12th International Conference on CANDU Fuel
Holiday Inn Kingston-Waterfront
Kingston, Ontario, Canada, 2013 September 15-18th

METALLURGICAL STRUCTURE MODIFICATION OF UO_2 PELLET DURING SINTERING - EXPERIENCE AT NFC, HYDERABAD, INDIA

N.Santra*, T.K.Sinha, A.K.Singh, S.Sairam, Smt Sheela and N.Saibaba

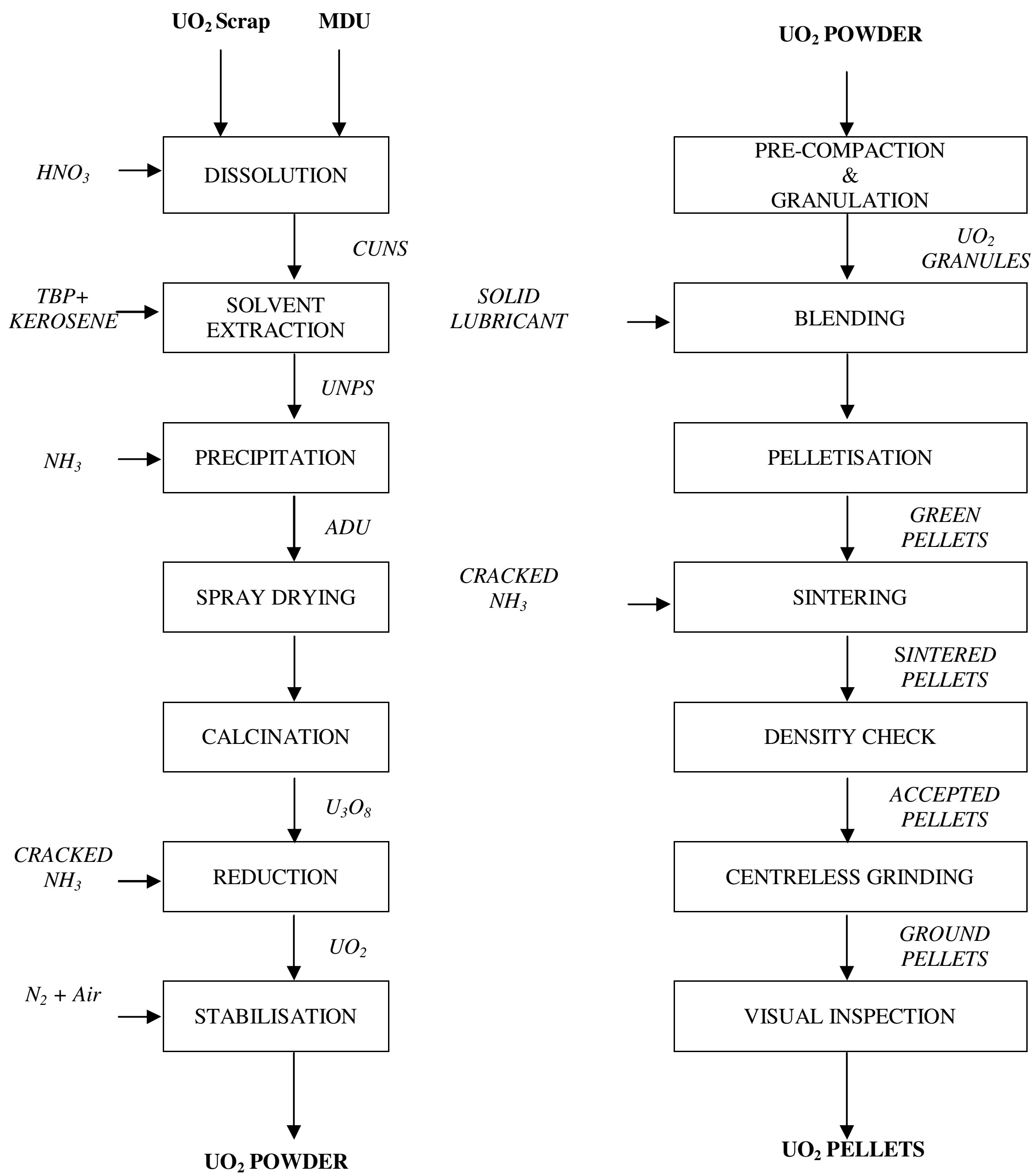
Nuclear Fuel Complex,
Dept. of Atomic Energy,
Govt. of India, Hyderabad
*santra@nfc.gov.in

