Study On Densification Behaviour Of UO_2 Material Using Dilatometry

K.Kapoor, A.L.Narayana, S.V.Ramana Rao, G.V.S.Hemantha Rao, R.K. Srivastava And R.Kalidas

Nuclear Fuel Complex,
Department of Atomic Energy,
Hyderabad, India

Abstract

High temperature dilatometer has been used for study on effect of various parameters on the shrinkage behaviour of the UO_2 powder compact. It is well known that the densification achieved on sintering is a function of powder characteristics, pressing and sintering parameters. For achieving sinter density in a close acceptable range it is required have a clear idea about the influence of these parameters on shrinkage characteristics. In the dilatometric laboratory tests, the linear shrinkage data from the dilatometer was obtained as a function some of these parameters. The runs were carried out in dilatometer under reducing atmosphere similar to production scale furnaces. Calculation of sintering rate exponent (n) was carried out and compared with literature data for the various possible sintering mechanisms like grain boundary diffusion, volume diffusion, surface diffusion etc. Microstructural features observed in the low density cases were correlated to the shrinkage behaviour in the dilatometer. The possibility of using a 'master shrinkage curve' for a given sintering cycle is explored. Comparison of the shrinkage curves for the lots before actual production with the master curve could be used as a screening test for the powder lots in order to predict the sintering behavior.

1.0 INTRODUCTION

Sintering is mass transport phenomenon driven by lowering of surface energy, occurring at elevated temperature. There are four important atomistic mechanisms, by which the mass can be transferred in a powder compact namely,

1. Evaporation-condensation
2. Surface diffusion
3. Volume diffusion from a) surface to neck and b) grain boundary to neck
4. Grain boundary diffusion

The mass transport through paths 1, 2 and 3a leads to coarsening, while mass transport through path 3b and/or 4 leads to densification. Mechanistic models are now available for verification of densification phenomenon during sintering [1]. An in-depth understanding of the shrinkage mechanisms is critical for attaining the required density in the sintered material. Characterisation of sintering phenomenon involves a) microstructural analysis and its correlation with densification, and b) evaluation of kinetic parameters for the underlying sintering mechanism. For this purpose, high temperature dilatometer combined with electron microscopy has been used in the laboratory studies. It is well known that the densification achieved on sintering is a function of many variables. These can be divided into three groups

namely, powder characteristics, pressing and sintering parameters. The influence of some of these parameters on the shrinkage behaviour has been studied using dilatometry. Previously studies using dilatometer were restricted to evaluation of kinetic parameters and study on affect of sintering variables on the shrinkage behaviour [2-6]. But, use of the dilatometric data for achieving sinter density in a close acceptable range in large scale production furnace has been not attempted. As always the laboratory test under well controlled conditions with a few samples gives only an idea about the performance of process parameters and material. It is expected to get some deviations in results with large scale production due to lack of material homogeneity combined with variations in the process parameters. Nevertheless, the laboratory data can give valuable information about the intrinsic material properties which can be used as a screening test for the material.

2.0 LABORATORY TESTS

Sintering tests were carried out in a high temperature dilatometer using a reducing atmosphere (5% H_2 in Argon). The unit consists of a vertical push rod system with weight balance for the push rod to have minimal force on the sample by weight of the rod. The sample temperature is monitored using a sealed Pt-Pt/Re thermocouple. The unit is calibrated using a standard sapphire sample for measurement of dilation/contraction. The data on the sample temperature and shrinkage was logged as a function of cycle time. For rate controlled sintering, special software was used to setup a constant shrinkage rate.

For the tests the powder compacts were made from the pre-compacted powder in the double acting hydraulic press with green density ranging from 5.6 to 5.8 g/cc.

3.0 RESULTS

3.1 Studies on Influence of Process and Material Parameters:

The influence of the various process and material parameters on the shrinkage behaviour has been studied and reported below.

