

Characterization and densification studies on ThO₂–UO₂ pellets derived from ThO₂ and U₃O₈ powders

T.R.G. Kutty^{a,*}, P.V. Hegde^a, K.B. Khan^a, T. Jarvis^a,
A.K. Sengupta^a, S. Majumdar^a, H.S. Kamath^b

^a Radiometallurgy Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

^b Nuclear Fuels Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

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Abstract

ThO₂ containing around 2–3% ²³³UO₂ is the proposed fuel for the forthcoming Indian Advanced Heavy Water Reactor (AHWR). This fuel is prepared by powder metallurgy technique using ThO₂ and U₃O₈ powders as the starting material. The densification behaviour of the fuel was evaluated using a high temperature dilatometer in four different atmospheres Ar, Ar–8%H₂, CO₂ and air. Air was found to be the best medium for sintering among them. For Ar and Ar–8%H₂ atmospheres, the former gave a slightly higher densification. Thermogravimetric studies carried out on ThO₂–2%U₃O₈ granules in air showed a continuous decrease in weight up to 1500 °C. The effectiveness of U₃O₈ in enhancing the sintering of ThO₂ has been established.

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1. Introduction

ThO₂ containing around 2–3% ²³³UO₂ along with ThO₂–3 to 4%PuO₂ is the proposed fuel for the forthcoming Indian Advanced Heavy Water Reactor (AHWR). The AHWR is being developed in India with the specific aim of utilising thorium for power generation since India has vast reserves of thorium and its resource profile needs a closed cycle involving utilisation

of thorium. The currently known Indian thorium reserves amount to 358,000 GWe-yr of electrical energy and can easily meet the energy requirements during the next century and beyond. AHWR is a vertical pressure tube type reactor cooled by boiling light water and moderated by heavy water. It incorporates several advanced passive safety features, e.g., heat removal through natural circulation. The reactor has been designed to produce 920 MW(th) at a discharge burn-up of fuel in excess of 24 MWD/kg U [1].

The goal of this work is to develop mixed thorium–uranium dioxide (ThO₂–UO₂) fuel by powder metallurgy technique using ThO₂ and U₃O₈ powders as the starting material. Generally, large scale production of nuclear fuel pellets is carried out by sintering the green compacts in high temperature in a reducing atmosphere

* Corresponding author. Tel.: +91 22 5505319; fax: +91 22 5505151.

E-mail address: tkutty@magnum.barc.ernet.in (T.R.G. Kutty).

at around 1700 °C [2]. ThO₂ being a very stable oxide, can be sintered in atmospheres such as air, hydrogen, Ar or vacuum. Due to its very high melting point, a sintering temperature as high as 1800 °C is required to attain above 90% theoretical density (TD). But with the addition of suitable additives the sintering of ThO₂ can be carried out at a temperature as low as 1250 °C in air. It is well known that the addition of aliovalent cations accelerates the sintering of ThO₂. The effect of an additive depends mainly on its valency [3]. But the additions of such additives increase the amount of undesired impurities in the fuel pellets. Therefore an attempt has been made in this study to use U₃O₈ as additive instead of the conventional Nb₂O₅ or CaO as the sintering aid for ThO₂.

For nuclear fuel ceramics such as UO₂, it is reported that the diffusion rate is slow under reducing condition and is fast under oxidising condition. Therefore, a change in the sintering atmosphere from reducing to controlled oxidizing conditions is very much advantageous to increase the interdiffusion rates [4–7]. Typical example is the Nikusi process [8] adopted by KWU. Cation mobility increases drastically in hyperstoichiometric oxide because of the large increase in cation vacancy concentration. A low temperature (≤1300 °C) short time sintering has been developed to take advantage of the very high cation mobilities in hyperstoichiometric uranium oxides [9,10]. This process results in large scale savings in energy, time and capital investment [11,12]. Since diffusion is largely dependent on oxygen potential of the sintering atmosphere, it will be worthwhile to determine the effects of a wide variety of atmospheres such as inert (Ar), reducing (Ar–8%H₂) and oxidising (CO₂ and air) atmospheres on the sintering behaviour of ThO₂–U₃O₈ using a dilatometer. So far, studies have not been reported on the above-mentioned composition in such a wide range of atmospheres. Hence, it is felt that the results of this study would be very useful to the manufacturers of such fuels.

The current thrust in nuclear technology is in the area of the development of a proliferation-resistant and environmentally friendly fuel which exhibits higher performance under irradiation [13–15]. A significant reduction in quantity and ‘quality’ of Pu may be achieved by replacing the ²³⁸U fertile component by ²³²Th [16–18]. The other advantages of the use of mixed ThO₂–UO₂ for existing light water reactors (LWRs) are as follows [17]:

- (a) less expensive than the current UO₂ fuel,
- (b) very resistant to nuclear weapons-material proliferation,
- (c) results in a more stable and insoluble waste form, and
- (d) generates less spent fuel per unit energy production.

