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EFFECT OF PARTICLE SIZE DISTRIBUTION OF UO_2 POWDER ON SINTERABILITY

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Abstract

Nuclear grade UO_2 pellets are produced worldwide through very well proven powder metallurgy route involving operations like granulation, final compaction and sintering, in which particle size distribution of the UO_2 powder plays an important role in final pellet quality. Virgin UO_2 powder produced through ADU route is fine in nature and has poor flowability. Granulation operation is carried out to improve its flowability. During final compaction, higher fraction of granules yield poorly packed green compacts whereas excess of fines lead to increased inter-particle friction. Hence, a judicial mix of fines (45-250 µm) and granules (250 - 2000 µm) is very important for obtaining the stipulated mechanical strength, density and dimensional control of the sintered pellets. In the present work, the weight fraction of granules and fines were varied to study the effect of particle size distribution of UO_2 powder on sintering quality, onset of sintering, sintering rate, linear shrinkage, grain size etc. using a high temperature dilatometer under reducing atmosphere. Variation of grain size with respect to the sintering environment has also been studied.

Keywords

Sinterability, Particle Size Distribution, Dilatometer, Sintering Quality, Reducing Atmosphere.

1 Introduction

NFC follows ammonium diuranate route for the production of nuclear grade UO_2 powder. The raw material, Uranium Ore Concentrate (UOC) is converted to nuclear grade stabilized UO_2 powder through wet route involving processes like dissolution, solvent extraction, feed conditioning, precipitation as ADU, drying, calcination, reduction and stabilization. Uranium dioxide (UO_2) fuel pellets are manufactured through well proven and established powder metallurgy route involving processes like precompaction and granulation and mixing with suitable

quantity of organic solid lubricant/binder. The green compacts formed by pressing the virgin UO_2 granules are then sintered in a reducing atmosphere at around 1700°C and are ground to get the required diameter. QC cleared UO_2 pellets are loaded into zircaloy tubes for further downstream assembly operations.

In pellet fabrication, chemical, physical and morphological characteristics of UO_2 powder play an important role in pelletization operations to achieve required sintered density and visual recovery[1]. UO_2 powder produced through ADU route has poor flowability owing to its morphology. In order to improve its flowability for proper die fill during final compaction operation, the UO_2 powder is precompacted, granulated and sieved to get the required granule shape and size.

Precompaction of the virgin UO_2 powder is accompanied by fracture of the particles which results in an increase in surface area. These fractured particles get interlocked together by Van der Waal's forces under precompaction load.

Higher fraction of the granules in green compacts leads to higher green density but inconsistent pellet integrity after sintering. Though fines help in filling the interstitial spaces, they exhibit higher interparticle friction, poor flowability and lower green density. Therefore, a judicial mix of fines and granules in granulated green powder plays a vital role in final compaction and subsequent sintering operation towards achieving final product quality.

The present work studies the effect of particle size distribution of UO_2 granules on the quality of the sintered pellets through the variation of weight fractions of granules and fines in UO_2 granulated powder. This paper studies the variation in the sintering quality (density, visual and geometrical integrity), onset of sintering, sintering rate, linear shrinkage, grain size etc. in the UO_2 pellets as responses.

2 Experimental

2.1 Fabrication of Green Pellets

The UO_2 powder characteristics and SEM image used for this study are shown in table 1 and figure 1 respectively. The particle size of the powder was measured by laser scattering method and the morphology was observed by scanning electron microscopy.

Table 1 Characteristics of Virgin UO_2 Powder

Property	UO_2
Oxygen to Metal Ratio	2.042
Bulk Density (g/cc)	1.95
Equivalent Boron Content (ppm)	0.3
Theoretical Density (g/cc)	10.97
Specific Surface Area (m^2/g)	3.1
Median Diameter (µm)	14.6