3.1.1 Effect of Heating Rate: In case of large scale sintering furnace the pellets are loaded in shrouds which are pushed in the muffle at regular intervals. The furnace profile and the pushing interval selected are the two main parameters for sintering cycle. In the present study, a furnace profile was selected with three different pushing intervals as variable namely, 30m, 60m and 90m. Tests were conducted in dilatometer simulating the heating cycles corresponding to a fixed furnace profile and variable pushing intervals. To ensure minimum variability in the samples, the source was from same powder lot and pressing was carried out in one cycle in a hydraulic press. Fig.1a and b gives the shrinkage (dl/Lo) curves for green compacts measured for the three cycles in the dilatometer as a function of time and temperature respectively. From these curves shrinkage rate (dl/Lo)/dt curves are obtained and evaluation of important parameters like onset of shrinkage temperature, maximum shrinkage rate and temperature of maximum shrinkage rate, was carried out. Following are the important observations from these curves:

1. The maximum shrinkage rate is higher for faster pushing interval and
2. The temperature at which highest shrinkage rate appears increased marginally with faster pushing interval.

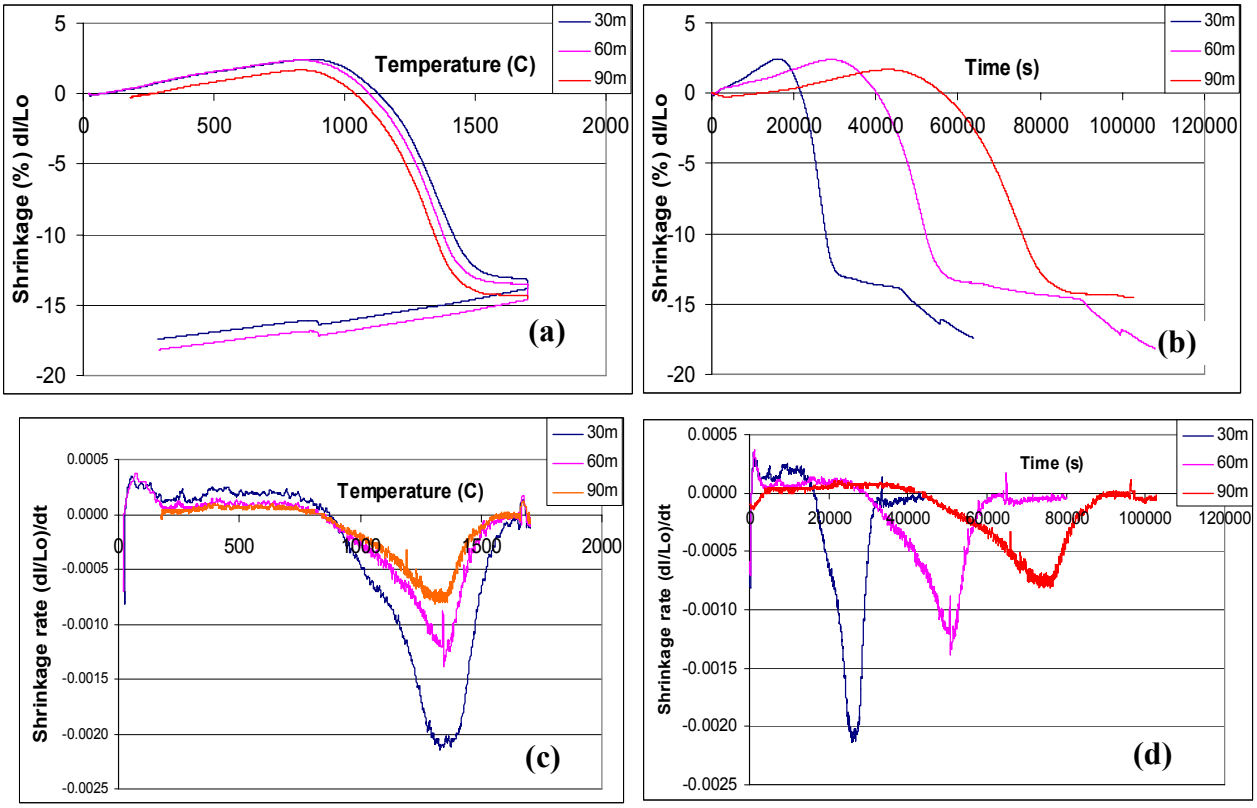

FIG. 1 EFFECT OF PUSHING INTERVAL (HEATING RATE) ON THE SHRINKAGE BEHAVIOUR OF UO_2 PELLETS.