ThO₂–UO₂ fuel is expected to exhibit better performance during LOCA due to its higher thermal conductivity and lower specific heat capacity and density in comparison to the case of UO₂ fuel for the same conditions. In terms of waste management issues, the Th containing fuel is found to create more ¹²⁹I and ²³⁴U due to the higher amount of ²³³U. However, the U fuel forms more ⁹⁹Tc, ²³⁷Np and ²³⁹Pu and some higher actinides [19–21]. Hence Th containing fuel not only reduces plutonium production but also reduces the isotopes responsible for the high fraction of the dose to the public [22,23]. With this background in mind, a study was undertaken on ThO₂–UO₂ fuel with the following objectives.

1. To fabricate high quality ThO₂–UO₂ pellets from ThO₂ and U₃O₈ powders as the starting materials.
2. To evaluate the shrinkage behaviour of ThO₂–2%U₃O₈ compacts in various atmospheres like Ar, Ar–8%H₂, air and CO₂.
3. To find out the effectiveness of U₃O₈ as a sintering aid instead of conventional ones like CaO or Nb₂O₅.
4. To evaluate the uniformity of uranium distribution in the above pellets after sintering.

2. Experimental

2.1. Preparation of green compacts

The green ThO₂ pellets and ThO₂–2%U₃O₈ pellets for this study were prepared by the conventional powder metallurgy technique. U₃O₈ powder was prepared by suspending the UO₂ particles in boiling water and then bubbling the air continuously through the suspension for about an hour. The suspension is then cooled, filtered to remove the oxidized UO₂ i.e., U₃O₈ particles, which are then further dried in oven to get the final U₃O₈ powder. The O/M ratio of the dried powder was 2.66. XRD pattern of the powder indicates that the crystal structure is orthorhombic. The procedure for the fabrication of ThO₂–2%U₃O₈ green pellets consists of the following steps:

- (a) milling of the as-received ThO₂ powder in a planetary ball mill to break its platelet morphology,
- (b) mixing/milling of the above milled ThO₂ powder with the required quantity of U₃O₈ powder for 4 h in a planetary ball mill with tungsten carbide balls,
- (c) double pre-compaction of the above prepared mixtures at 150 MPa,
- (d) granulation of the pre-compacts, and
- (e) final cold compaction of the granulated powder at 300 MPa into green pellets.

Table 1
Characteristics of ThO₂ and U₃O₈ powders

Property	ThO ₂	U ₃ O ₈
Oxygen to metal ratio	2.00	2.66
Apparent density (g/cm ³)	0.70	1.2
Total impurities (ppm)	<1200	<800
Specific surface area (m ² /g)	1.53	2.15
Theoretical density (g/cm ³)	10.00	8.34
Molecular weight (g/mol)	264	842
Volume (cm ³ /mol U)	26.4	33.613
Volume relative to ThO ₂	1.000	1.273

A few control samples of ThO₂ were also prepared under identical conditions with CaO and Nb₂O₅ as dopants. For this, ThO₂ powder and the required quantity of additive (0.5wt% CaO or 0.25wt% Nb₂O₅) were milled for 4 h in a planetary ball mill with tungsten carbide balls. The concentrations of the dopants to be added depend on its effectiveness in generating lattice defects. They should be added in bare minimum quantities to reduce the amount of impurities in the sintered pellets. The study conducted by authors' laboratory on ThO₂ has shown that best optimum properties (like density, grain size etc.) were obtained with 0.25 wt% Nb₂O₅ and 0.5 wt% CaO. Hence we have adopted these concentrations.

Green density of the compacts was around 67% of the theoretical density. To facilitate compaction and to impart handling strength to the green pellets, 1 wt% zinc behenate was added as lubricant/binder during the last 1 h of the mixing/milling procedure. The green pellets were about 8.15 mm in diameter and around 7 mm in length. The characteristics of the starting ThO₂ and U₃O₈ powders used in this study are given in Table 1.

2.2. Dilatometry

The shrinkage behaviour of pellets of pure ThO₂, ThO₂-2%U₃O₈, ThO₂-0.5%CaO and ThO₂-0.25%Nb₂O₅ was studied using a high temperature horizontal dilatometer (Netzsch, model 402E). The dilatometry was carried out under the following condition:

Table 3
Metallic impurities in the sintered ThO₂ pellet containing 2%U₃O₈

Element	Impurity (ppm)
Na	15
Al	7
Mg	6
Si	<100
Fe	15
Cr	<1
Co	<5
Ni	<1
Mo	<5
W	<50
Cu	1.5
B	<0.6

- force on the sample 0.2 N.
- Gas flow 0.012 m³/h.
- Heating rate 6 °C/min.

