4.5 DEVELOPMENT OF MASTER SINTERING CURVE AND SINTERING KINETICS STUDIES ON (Th-U)O$_2$ MOX PELLETS

The sintering parameters of many ceramic products are still decided by the ancient method of trial and error basis. The theory of Master Sintering Curve (MSC) provides a new insight into the sintering phenomena. MSC enables the prediction of the densification behaviour under arbitrary time-temperature excursions with the help of a minimum number of preliminary experiments. The procedure for development of a master sintering curve for AHWR fuel of composition ThO$_2$-3%UO$_2$ is described below:

Theory of Master Sintering Curve

The master sintering curve is derived from the densification rate equation of the combined-stage sintering model. The parameters in the sintering rate equations can be separated into two parts: (a) those related to the microstructure and (b) those related to time and temperature terms. These parts, which are on the opposite sides of the equation, are then related to each other experimentally. The temperature-dependent side of the equation can be represented by

$$\theta = \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt$$  \hspace{1cm} (1)

where $Q$ is the sintering activation energy, $R$ is the gas constant, $t$ is the instantaneous time and $T$ the absolute temperature. The relationship between density $\rho$ and $\theta$ is defined as the master sintering curve. For the construction of MSC, the integral of equation (1) and density should be known.

Activation energy of sintering

For construction of Master sintering curves ($\rho$ versus $\theta$), correct value of activation energy is required which can be available from literature or can be estimated with good precision from $\rho$ versus $\theta$ data. To estimate the activation energy for sintering, firstly, a particular value of activation energy is chosen and $\rho$ versus $\theta$ curves are constructed for each heating rate. If the curves fail to converge, a new value of activation energy is chosen and the calculations are repeated. This procedure continues until all the curves converge and the corresponding activation energy is the true activation energy for sintering. If the correct value of $Q$ is chosen, all of the data converges to a single curve. The best estimate of $Q$ will be the value of the minimum in the plot of mean residual squares versus activation energy.

Experimental

The green pellets of ThO$_2$-3% UO$_2$ for this study were prepared by the conventional powder metallurgy route. The procedure adopted for the fabrication of ThO$_2$-3% UO$_2$ green pellets are as follows:

a) milling of the as-received ThO$_2$ powder in a planetary ball mill
b) mixing/milling of the above milled ThO$_2$ powder with the required quantity of UO$_2$ powder for 4 h in a planetary ball mill with tungsten carbide balls
c) double precompaction of the above mentioned mixtures at 150 MPa
d) granulation of the precompacts
e) final cold compaction of the granulated powder at 300 MPa into green pellets of about 8 mm diameter and 7mm long.

To determine the shrinkage of (Th-U)O$_2$, a push rod type high temperature horizontal dilatometer was used. The dilatometric experiments were carried out using a flow rate of 18 l/h. The heating rate used for the above studies was 6, 12 and 20°C/min. For the determination of activation energy, the density data for ThO$_2$-UO$_2$ compacts obtained from the dilatometric data, and $\theta$ values obtained from the equation (1) are employed. A $\rho$-$\theta$ curve is then constructed for all the heating profiles for a chosen value of activation energy. The mean residual squares for the various values of activation energy have been calculated and the minimum has been found to be for 500 kJ/mol.
From the knowledge of the activation energy, \( \theta \) values are determined using (1) and are plotted against density (p). Such plot (master sintering curve) for ThO\(_2\)-3\%UO\(_2\) has been shown here.

**Discussion**

The following conclusions are drawn from the above study:

The concept of MSC can be used to calculate the activation energy for sintering. The activation energy for sintering for ThO\(_2\)-3\%UO\(_2\) was found to be 500 kJ/mol. The sinterability of powder compacts made from different powders and fabrication procedures under different thermal histories, can be characterized through the master sintering curve. The MSC curve can also be used as an aid to compare the sinterability of different powders and to know the effects of additives, atmosphere and fabrication procedure of sintering.