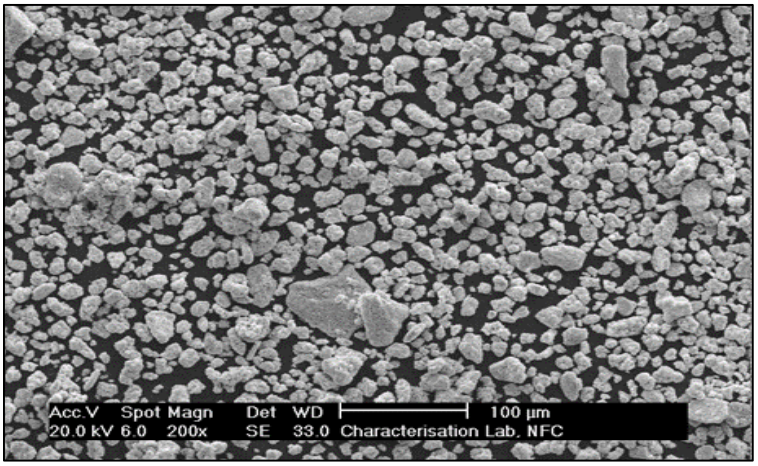

Figure 1 Typical SEM of UO_2 Powder produced through ADU Route

The virgin UO_2 powder was precompacted at low pressure, granulated and then sieved in a vibro-siever with 60 mesh (250 µm) sieve. The + 60 fraction is termed as granule and – 60 fraction is termed as fines. These granules and fines were separately collected and mixed in varied proportions to form different binary compositions of granulated green powder. The weight fraction of granules in granulated green powder was selected as 40, 50, 70, 80 and 90 weight % respectively. To this, 0.3 weight % of solid organic lubricant was added for reducing the die-wall friction and was then compacted in standard double acting hydraulic press at a compaction pressure of 270 MPa into green pellets having length in the range of 16 - 19 mm and diameter around 15 mm. The final compaction pressure was adjusted to get green compacts having density of 52 - 53% T.D.

2.2 Dilatometry

The shrinkage behaviour of the UO_2 compacts having various weight fractions of granules in reducing atmosphere was studied using a high temperature vertical configuration single push

rod type dilatometer (make: Linseis, model: L75V1750S). The sample rests between the spring loaded push rod and a stopper (end support) inside a sample holder all of which are made of Al_2O_3 material. The change in length of green compact was transmitted through the frictionless push rod to an LVDT transducer which was maintained at a constant temperature by means of chiller unit. The temperature of the furnace was measured by Type B thermocouple (Pt - 30/6% Rh) and sample temperature was measured by type C thermocouple (W - 5/26% Re) placed just beside the sample. A nominal force of 300 mN was applied on the sample through the push rod. The sample mounted in dilatometer has been shown in figure 2.

Figure 2 Actual Image of Sample mounted in a dilatometer

The dilatometer experiments were carried out in N_2 – 5% H_2 premixed gas atmosphere using a flow rate of 9 lph (150 sccm/min). Initial heating rate of 10°C/min up to 400°C and 2°C/min from 400°C to 1700°C was selected. The pellet was isothermally held at 1700°C for 1 h to ensure complete sintering. The cooling rate was controlled at 30°C/min up to a temperature of 400°C. The temperature profile selected for the experimentation is shown in figure 3.

Temperature as per the set temperature profile was achieved with the help of feedback loop type in-situ data acquisition and control system. Correction in the final expansion values was done by subtracting the system expansion with the help of blank run.