It is found that only one single mechanism is acting during the initial stages of sintering in all the three cases. The final density achieved in the three cases is given in table 1:

TABLE 1: IMMERSION DENSITY MEASURED FOR THE PELLETS SINTERED WITH DIFFERENT PUSHING INTERVAL (HEATING RATE).

SNo	Pushing Interval	Measured Density (g/cc)
1	30 m	10.38
2	60 m	10.62
3	90 m	10.68

As it can be seen from the shrinkage curves and the measured sintered density, the heating rate has a significant influence on the densification process.

Even if the mechanism involved during the densification process in the three cases may be similar, the final density achieved is influenced by the heating rate.

3.1.2 Powder Characteristics: Powder characteristics (morphology, crystallite (domain) size, surface area, O/U ratio etc) are important parameters which influence the shrinkage behaviour of the green compact. In the present study, the powders from two sources with some difference in processing routes were taken.

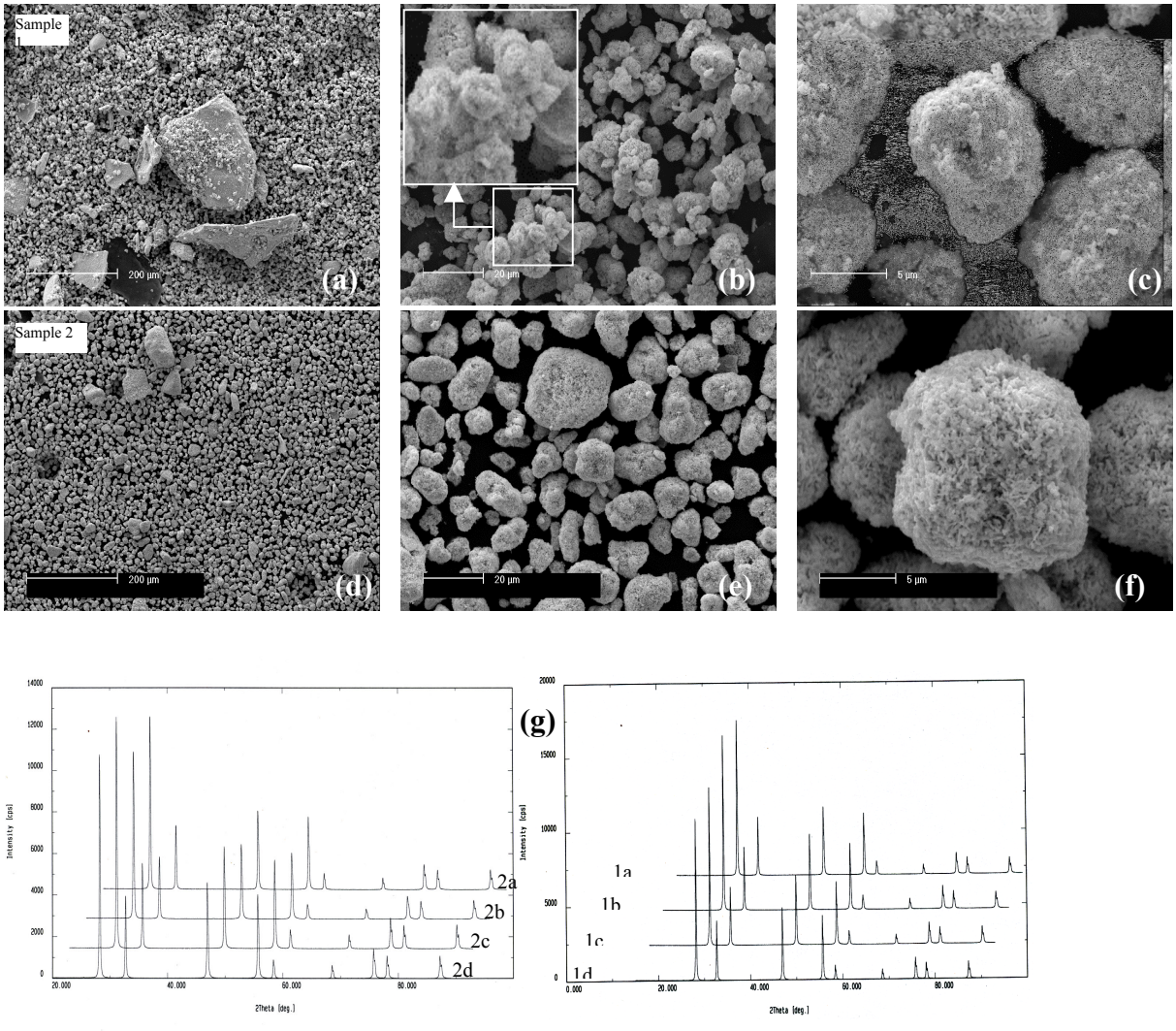

FIG 2. MORPHOLOGY OF POWDER AS SEEN IN SCANNING ELECTRON MICROSCOPE, FOR TWO SAMPLES. SAMPLE 1 (a, b AND c), AND SAMPLE 2 (d, e AND f) AS SEEN AT DIFFERENT MAGNIFICATIONS. (g) XRD SCANS FOR THE TWO SOURCES OF POWDER FOR DIFFERENT LOTS SHOWING SINGLE PHASE NATURE (ONLY UO_2).

It can be seen from fig. 2 (a to c) that the particles from sample 1 consists of agglomerates with some very large size particles (as seen at low magnification 2(a)). The agglomerated particles appear to have pre-sintered during the process of drying of ADU cake, which could be due to use of higher drying temperature for active powder. In the other case of sample-2 (fig.2 (d) to (f)), the particles are very much

rounded shape with individual identity. However, the surface morphology, of the particles from the two routes, as seen at high magnification, was identical. Several samples from the two routes were taken for XRD. The XRD pattern for the two sources showed all the 9 characteristic peaks of UO_2 and was similar. Green pellets samples from these two sources were subjected to dilatometry for study of shrinkage behaviour. Fig. 4 shows the shrinkage behaviour for the powder from the two sources.