ABSTRACT: Nuclear Fuel Complex (NFC), Department of Atomic Energy (DAE) produces UO_2 fuel pellets by powder compaction, high temperature sintering followed by centreless wet grinding method from the stabilized UO_2 powder generated through ADU-route. Enhancement of fuel burn up of the Indian PHWRs becomes very important in order to effectively utilize the fuel to the maximum extent inside the reactor. Burn up is mainly limited by increased fission gas release from the fuel during reactor operation. Without introducing much change in the design, rate of release of fission gas can be reduced through enlargement of UO_2 grain size. In Powder Metallurgical (PM) route of fuel fabrication, trials were taken by doping various oxide powder additives like TiO_2, Al_2O_3, SiO_2, Nb_2O_5 and Cr_2O_3. The dopant normally goes into the solid solution of parent matrix during sintering at 1700^0C and thus enhance the rate of diffusion. Aliovalant dopant can alter the defect chemistry of the parent material either by creating vacancy or interstitial. It is apparently understood that the combination of above mechanisms are responsible for structural modification of UO_2. Hence selection of dopant remains largely empirical. It has been observed at NFC Hyderabad that the Cr_2O_3 is the most suitable for achieving average UO_2 grain size of about 70 micron and 98%TD of the sintered pellet. The paper discusses about the various experimental trials, sintered densities, metallographic examination, effect of different quantities, analysis and result obtained thereof:

Introduction

Ceramic uranium dioxide (UO_2) in the form of cylindrical sintered pellets are widely used as nuclear fuel material for power generation all over the world. Quality specification is very stringent in terms of fuel density and integrity for the natural UO_2 pellet used in Indian PHWR's. Effective utilization of nuclear fuel inside the reactor is of prime importance w.r.t fuel burn up and to avoid frequent refueling in the reactor. Fission product gases like Cesium (Cs), Tellurium (Te), Iodine (I) etc generates from the fuel lattice during reactor operation. They are corrosive in nature and once release from the fuel matrix, come into contact with Zr-alloy clad and corrode them by stress corrosion cracking (SCC). Fuel assembly needs to be removed from the reactor prematurely with partial utilization of fissile materials. Retention of fission gases may be possible by the modification of the microstructure of pellets. An enlarged UO_2 grain is expected to retain more fission gases over a larger period of time inside the reactor. Introduction of optimized quantity of suitable sintering aid can promote grain growth and density during high temperature sintering in reducing cracked ammonia atmosphere.