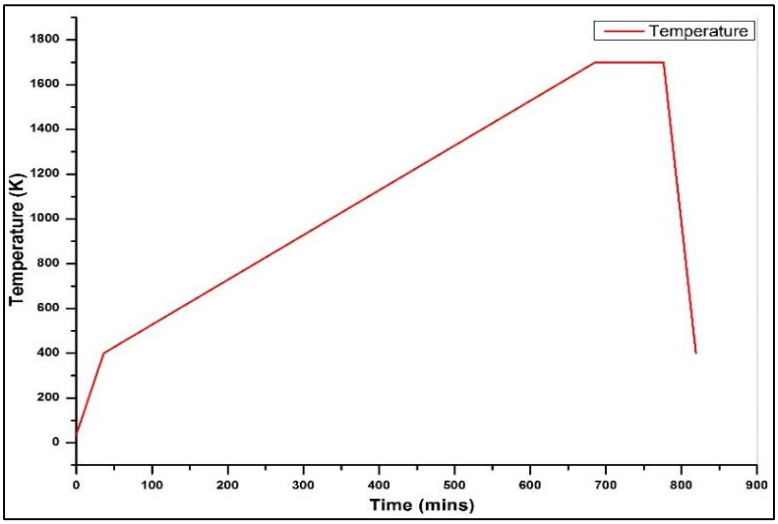

Figure 3 Sintering Temperature Profile

3 Characterization

The density values of sintered UO_2 pellet measured by dilatometer were compared with the help of immersion technique and found to be in close agreement. The microstructure analysis, the sintered pellets were mounted in Bakelite and ground using successive grades of emery paper. The final polishing was done using diamond paste. The etching was carried out using a mixture of 90% hydrogen peroxide and 10% of concentrated sulphuric acid. Further, onset of sintering, sintering rate and linear shrinkage were determined from dilatometer system data.

4 Results

To verify the repeatability of the measurements, each experimental run was carried out twice. The green and sintered density of the pellets are summarised in table 2 and it is observed that the green and the sintered density increases with granules weight fraction. This is probably because of higher density and flowability of granules.

Table 2 Green and Sintered Density of the Pellets

Granule Wt. %	Green Density (g/cc)	Sintered Density (g/cc)
40	5.73	10.352
50	5.76	10.367
70	5.77	10.369
80	5.78	10.394
90	5.79	10.397

Figure 4 compares the expansion (dl/l_0 vs Temperature) of UO_2 pellets as a function of weight fraction of granules in reducing atmosphere, where l_0 is the initial length of the pellet and dl is the incremental length.