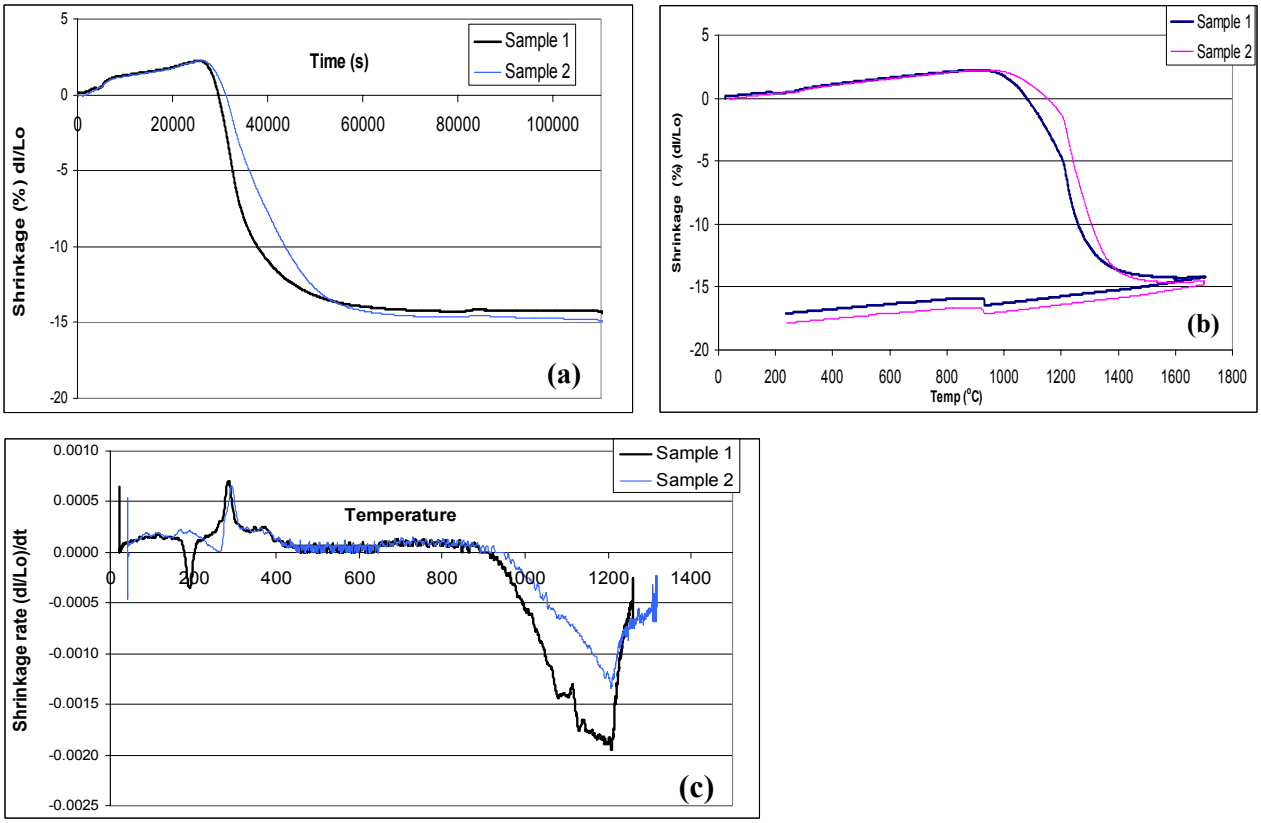

FIG.3 THE SHRINKAGE CURVES FOR UO_2 PELLETS SAMPLE 1 AND 2 SHOWING (a) SHRINKAGE VS TIME (b) SHRINKAGE VS TEMPERATURE AND (c) SHRINKAGE RATE VS TEMPERATURE.

From the shrinkage curves for the two samples it can be seen that

1. Sample 1 has high initial shrinkage rate,
2. For Sample 1, the initial high shrinkage rate sharply falls on reaching a maximum value, while for sample 2 the shrinkage is maintained at the higher temperatures.

It is attempted to explain the differences in the shrinkage behaviour of the two samples with morphological features observed. In case of the sample 1 the high initial sintering rate could be due to active nature of the powder. Generally, during densification the shrinkage and pore removal takes place concurrently. For high densification there should be some driving force left for the final pore removal at the

end stage. High shrinkage rate in case of sample 1 exhausts this driving force faster, leaving no or little force for final pore removal. This can be seen by looking at the shrinkage curve for sample 1, although there is a fast shrinkage at the initial stage but there is a very minimal shrinkage at the end stage. It was observed that the particles have tendency to form agglomerates in case of dried powder for sample 1.

Even though the drying temperature was lower, due to active nature such agglomeration is likely to occur. The active nature not only includes the surface features (external morphology) but it also includes the internal structure of the powder particles. The size of the individual crystallite domains, internal microstrains and density of crystallographic defects are important features of the powder internal structure. These can be quantified by using X-ray diffraction techniques. But, as of now these techniques are under development for UO_2 and hence the results will be reported at a later date.

3.2 Rate Controlled Sintering

A fundamental understanding of the sintering mechanisms operating during the densification process is studied by using dilatometry [7, 8]. Densification behaviour of UO_2 pellets has been studied using a dilatometer in reducing atmosphere.