The process flow sheet for the production of UO_2 powder and pellets at NFC :-

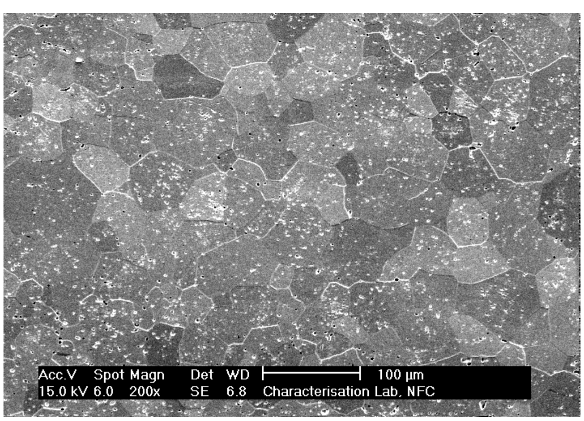


1. Experimental method

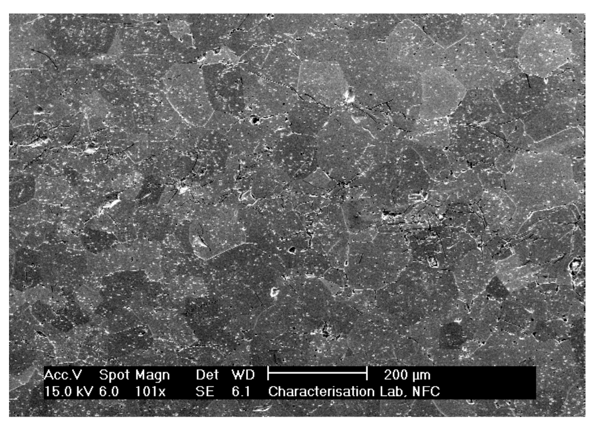
Five categories of sintering aids in the form of ceramic oxide powder additives viz. Nb_2O_5, Al_2O_3, TiO_2, Cr_2O_3 and SiO_2 were selected for the trial with ADU-ex UO_2 powder. The median size of the UO_2 powder agglomerate is about 12-14 micron. The initial O/U ratio of the powder was 2.045 and BET specific surface area was 2.9-3.1 m^2/g. The additives are incorporated in UO_2 granules which were produced in pre-compaction of as received UO_2 powder at about 80-100 MPa pressure to make the powder free flowable for final compaction. These powders were added very less quantity so are called as powder dopants. They were mixed thoroughly with UO_2 powder granule in varying quantities of 0.2wt%, 0.3wt%, 0.4wt%, and 0.5wt% for each category of blend. Quantities are chosen in view that the optimum results should come with the lowest quantity dopant addition. Total twenty numbers of blends were prepared with the above combination taking the same precipitation lot of ADU-ex UO_2 powder in order to avoid variability in UO_2 powder characteristics. Homogenization of additive mixing were ensured by preparing master blend at first with highest quantity of dopant and then making dilution as per the various percentages required for the trials. Powder blends were compacted in double acting die compaction with admixed solid lubricant (0.3wt%) at a pressure of about 275-300 MPa to obtain green density in the range of 52-54%TD as in the regular production. Pellets were sintered in high temperature (1700ºC) continuous pusher type sintering furnace having six different temperature zones along with regular production of conventional nuclear grade UO_2 pellets without any dopants for comparison. Soaking period of 9-10 hrs was ensured at temperature 1700°C. Cracked ammonia atmosphere were maintained inside the furnace as reducing atmosphere. All the other parameters of powder compaction and sintering were maintained same as in the regular commercial production. The sintered pellet samples were selected randomly for sintered densities and metallographic examination. Pellet samples were cut, polished and etched with 10% H_2SO_4 + 90% H_2O_2 solution to reveal the microstructure in SEM. Repeated trials were carried out with changing the lot number of ADU-ex UO_2 powder keeping the other parameters in same condition. Chemical compositional analysis of sintered pellets were carried out for confirming homogenization, presence of additives and calculation for neutron absorption factor in the reactor.

2. Microstructures

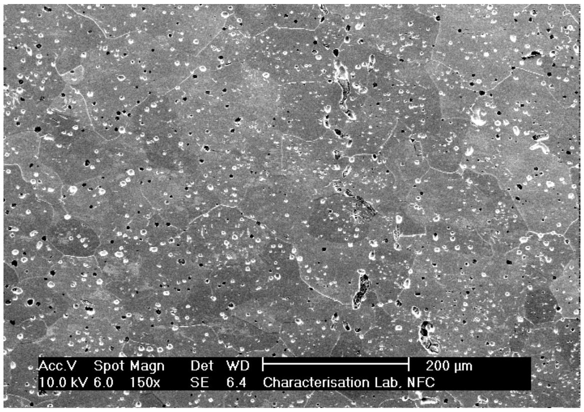
SEM photo micrographs for the pellets having two different quantities lowest 0.2 wt% and the highest 0.5 wt% of dopant in each category are analyzed here for grain size measurement.