The dilatometric data were obtained in the form of curves of dimension against time and temperature. In the push rod type dilatometer, the sample rested between the push rod and a stopper. Length changes were transmitted through the frictionless push rod to an LVDT transducer. The accuracy of the measurement of change in length was within ±0.1 μm. A calibrated thermocouple was placed just above the sample to record the sample temperature. The dilatometric experiments were carried out with four different cover gases, Ar, Ar-8%H₂, CO₂ and air. The impurity contents of the cover gases used in this study are given in Table 2. The selection of the temperature programme was made by a computer via data acquisition system. The shrinkage of a standard sample (POCO graphite, NIST) was measured under identical conditions in order to correct for the differences in shrinkage between the sample holder and the sample. Table 3 gives typical impurity contents of a sintered pellet.

2.3. Characterization

The ThO₂-2%U₃O₈ pellets were characterized by the following techniques.

Table 2
Impurity contents of different sintering atmospheres (volume ppm)

Sintering atmosphere	Oxygen (vppm)	Moisture (vppm)	CO ₂ (vppm)	CO (vppm)	N ₂ (vppm)	Oxides of N ₂ (vppm)	Hydrocarbon (vppm)
Argon	4	4	1	1	10	1	1.5
Argon + 8% hydrogen	4	4	1	1	10	1	2
CO ₂	300–400	10	–	5	50	15	2

Table 4
Density of the sintered ThO₂-2%UO₂ pellets in different atmospheres

Sintering atmosphere	Heating rate (°C/min)	Maximum sintering temperature (°C)	Density (% TD)	Phases present
Ar	6	1600	87.0	Fluorite type fcc
Ar-8%H ₂	6	1650	86.6	Fluorite type fcc
Air	6	1625	95.2	Fluorite type fcc
CO ₂	6	1650	94.4	Fluorite type fcc

- Thermogravimetry
- XRD
- Density
- Metallography
- SEM
- EPMA

The O/M ratio and XRD of all the samples covered in this study was evaluated after sintering. The O/M ratio was measured thermogravimetrically and the phase content was estimated using X-ray diffractometry and metallography. The X-ray diffraction patterns of the pellets were obtained by using CuK_α radiation and graphite monochromator. The green density was measured geometrically and sintered density was determined following the Archimedes method. Table 4 gives typical values of their density. The phases present, heating rate used for the present study and maximum sintering temperature employed are also shown in Table 4. For metallography, the pellets sintered in Ar-8%H₂ and air were mounted in Araldite and ground using successive grades of emery paper. The final polishing was done using diamond paste. The pellets were removed from the mount by dissolving the mount in acetone and then etched thermally by holding them at 1600°C for 4h in air. The grain size was determined by the intercept method. The microstructure was then characterized by SEM. The uranium distribution in the sintered pellet was determined by EPMA.

3. Results

Fig. 1 shows the shrinkage behaviours of ThO₂-2%U₃O₈ pellets in Ar, Ar-8%H₂, CO₂ and air. The $d(l/l_0)$ (l_0 : initial length) versus temperature curves can be classified into two distinct groups which show different behaviours. The curves for Ar and Ar-8%H₂ atmospheres almost coincide while those for oxidizing atmospheres like air and CO₂ also coincide but lie below the former at temperatures above 600°C. Fig. 2 shows shrinkage rate versus temperature for the above composition. From the above figures, it is clear that the onset of shrinkage occurs at around 1000°C in Ar for ThO₂-2%U₃O₈ pellets. The maximum shrinkage rate occurs at around 1200°C for both the air and CO₂ sintered

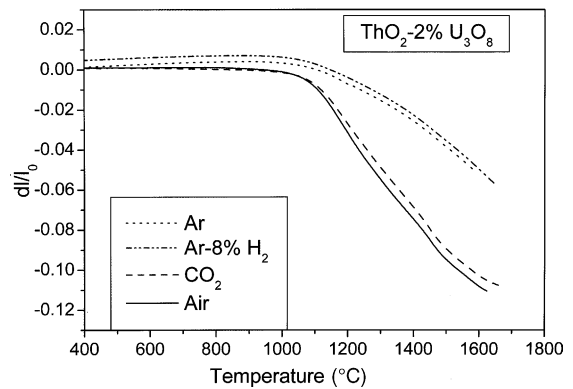


Fig. 1. Shrinkage curves for ThO₂-2%U₃O₈ pellets obtained in Ar-8%H₂, Ar, CO₂, and air atmospheres.