$$Relative\ Expansion\ (\%) = \frac{dl}{l_0} \times 100$$

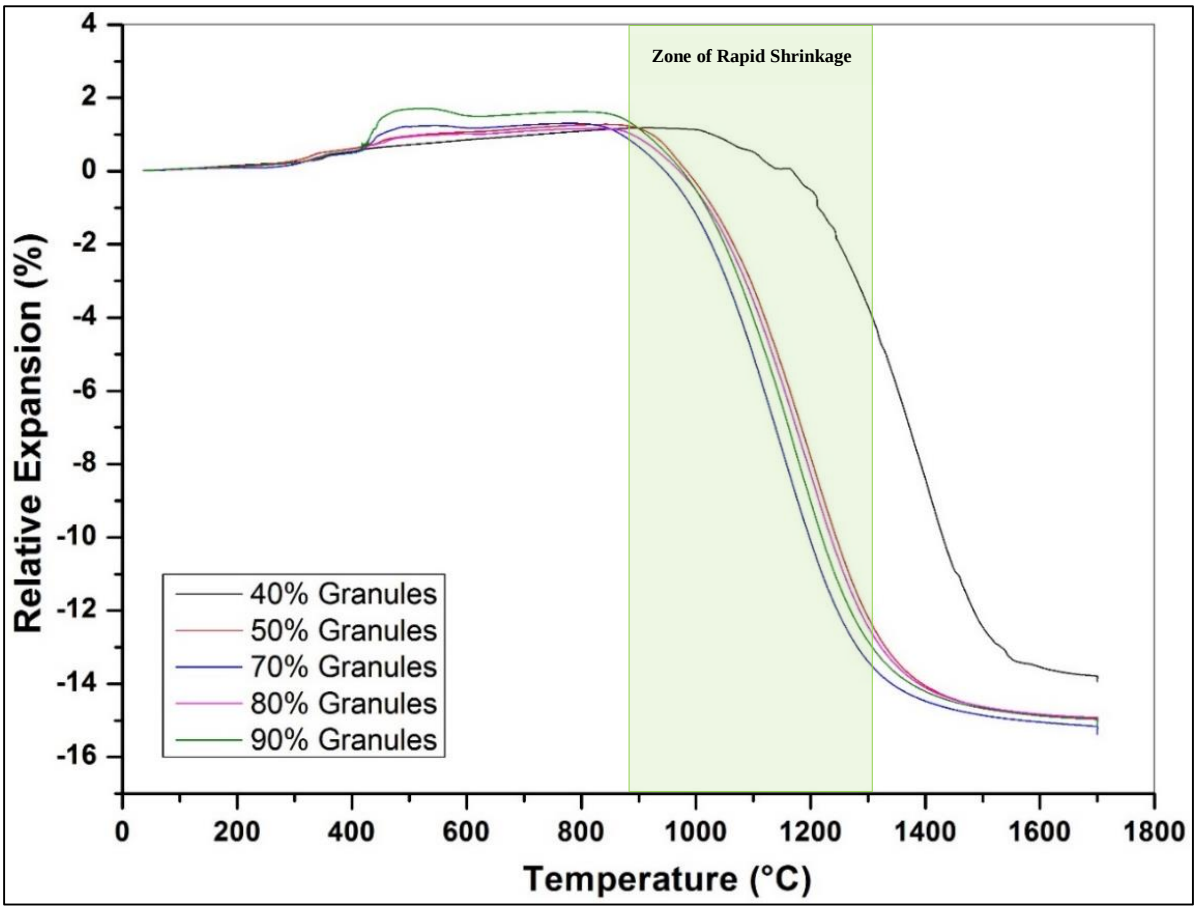

Figure 4 Shrinkage Curve for UO_2 Pellets as a function of Weight Fraction of Granules

It can be seen from the shrinkage curve that zone of rapid shrinkage shifts towards lower temperatures with increase in granule weight fraction.

Figures 5 (a) to 5 (e) shows the onset of sintering for different granule weight fraction UO_2 green compacts. The onset shrinkage temperature was obtained from the shrinkage curves and was determined the point at which it deviates from its linear paths [2].

