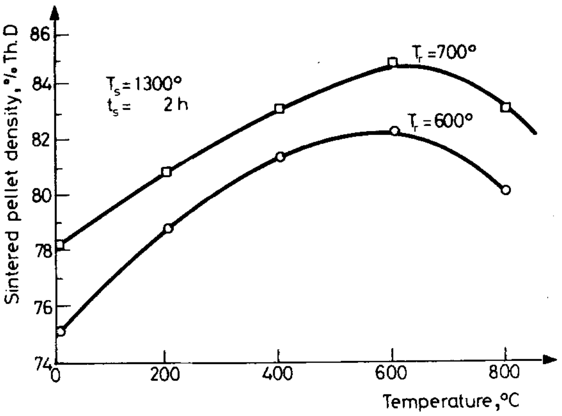

Fig. 5 Effect of reduction and calcination temperature on density of sintered UO_2 pellets (sintering atmosphere H_2)

changed during storage in air, and that the amount of oxygen uptake increased with the specific surface area of the powders [13].

Effect of furnace atmosphere on sintered sphere density

Figure 6 shows the relation between the temperature of calcination of UO_3 spheres and their sintered density in both hydrogen and argon atmospheres. It is clear from this Figure that, at the same calcination and sintering temperature, lower densities are achieved in argon atmosphere than in hydrogen atmosphere. This is

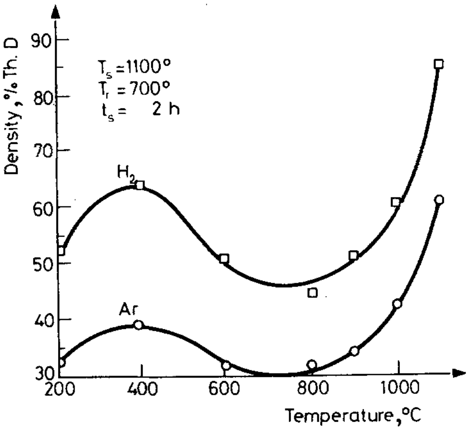

Fig. 6 Effect of sintering atmosphere on sintered sphere density

probably due to the reduction ability of hydrogen as compared to argon in contact with reoxidized microspheres.

Effect of sintering temperature on sintered pellet density

Figure 7 shows the relation between the sintering temperature and the sintered pellet density. It is seen that the sintered pellet density increases on increase of the sintering temperature. On the other hand, the sintered pellet density at 1400° was about 94% Th.D. for pellets made from calcined and then reduced spheres, while the sintered pellet density was only about 82% Th.D. for pellets made from the calcined microspheres. This is because the pellets made from calcined spheres developed cracks during sintering, because of degassing (due to the high O/U ratio = 2.67), and the volume reduction which occurred due to the transformation of U_3O_8 (at T_c = 600°) to UO_2 during sintering was sufficient to crack the pellets and thereby lower the sintered pellets density. In contrast, the pellets made from calcined-reduced spheres were crack-free in general, and therefore reached higher densities.

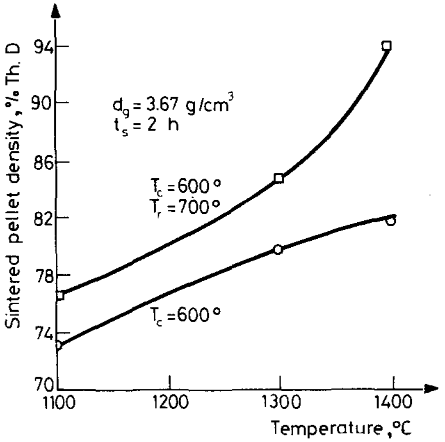

Fig. 7 Effect of sintering temperature on density of sintered UO_2 pellets (sintering atmosphere H_2)

Conclusions

The results of sintering and pelletization studies indicate that:

(i) At the same sintering temperature, the density of spheres reduced/sintered in ammonia atmosphere was higher than that in hydrogen atmosphere.

(ii) The density of sintered spheres reduced at 700° was higher than at any other reduction temperature.

(iii) At the same sintering temperature, lower sintered sphere densities were achieved in argon atmosphere than in hydrogen atmosphere.

(iv) The sintered pellet density increases with temperature, and the density of sintered pellets fabricated from calcined and reduced spheres is higher than that of pellets fabricated from only calcined spheres.

References

1 M. Kadner and J. Baier, Kerntechnik, 18 (1976) 413.
2 H. J. Engelmann, Kernenergie, 26 (1983) 93.
3 R. L. Beatty et al., Report ORNL (1978) 5469.
4 A. L. Lotts and R. L. Beatty, Report ORNL–TM (1979) 6746.
5 H. Nickel, Report Jul. (1970) 687.
6 N. L. Billison, Report DPTN (1973) 418.
7 P. A. Haas, Report ORNL–TM (1978) 3978.
8 A. S. Abdel Halim, Report KFA–2 BB, (1982) 7/82.
9 Symposium on Sol-Gel Processes and Reactor Fuel Cycles, Goltinburg 1970, Conf.–700502.
10 Proc. for Fuel Fabrication, IAEA–161, Vienna, 1974.
11 H. D. Ringel and E. Zimmer, Trans. Amer. Nucl. Soc., 292 (1977) 27.
12 F. H. Hammad, A. F. Bishay, A. S. Abdel-Halim and A. M. Elaslaby, IAEA SM–288/52, P (1986).
13 J. Belle, Uranium dioxide properties and Nuclear Applications, Ed. J. Belle, USAEC Washington, D.C., 1961.
14 K. C. Radford and M. J. Pope, Ceram. Bull., 56 (1977).
15 H. Abrasm, Metallography, 4 (1971) 59, 78.
16 R. B. Matthews and P. E. Hart, J. Nucl. Mat., 92 (1980) 207.
17 S. M. Teigs, P. A. Haas and R. D. Spence, ORNL–TM (1979) 6906.

Zusammenfassung — Über interne Gebildungsprozesse hergestellte UO_3 Mikrokugeln wurden reduziert und gesintert. Dafür wurden Wasserstoff- und Argonatmosphären verschiedene Zeit lang bei Temperaturen zwischen 1100 °C und 1400 °C verwendet. Es wurde festgestellt, daß die Dichte des gesinterten Materials bei einer Reduktionstemperatur von 700 °C am größten ist. Bei gleichen Sinter- und Reduktionstemperaturen erreicht man in Argon eine geringere Dichte als in Wasserstoff. Mehr als 98% Th.D. kann man erreichen, indem man die UO_3 Kugeln bei 400 °C eine Stunde lang kalziniert, bei 700 °C reduziert und dann zwei Stunden lang bei 1400 °C in Wasserstoffatmosphäre sintert.

Резюме — Микросферическая трехокись урана, полученная методом внутреннего желатирования, была подвергнута восстановлению и спеканию. Процессы проводились с различной продолжительностью в интервале температур 1100–1400° в атмосфере водорода и аргона. Найдено, чти плотность спекания была более высокой для сферических частиц трехокиси урана, подвергнутых восстановлению при 700°, чем при других температурах восстановления. При той же самой температуре спекания и восстановления в атмосфере аргона были достигнуты более низкие плотности по сравнению с таковыми в атмосфере водорода. Более чем 98% абсолютно сухой трехокиси урана было получено путем обжига сферической трехокиси урана при температуре 400° в течении 1 часа, с последующим восстановлением ее при 700°, а затем спеканием ее в атмосфере водорода в течении 2 часов при температуре 1400°.