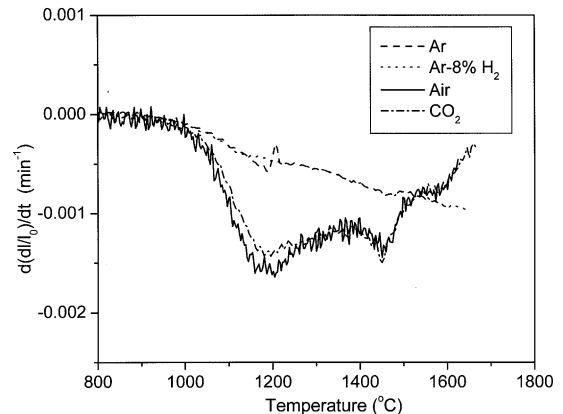


Fig. 2. Shrinkage rate of ThO₂-2%U₃O₈ pellets obtained in Ar-8%H₂, Ar, CO₂, and air atmospheres plotted against temperature.

samples. It is evident from the shrinkage rate curves that the ThO₂-2%U₃O₈ samples behave identically in both air and CO₂ atmospheres. The onset of shrinkage occurs in air and CO₂ at a much lower temperature (900°C) than that found for Ar and Ar-8%H₂. Among the four atmospheres covered in this study, the best in terms shrinkage is air. The shrinkage rate curves for Ar and Ar-8%H₂ are smooth while those for CO₂, especially for air, show many oscillations especially in the

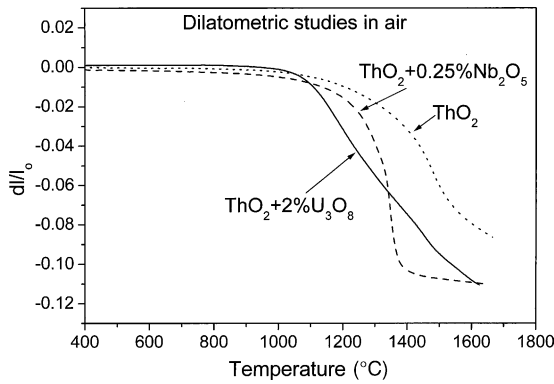


Fig. 3. Shrinkage curves for ThO_2 -0.25% Nb_2O_5 and ThO_2 -2% U_3O_8 obtained in air. The shrinkage curve for pure ThO_2 is also shown.

temperature range of 800–1600 $^{\circ}\text{C}$. This may be due to some micromechanisms occurring in the pellet during the sintering. It is probable that U_3O_8 may be getting reduced to a series of lower oxide. However, further work is required to confirm this. Similar observations were noted for PuO_2 when sintered in Ar -8% H_2 [24,25].

Fig. 3 shows the shrinkage behaviours of pure ThO_2 and ThO_2 -0.25% Nb_2O_5 as dopant in air. For comparison, the shrinkage curve of ThO_2 -2% U_3O_8 in air is also shown in the figure. The effect of dopants on shrinkage is clear: the onset of sintering shifts towards to the lower temperature on the addition of a dopant. For pure ThO_2 , the sintering commences only at temperatures above 1100 $^{\circ}\text{C}$, while it starts at about 960 $^{\circ}\text{C}$ for the ThO_2 -2% U_3O_8 pellet. Fig. 4 shows shrinkage rate for the above compositions as a function of temperature. The maximum shrinkage rate for pure ThO_2 occurs at 1480 $^{\circ}\text{C}$ while that occurs at a much lower temperature (1345 $^{\circ}\text{C}$) for ThO_2 -0.25% Nb_2O_5 .

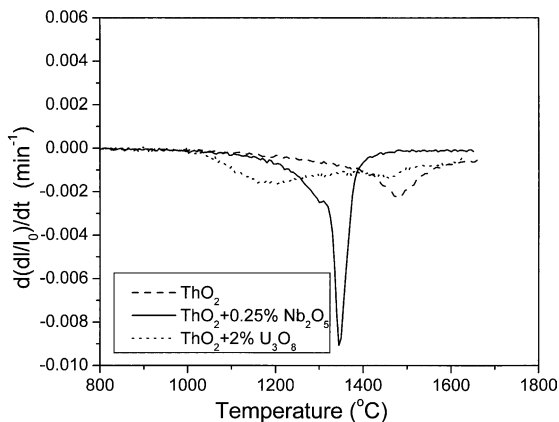


Fig. 4. Shrinkage rate versus temperature curves for ThO_2 , ThO_2 -0.25% Nb_2O_5 and ThO_2 -2% U_3O_8 pellets obtained in air.