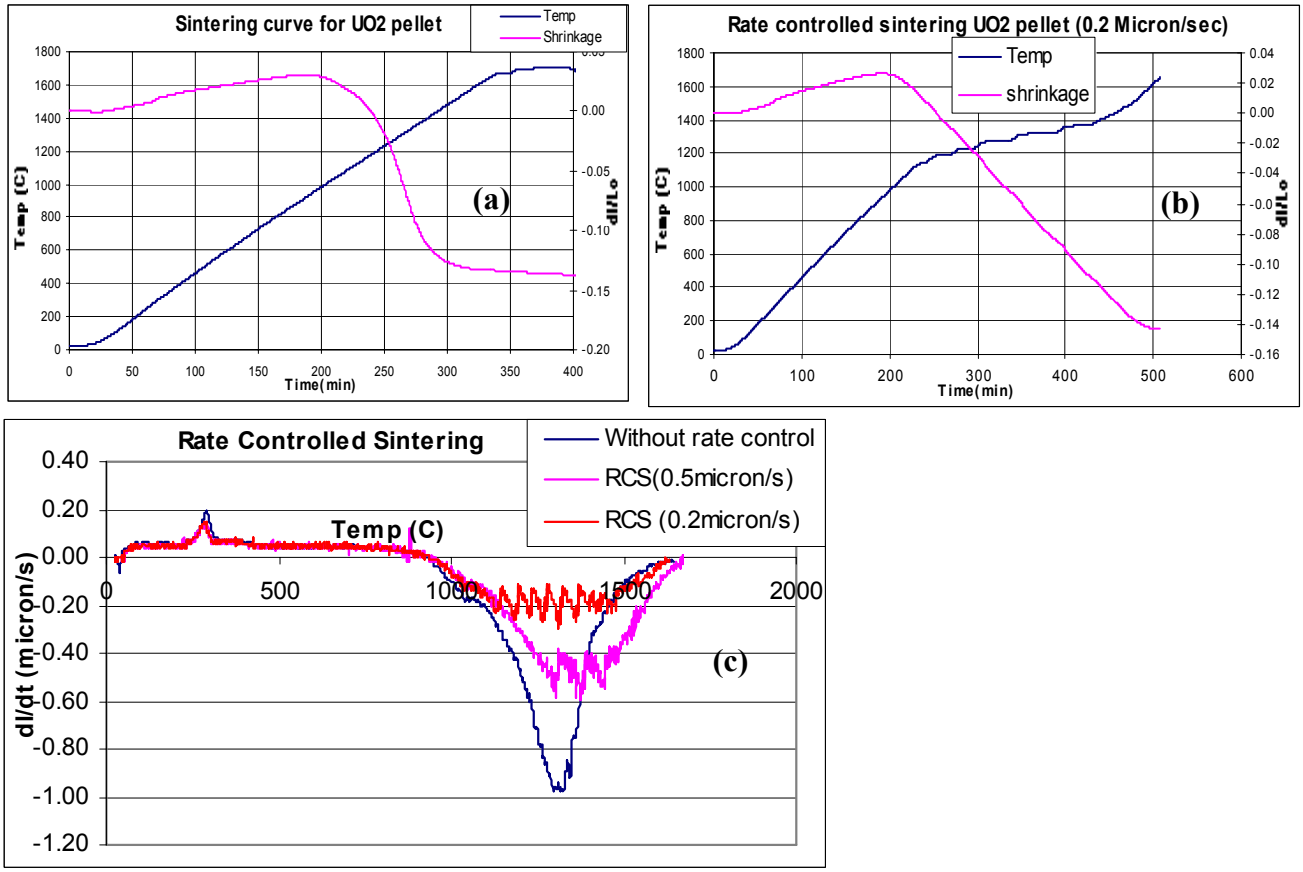

FIG. 4: (a) SHRINKAGE CURVE WITH A CONSTANT HEATING RATE OF 5°C/MIN (b) SHRINKAGE CURVE FOR RATE CONTROLLED SINTERING, AT CONSTANT SHRINKAGE RATE OF 0.2 μm/s AND (c) AND 0.5 μm/s CONSTANT SHRINKAGE

RATES ALONG WITH NON-RATE CONTROLLED CURVE FOR COMPARISON PURPOSE.