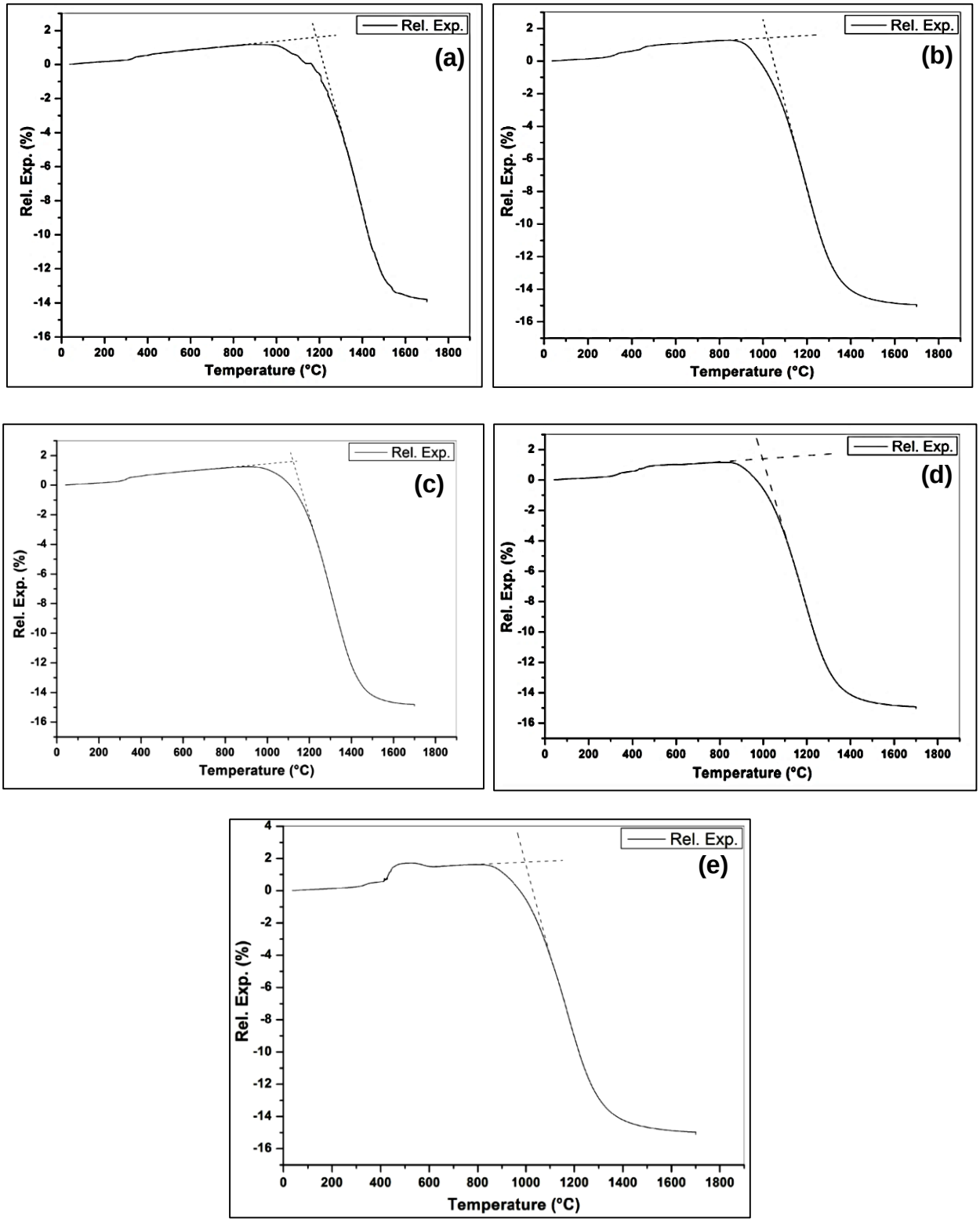

Figure 5 Onset of Sintering for (a) 40 granule % (b) 50 granule % (c) 70 granule % (d) 80 granule % (e) 90 granule % pellets

From the figures, it can be observed that with increase in the weight fraction of granules, the onset temperature of sintering shifts towards lower temperatures. For highest weight fraction, the onset temperature of sintering is around 960°C whereas for lowest weight fraction, the onset temperature of sintering is around 1200°C.

Figures 6 (a) to 6 (e) show the sintering rate of the pellets. The shrinkage rate (dl/dt) has been normalized by dividing it with the initial length of the pellets. The normalised shrinkage rate $((dl/l_0)/dt)$ has been plotted as a function of temperature to ascertain the temperature for maximum shrinkage. From the curves that the temperature of maximum shrinkage is observed at around 1200°C for all the granule compositions. The maximum shrinkage rate for all the compositions was observed to be around 0.002 min^{-1}.

Figures 7 (a) to 7 (e) show the metallographic images of the pellets. The pellets have been polished and etched as per the method described above. The etched pellets have been observed under an optical microscope at 500x magnification. It can be observed from the microstructure analysis that the grain size increases with increase in the weight fraction of granules. The biggest grain size is obtained for the 90 granule % pellet whereas the smallest grain size is obtained for 40 granule % pellet.

5 Discussions

It is well established that sinterability of powders depends upon particle size, morphology and specific surface area. Sintering being a diffusion controlled process, close inter particle contact and small particle size enhances sinterability. In the precompaction process, fracturing of UO_2 particles leads to an increase in surface area and enhanced inter-particle contact. The granules so formed after precompaction will consist of smaller UO_2 particles with increased surface area and enhanced interparticle contact. This explains early onset of sintering for pellets having higher granule fraction.

Sintering process starts with neck formation followed by pore shrinkage, pore elimination and grain growth. An early onset of sintering indicates that the particles enter into neck formation and subsequent sintering stages much earlier. Thus, in pellets with higher granule percentage,

densification is achieved at lower temperatures and further sintering at higher temperatures lead to grain growth. This is evident from comparison of photo micrographs as shown in figure 7.