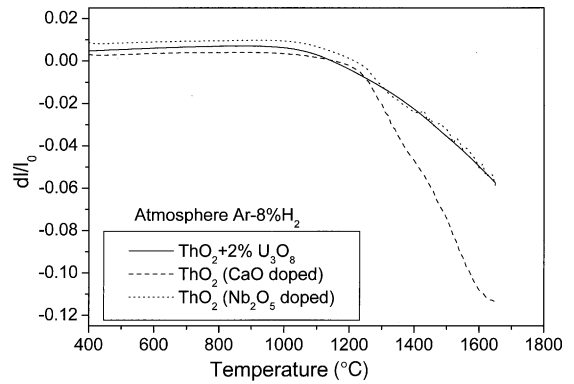


Fig. 5. The effect of dopants on the shrinkage behaviours of ThO_2 -0.5% CaO , ThO_2 -0.25% Nb_2O_5 and ThO_2 -2% U_3O_8 in Ar -8% H_2 .

It is possible to compute the shrinkage levels at two different temperatures from Fig. 3 and also the effect of additives on the shrinkage at a particular temperature. At 1400 $^{\circ}\text{C}$, the shrinkage is 3% for pure ThO_2 , 7.5% for ThO_2 -2% U_3O_8 and 11% for ThO_2 -0.25% Nb_2O_5 . The effect of Nb_2O_5 is very significant especially in the temperature range of 1300–1400 $^{\circ}\text{C}$, and above 1400 $^{\circ}\text{C}$, the rate of shrinkage decreases drastically with increase in temperature. On the other hand, the shrinkage rate is almost constant for ThO_2 -2% U_3O_8 from 1100 to 1600 $^{\circ}\text{C}$.

Fig. 5 compares the shrinkage behaviour of ThO_2 -2% U_3O_8 and ThO_2 containing different additives in Ar -8% H_2 atmosphere. The shrinkage is almost identical for both ThO_2 -2% U_3O_8 and ThO_2 -0.25% Nb_2O_5 . ThO_2 -0.5% CaO , showed the best behaviour in reducing atmosphere yielding a maximum shrinkage of $\sim 12\%$ at 1600 $^{\circ}\text{C}$. In comparison the shrinkage for both ThO_2 -2% U_3O_8 and ThO_2 -0.25% Nb_2O_5 are about half ($\sim 6\%$) at the same temperature.

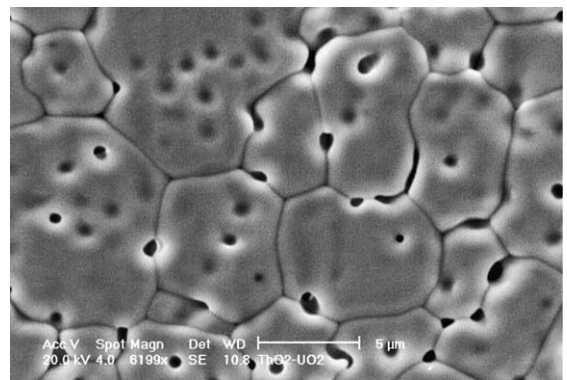


Fig. 6. Microstructure of a ThO_2 -2% U_3O_8 pellet. This pellet was sintered in air and etched thermally.

Fig. 6 shows the microstructure of a $\text{ThO}_2\text{-}2\%\text{U}_3\text{O}_8$ pellet sintered in air. The grain size is uniform. The average grain sizes are 3.0 and 3.75 μm for the pellets sintered in $\text{Ar-}8\%\text{H}_2$ and air atmospheres respectively. The EPMA data show that uranium distribution is uniform for these samples.

The significant observations are summarized below.

1. Among the four atmospheres, Ar, $\text{Ar-}8\%\text{H}_2$, air and CO_2 , the best atmosphere in terms shrinkage was found to be air.
2. The onset of sintering commenced at a temperature which is about 100–120 °C lower in oxidizing atmosphere than in the reducing and inert atmospheres.
3. The maximum shrinkage rate was found to occur at around 1200 °C for both air and CO_2 sintered samples.
4. A large number of oscillations appeared in the shrinkage rate curves for pellets sintered in air.