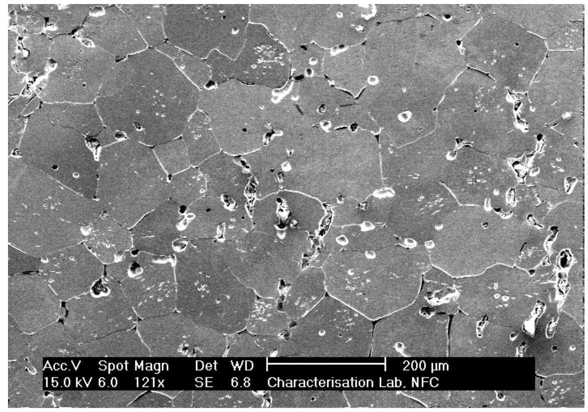
0.2 wt% Cr_2O_3



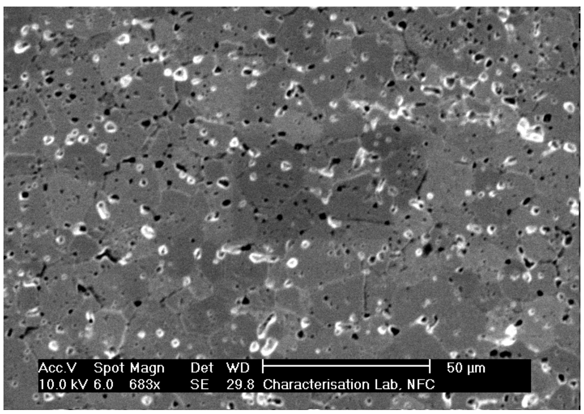
0.5 wt% Cr_2O_3



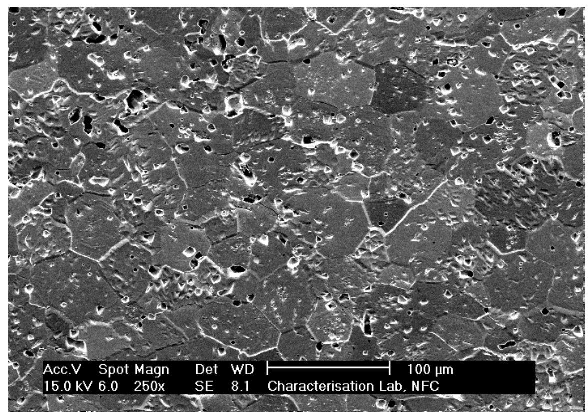
0.2 wt% TiO2