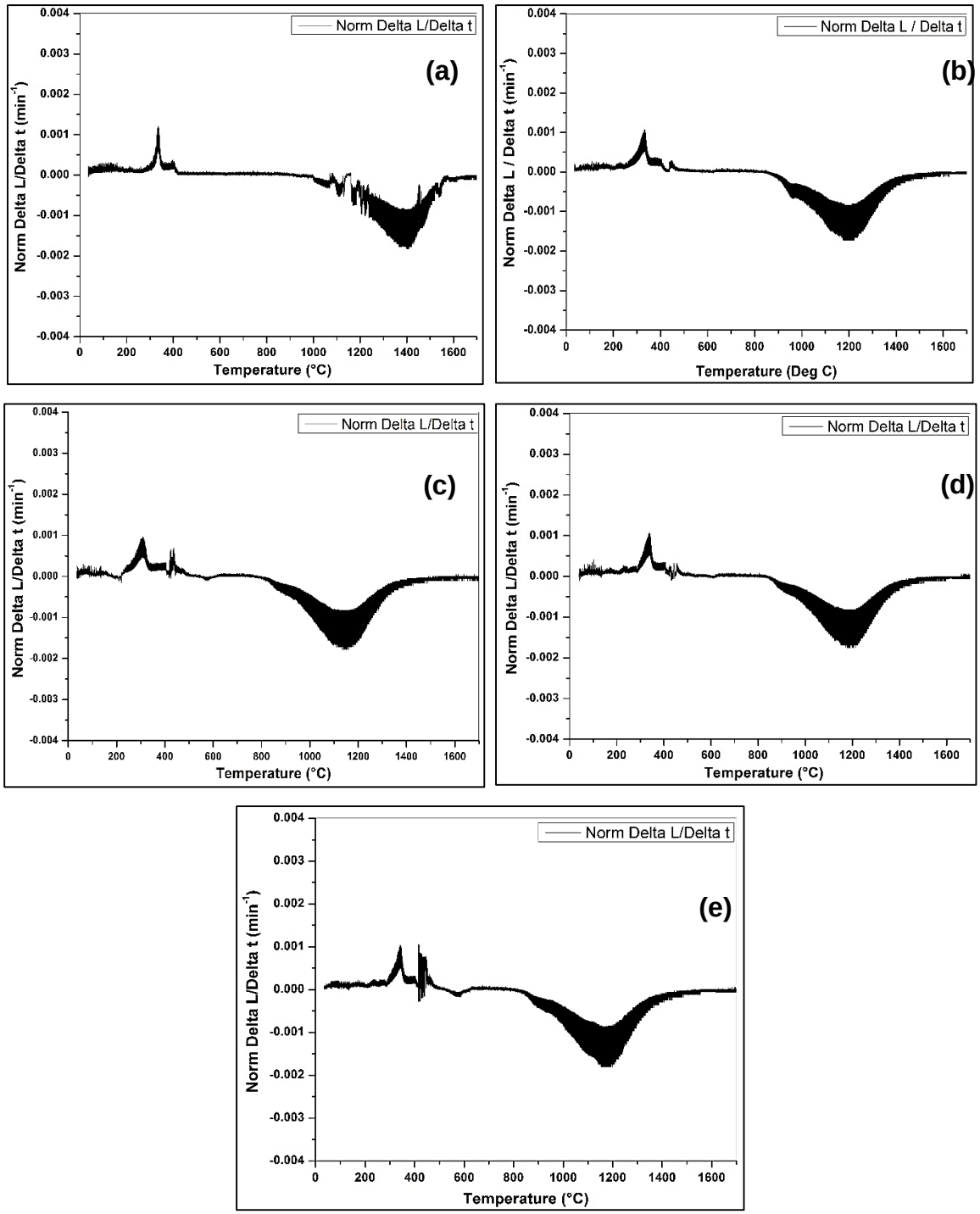

Figure 6 Shrinkage Rate curve for (a) 40 granule % (b) 50 granule % (c) 70 granule % (d) 80 granule % (e) 90 granule % pellets