The mechanism for the initial stage of sintering was determined using rate controlled sintering (RCS) technique. It was found that the densification during sintering in reducing atmosphere occurs above 900°C. The experimental shrinkage curve is fitted in the empirical equation

$$\Delta l/L_o = Y = [K(T)t]^n \quad (1)$$

where L_o is the initial length of the sample, Δl is the instantaneous change in the length K(T) is Arrhenius constant, t is the time and n is a constant whose value depends on the sintering mechanism. To know the operating mechanisms, value of the sintering rate index 'n' for various sintering mechanisms models is compared with the experimentally obtained value. For such a study, shrinkage is monitored in small isothermal steps in the temperature range of 900 to 1300°C which is possible only in rate controlled sintering. Under such a set-up temperature of the sample is controlled to achieve a fixed shrinkage rate. Using the data from the isothermal steps, the slope of the plot of the $\log\{d(\Delta l/L_o)/dt\}$ against the log(t) is calculated (which is equal to n-1) and from the intercept of these plot.

Fig. 4b shows the temperature profile for the sample when a constant shrinkage rate is set-up with a number of isothermal steps. At these isothermal steps the shrinkage data is used for calculation of sintering rate exponent.

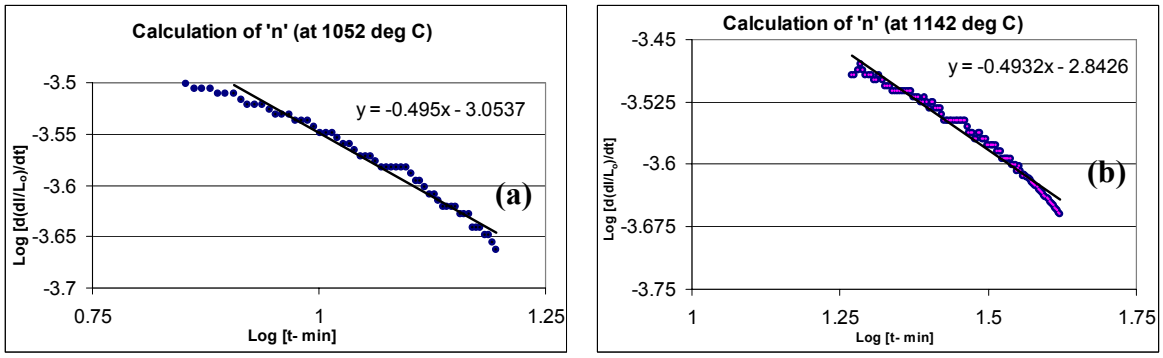

FIG.5: CALCULATION OF SINTERING RATE EXPONENT AND ACTIVATION ENERGY. THE SLOPE OF THE CURVE GIVES THE VALUE OF (n-1) AT (A) 1052°C AND 1142°C (B).

From the above calculation the value of the exponent n was estimated as about 0.5, the literature data for the exponent is very close to that of volume diffusion through grain boundary which is equal to 0.49 [9].

3.3 Master Shrinkage Curve

As seen above, the shrinkage characteristics is influenced by material and process parameters. It is important to evaluate the lots before sintering in large quantities to achieve density within a narrow acceptable range. For this, a sinterability test is practiced in which a small quantity of lot (50 Kg) is sintered for

evaluation of the powder performance. In the present study, an alternative test using dilatometer is carried out simulating production condition. The possibility of using a 'master shrinkage curve' for a given sintering cycle to evaluate the performance of the powder is explored. Comparison of the shrinkage curves for the lots before actual production with the master curve could be used as a screening test for the powder lots in order to predict the sintering behavior, which would be advantageous than the cumbersome sinterability test. The master shrinkage curve was obtained as an average of 3 curves which yielded density in the range of 10.60- 10.66 g/cc. As the shrinkage rate curve gives the maximum information about the shrinkage behaviour the master shrinkage curve was converted to shrinkage rate curve and compared.