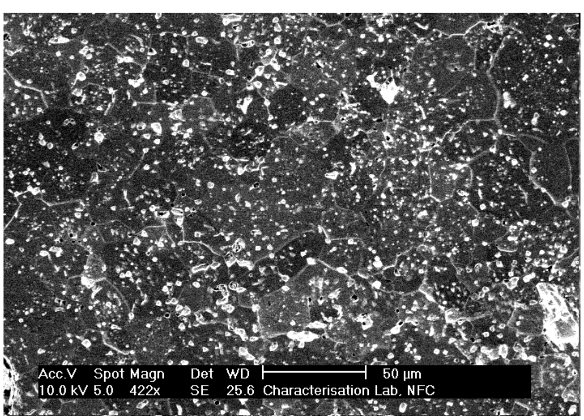
0.5 wt% TiO2



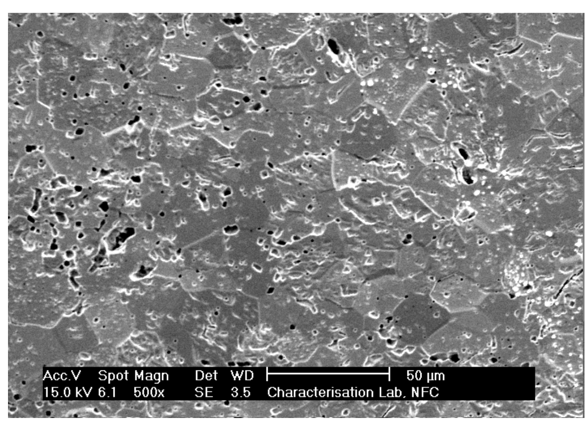
0.2 wt% Nb_2O_5



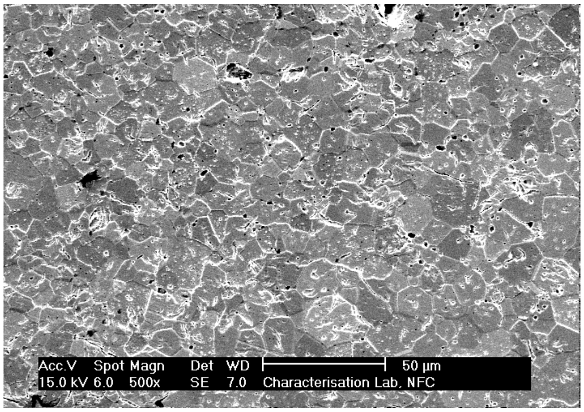