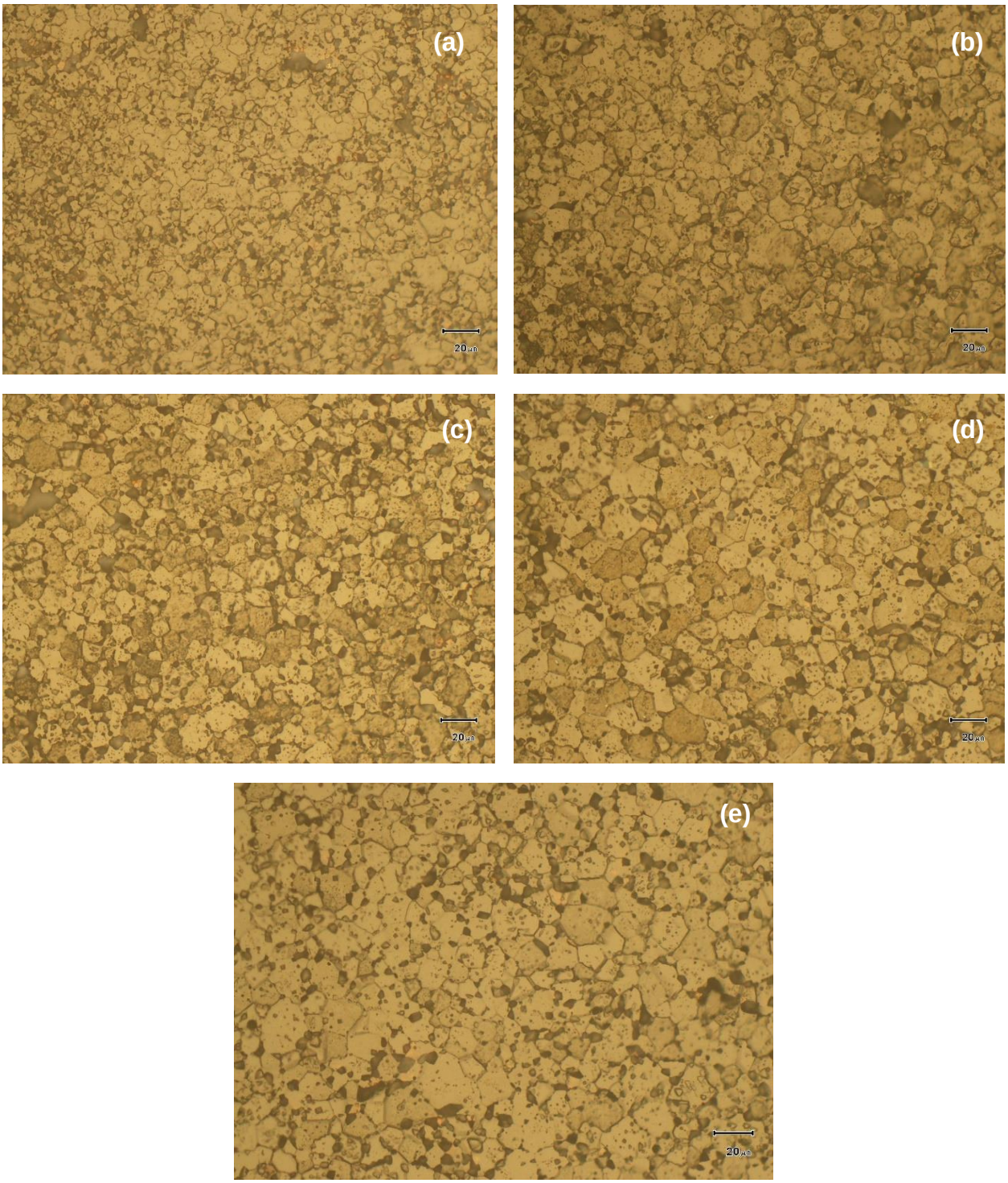

Figure 7 Metallography images of (a) 40 granule % (b) 50 granule % (c) 70 granule % (d) 80 granule % (e) 90 granule % pellets taken in an optical microscope at 500x magnification

6 Conclusions

The sintering behaviour of green UO_2 compacts having various weight fraction of granules and fines were studied under reducing atmosphere and the following conclusions were drawn:

1. The zone of rapid shrinkage shifts to the low temperatures with an increase in the weight fraction of granules in the powder.
2. The onset of sintering for 40 granule % pellet has been seen to be around 1200°C and it lowers with the increase of granule %.
3. The maximum rate of shrinking was constant at 0.002 min^{-1} for all compositions. It was observed at 1400°C for 40 granule % pellets and at 1200°C for all other granule fractions.
4. The biggest grain size has been observed for 90 granule % pellets whereas the smallest was observed for 40 granule % pellets.
5. Fracturing of UO_2 particles during precompaction operation, leads to an increase in surface area and enhanced inter-particle contact. The granules formed, is an aggregate of smaller UO_2 particles having increased surface area and enhanced interparticle contact.
6. In pellets with higher granule percentage, densification is achieved at lower temperatures and further sintering at higher temperatures lead to grain growth.

7 Acknowledgements

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8 References

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