In the present experiment, shrinkage curve for three categories of powder were taken namely, acceptable sinter density (10.45 to 10.75 g/cc) low density (>10.45 g/cc) and c) high density > 10.75 g/cc. These categories were made based on the sinter density evaluation of the powder lots made to pellets in large quantity. Fig.6 a, b and c shows the comparison of the master curve with the acceptable, low and high density respectively. Along with these curves the 'difference curves' were also plotted. These curves signify the difference in the master and the sample curve. There appears a good trend, wherein the low and high density material has a distinct difference from the master curve. The master shrinkage curve has onset of shrinkage at 910°C above the coarsening-densification transition temperature determined by Balakrishna et.al [10] indicating that in low density material the mechanisims leading to lower density are operating at much higher temperature (about 1200°C).

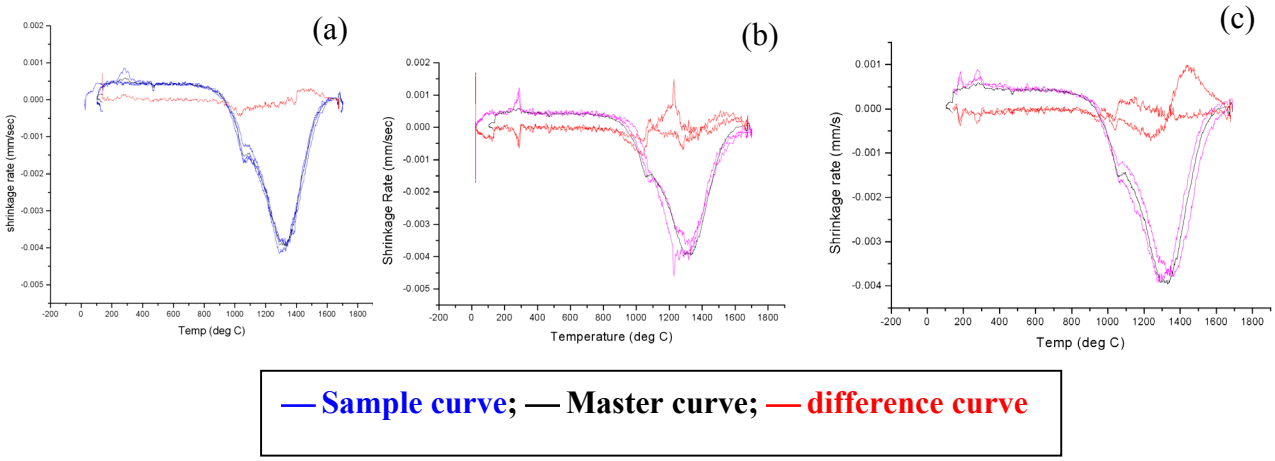

FIG. 6: SHRINKAGE RATE CURVES FOR SAMPLES AND ITS COMPARISON WITH MASTER SHRINKAGE CURVE PLOTTED WITH THE DIFFERENCE IN THE CURVES (A) SAMPLES WITH ACCEPTABLE DENSITY (B) SAMPLES WITH LOW DENSITY (> 10.45 g/cc) AND (C) SAMPLES WITH HIGH DENSITY (>10.75 g/cc)

4.0 CONCLUSIONS

1. The shrinkage characteristics of the UO_2 powder was seen to be affected by the heating rate, which is controlled by the pushing duration in the continuous sintering furnace.
2. Similarly, the morphology of the powder is a key factor and plays a vital role in the shrinkage characteristics of the powder. Very active nature of powder leads to high shrinkage rates initially, but lower density in the end of the cycle.
3. In the initial stages of the sintering of UO_2, the volume diffusion through the grain boundary appears to be mechanisim of the sintering. This was inferred by evaluating the sintering rate exponent calculated by using the rate controlled sintering, which is very close to the literature data for this mode of sintering.
4. A master shrinkage curve has been used to evaluate the sintering characteristics of powder lots. There appears a reasonable distinction for the curves which show poor or very high sintering characteristics when compared with the master curve.

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