4. Discussion

From the above results, it was clear that high density $\text{ThO}_2\text{-UO}_2$ pellets could be fabricated from $\text{ThO}_2\text{-U}_3\text{O}_8$ green compacts without the addition of any dopants or sintering aids. The U_3O_8 enhanced the sintering of ThO_2 compacts and the degree of enhancement depended upon the sintering atmosphere. At 1300 °C, in air, the shrinkage was just under 2% for pure ThO_2 , but for the same temperature, it was about 4% and 5.5% respectively for $\text{ThO}_2\text{-}0.25\%\text{Nb}_2\text{O}_5$ and $\text{ThO}_2\text{-}2\%\text{U}_3\text{O}_8$ (see Fig. 3). These results are very important for the large scale fabrication of $\text{ThO}_2\text{-UO}_2$ sintered pellets since this procedure will lead to large scale savings in money since no costly cover gases like Ar or Ar-H_2 are required. Normal air is used as the cover gas. Also costly furnaces with heating elements and sintering boats made of Mo or W are not required.

Solid state sintering is a complex process divided into three stages in which different mechanisms may be operative. The details of the theory of sintering are given elsewhere [26–38]. ThO_2 is the only stable oxide of Th–O system in the condensed state and it has very little non-stoichiometry compared to UO_2 . Th^{4+} is the only valence state of thorium [39–41]. U_3O_8 is one of the most kinetically and thermodynamically stable forms of uranium [6,42,43]. Although U_3O_8 is a stable oxide of uranium at room temperature it dissociates into UO_2 above 1100 °C when heated in air or inert gas like Ar. U_3O_8 can be completely reduced to UO_2 when heated in pure H_2 at about 700 °C [44–46]. Hund and Niessen [47] have studied the entire range of $\text{ThO}_2\text{-U}_3\text{O}_8$ system and reported the presence of U_3O_8 phase in addition to the solid solution for the higher U_3O_8 compositions. But for the composition containing lower U_3O_8 content, a single phase

structure has been reported. The significance of U_3O_8 addition for enhancing sintering, especially in UO_2 , has discussed by many authors. Chevrel et al. [48] indicated that the composition of $\text{UO}_{2.25}$ appeared to be the most appropriate for the low temperature sintering which is obtained by the addition of U_3O_8 powder to UO_2 . Harada [49] suggested to adjust the oxygen partial pressure to the boundary between single phase UO_{2+x} and $\text{UO}_{2+x}\text{-U}_3\text{O}_{8-z}$. It is reported that in solid state the solubility of U_3O_8 in ThO_2 is negligible [50,51]. With this background in mind, we will analyze the shrinkage behaviours of $\text{ThO}_2\text{-U}_3\text{O}_8$ compacts in various atmosphere covered in this study.

4.1. Ar

The densification behaviour of $\text{ThO}_2\text{-U}_3\text{O}_8$ in Ar has been found to be similar to that in $\text{Ar-}8\%\text{H}_2$. At all temperatures, shrinkage was found to be marginally larger for Ar atmosphere. Since ThO_2 always exists as stoichiometric ThO_2 and UO_2 does not exist as UO_{2-x} , the only possible deviation from stoichiometry for $\text{ThO}_2\text{-UO}_2$ system is to exist as MO_{2+x} . If U_3O_8 is reduced to $\text{UO}_{2.00}$ at the sintering temperature, then the defect concentration in $\text{ThO}_2\text{-UO}_2$ pellets will be very small and the driving force for sintering will be less and therefore sintering will be retarded. The present does not indicate this, which means that U_3O_8 has not been fully reduced to $\text{UO}_{2.00}$ at the sintering temperature.

To confirm this hypothesis thermogravimetry has been carried out on $\text{ThO}_2\text{-U}_3\text{O}_8$ in Ar and the resulting thermogram is given in Fig. 7. Here the percentage of weight change is plotted against temperature when the powder of $\text{ThO}_2\text{-U}_3\text{O}_8$ sample was heated in Ar at a heating rate of 6 °C/min. The initial weight loss up to 400 °C is due to the evaporation of moisture and the binder. It is evident that even at 1400 °C the loss in weight

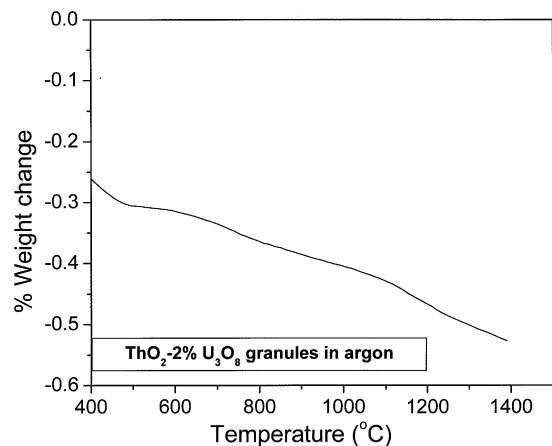


Fig. 7. Weight change obtained by thermogravimetry for $\text{ThO}_2\text{-}2\%\text{U}_3\text{O}_8$ powder heated in Ar atmosphere.

has not been completed indicating that U_3O_8 still exists as UO_{2+x} at this temperature. Since D^U is proportional to x^2 [52], an appreciable amount of sintering has taken place in Ar atmosphere.