0.5 wt% Nb_2O_5



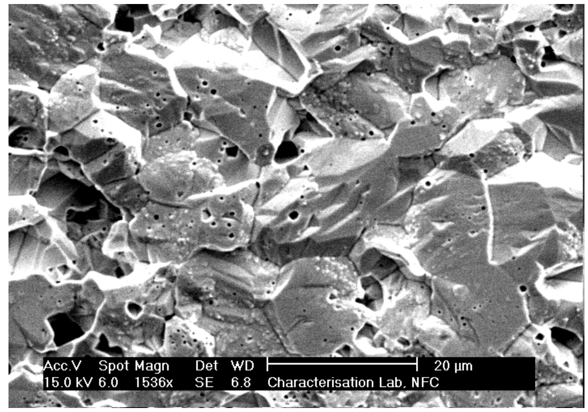
0.2 wt% Al_2O_3



0.5 wt% Al_2O_3



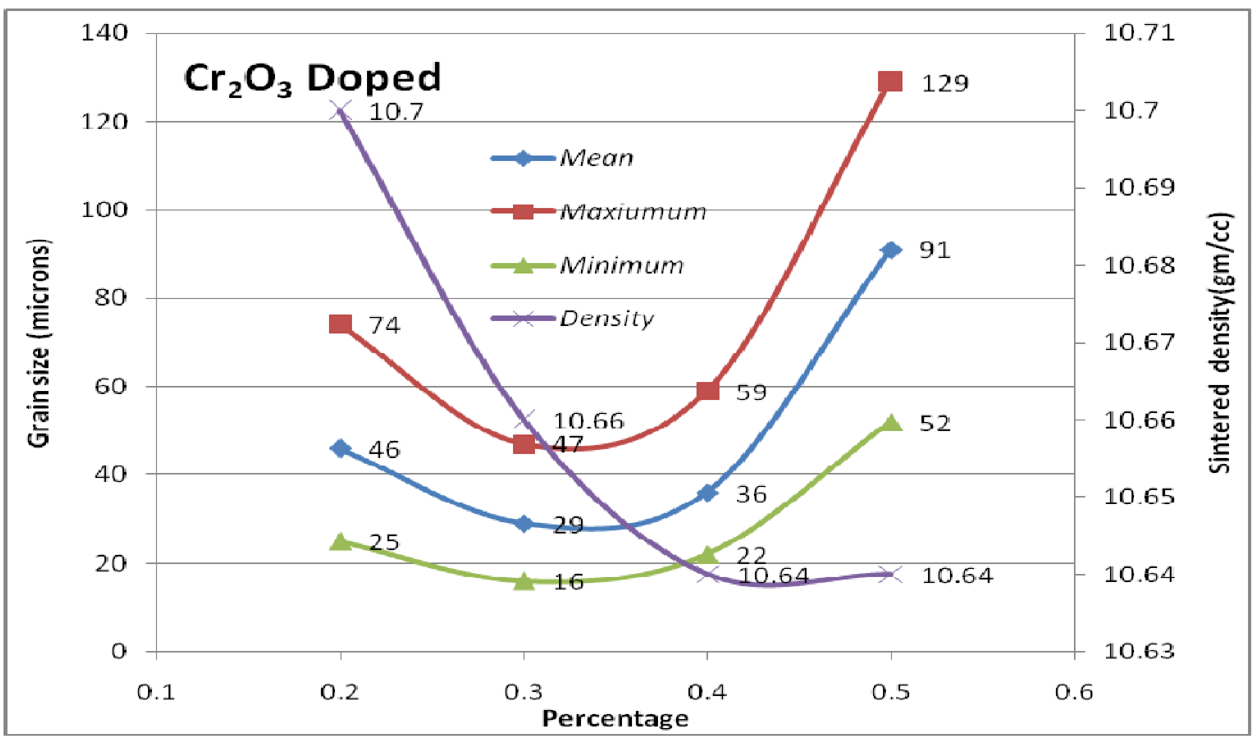
0.2 wt% SiO_2