4.2. Ar–8% H_2

In Ar–8% H_2 , the shrinkage behaviour of ThO_2 – U_3O_8 was found to be slightly inferior to that in Ar. Many authors [53–59] have studied the reduction of U_3O_8 to UO_2 in H_2 atmosphere. The rate controlling step in reduction of U_3O_8 in H_2 , was absorption of H_2 molecule on the oxide surface [57]. The rate equation can be expressed as [58]:

$$dF/dt = 7.65 \times 10^8 \times (PA/T^{3/2}) \exp(-27,700/RT), \quad (1)$$

where F is the fraction remaining to be reduced in t seconds, P is the H_2 partial pressure and A is the specific area.

Recently, Perrin et al. [59] have studied in detail the reduction of U_3O_8 into UO_2 by hydrogen. They found that the overall transformation proceeded through three successive stages. Firstly the oxygen stoichiometry of U_3O_8 was changed into U_3O_{8-x} ($x = 0.2$). This was followed by the transformation of U_3O_{8-x} into U_4O_9 . Finally, the reduction of U_4O_9 to UO_2 occurred. The first stage was controlled by a surface reaction step. In the second stage, the rate-limiting step for the inward growth of U_4O_9 was the reactive desorption of water at the surface of the particles. In stage three, a similar rate-limiting step was assumed for the growth of UO_2 from U_4O_9 .

It has been reported that U_3O_8 powder can be completely reduced to UO_2 in hydrogen even at low temperatures as low as 480 °C. While it takes only about 15 min at 575 °C for the full conversion of U_3O_8 to UO_2 , it takes around 2 h at 479 °C for the completion of the reaction [58]. This means that U_3O_8 present in ThO_2 – U_3O_8 compacts of present study will be reduced to UO_2 at around 600 °C which suggests that ThO_2 – U_3O_8 will become ThO_2 – UO_2 . Since no dopants are included in this compact, sintering will be retarded as ThO_2 and UO_2 are present as perfect stoichiometric compounds. But the present results are to the contrary and the sintering has been enhanced by the addition of U_3O_8 in Ar–8% H_2 atmosphere. The onset of sintering occurs at around 1020 °C. This confirms that U_3O_8 is not fully reduced to UO_2 at this temperature, but remains as UO_{2+x} . This observation is in agreement with the fact that the rate of reduction of U_3O_8 in Ar–8% H_2 atmosphere is surface controlled. It may be possible to reduce U_3O_8 to $UO_{2.00}$ in Ar–8% H_2 atmosphere even at 700 °C if it is in powder form. Since in this study, we used a green pellet having around 67% TD, the reduction of U_3O_8 to UO_2 could not be completed since the gas

would have to permeate through the dense mass of pellet. The reduction might have therefore occurred only on a few surface layers but the inner layers still remained as UO_{2+x} . Thus the presence of higher concentration of oxygen interstitials resulted in large shrinkage.

4.3. Air and CO_2

This study shows that air is the best atmosphere for sintering of ThO_2 – U_3O_8 compacts. A density of ~95% TD is obtained in air. This again shows that U_3O_8 has not been fully reduced to stoichiometric $UO_{2.00}$ on heating in air even at 1600 °C. To confirm this, thermogravimetry of ThO_2 – U_3O_8 has been carried out in air up to 1500 °C and the resultant thermogram is given in Fig. 8. The decrease in weight up to 400 °C is due to the evaporation of moisture and burning out of binder. From 700 °C to 1500 °C, the weight loss is gradual and continuous. Even at the highest temperature, the weight loss is not complete indicating that U_3O_8 is not fully reduced to stoichiometric $UO_{2.00}$.

Ackermann and Chang [60] observed that increasing the temperature at constant oxygen (0.21 atm) pressure allowed U_3O_8 to become non-stoichiometric (U_3O_{8-z}). The maximum temperature for stoichiometry at 0.21 atm of O_2 is determined to be 600 °C, in agreement with Cordfunke and Aling [61] and Rodriguez et al. [62]. The general trend of these measurements agrees with the non-stoichiometric behaviour above 600 °C in air. For higher oxidation temperatures, the true final composition of the U_3O_{8-z} oxide is determined by the following relation [44]:

$$O/U = 1.3752 + 0.0046875T - 6.1855 \times 10^{-6}T^2 + 3.5194 \times 10^{-9}T^3 - 7.3925 \times 10^{-13}T^4, \quad (2)$$

where T is $600 < T < 1223$ °C.

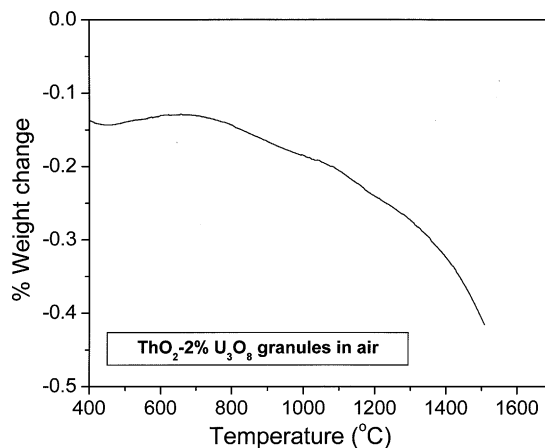


Fig. 8. Weight change obtained by thermogravimetry for ThO_2 –2% U_3O_8 powder when heated in air.

The O/U values of U_3O_{8-z} oxide at 1000, 1100 and 1200 °C are calculated 2.637, 2.633 and 2.627 respectively. This means that on increasing the temperature, there is a considerable amount of deviation from stoichiometry generating more point defects. As the defect concentration increases, the driving force for sintering also increases [63,64,3]. It can be seen from Fig. 1, the maximum shrinkage rate occurs at around 1200 °C, which is in agreement with the above results. In terms of defects, U_3O_8 phase has not been studied as extensively as UO_2 . The defect structures of substoichiometric U_3O_8 at lower temperature and or high $p(O_2)$ appear to be randomly distributed doubly charged oxygen vacancies. However at high temperature and or low $p(O_2)$ complex defect structures appear. Chervel et al. [48] have shown that the decomposition of U_3O_8 produces a network of fine pores enabling the samples richer in U_3O_8 to maintain high specific area at equivalent densification levels. The presence of high specific area for U_3O_8 containing samples constitutes a reserve of additional energy for sintering. Self-diffusion measurements of U in U_3O_8 have been carried out by Glasser Leme and Matzke [65] who reported an activation energy of for uranium migration of 2.4 eV by applying a thin layer of ^{233}U and observing the penetration profile following different annealing steps. This activation energy is much less than that for the self-diffusion of uranium in UO_2 (5.6 eV) [5]. Hence diffusion is expected to take place much faster in U_3O_8 phase.

Thermogravimetric studies carried out on U_3O_8 powder at authors' laboratory show that U_3O_8 powder cannot be reduced to stoichiometric UO_2 in air even on isothermally holding the powder at 1400 °C for 3 h. The oxygen potential of the furnace will not allow U_3O_8 to reduce easily to stoichiometric UO_2 . XRD evaluation on $ThO_2-U_3O_8$ pellets sintered in air at 1400, 1500 and 1600 °C showed only single phase. The detailed microstructural analysis on above pellets did not show any evidence of unreacted U_3O_8 . From the above findings, one can conclude that the overall densification of the $ThO_2-U_3O_8$ compacts is probably caused by the following sequence of events:

1. formation of defective U_3O_{8-z} structure,
2. decomposition of U_3O_{8-z} to UO_{2+x} ,
3. solid solution formation between ThO_2 and UO_{2+x} , and
4. sintering of $(Th-U)O_{2+x}$ solid solution.

5. Conclusions

High density ThO_2-UO_2 pellets have been fabricated by powder metallurgy route using ThO_2 and U_3O_8 powders as the starting materials. The densification behaviour of ThO_2 containing around 2% U_3O_8

was evaluated using a high temperature dilatometry in four different sintering atmospheres Ar, Ar–8% H_2 , CO_2 and air. The sintered pellets were characterized in terms of uranium distribution and grain size and the following conclusions were drawn:

- (a) Air was found to be the best medium for sintering among the different atmospheres covered in this study.
- (b) For Ar and Ar–8% H_2 atmospheres, the densification was found to be slightly higher in Ar.
- (c) Thermogravimetric studies carried out in Ar on $ThO_2-2\%U_3O_8$ granules showed a continuous decrease in weight even at 1400 °C. Weight loss studies in air for these granules up to 1500 °C indicated that U_3O_8 was not reduced to stoichiometric UO_2 even at that temperatures.
- (d) The reduction of U_3O_8 in H_2 was probably controlled by the rate of reaction at the surface of the oxide particles and the reaction rate depended upon the green density of the pellet.
- (e) Addition of small quantities of U_3O_8 to ThO_2 enhanced sintering and high quality ThO_2-UO_2 pellets could be made without the use conventional dopants like CaO and Nb_2O_5 thus reducing the impurity level in the pellets.

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