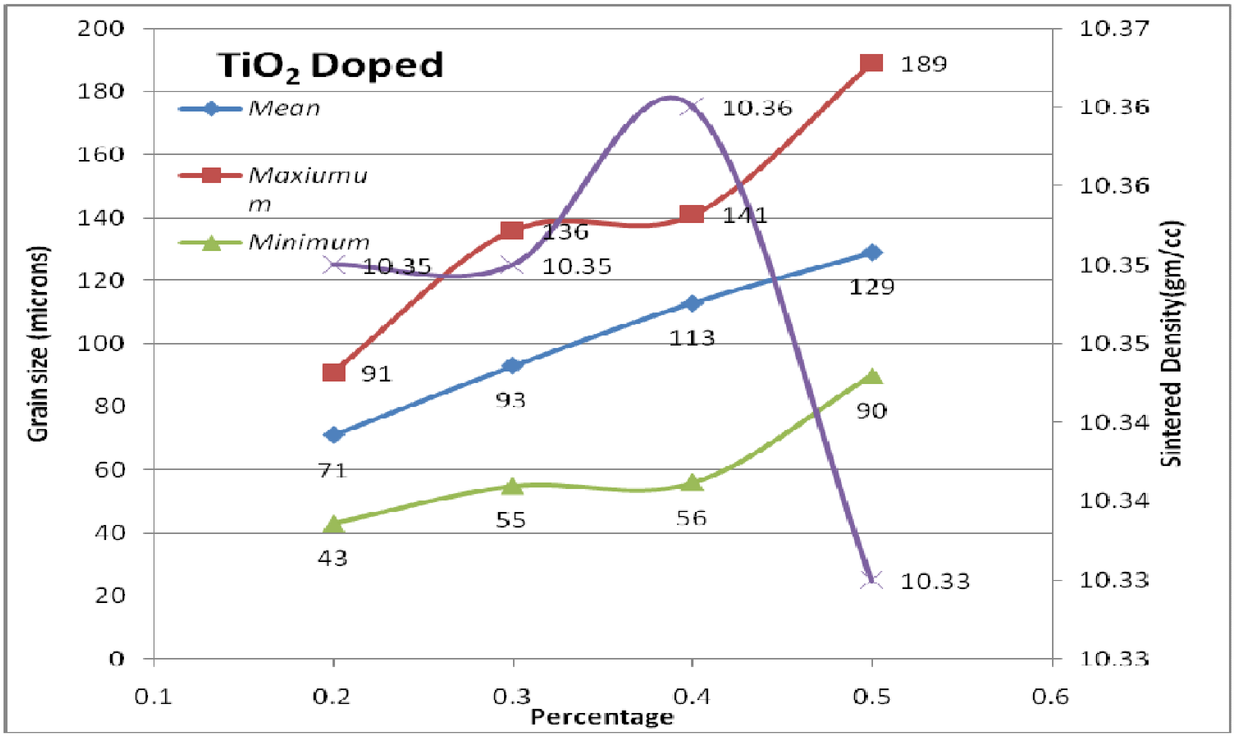


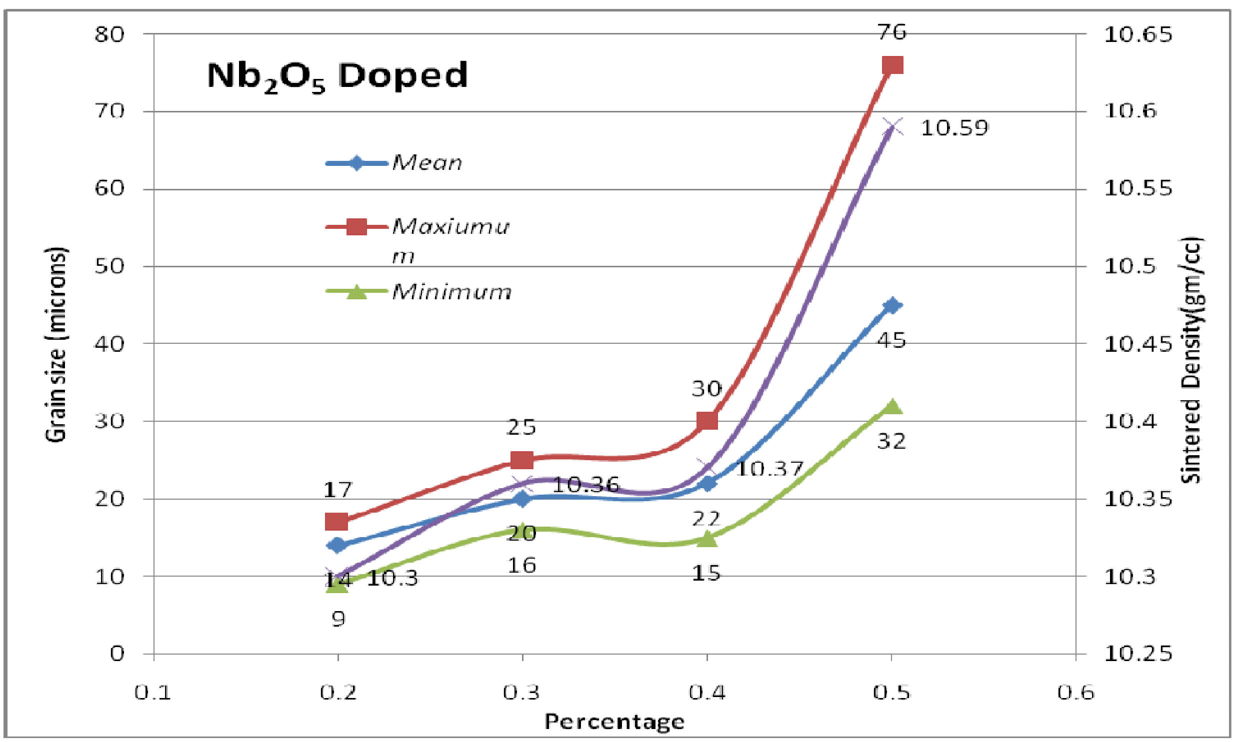
0.5 wt% SiO_2

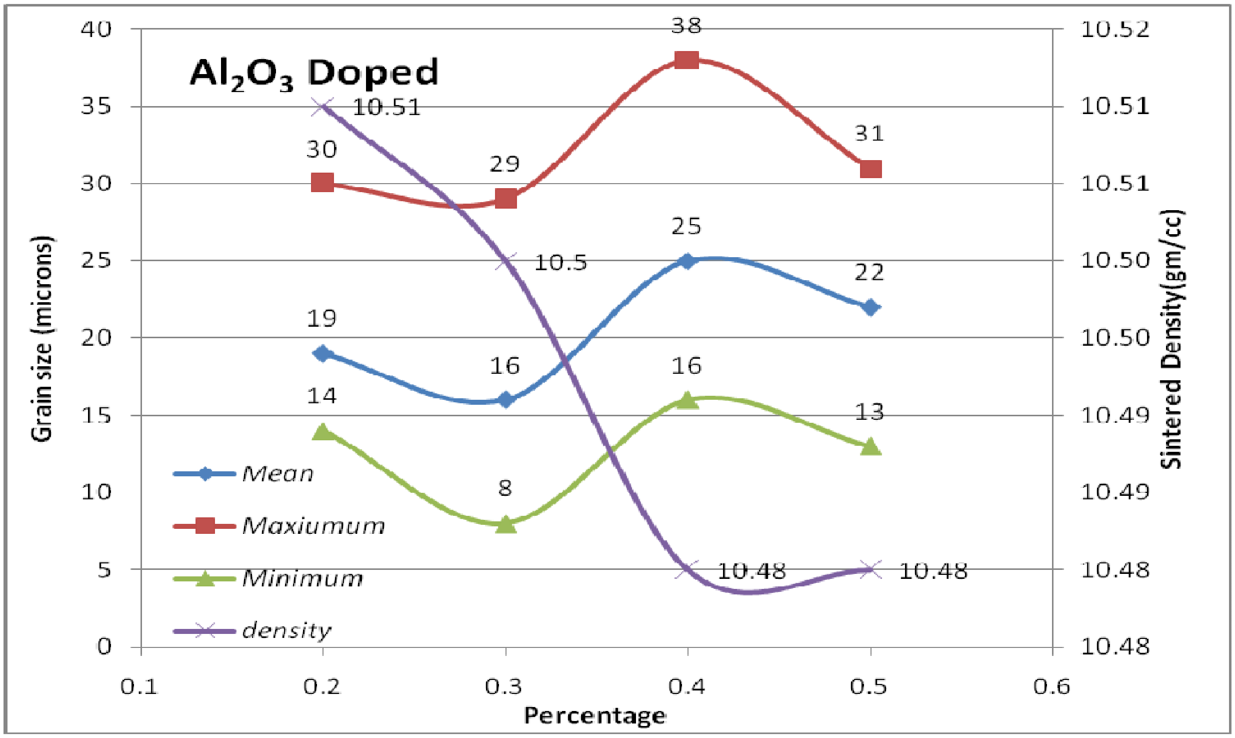
3. Graphical representations on effect of dopants

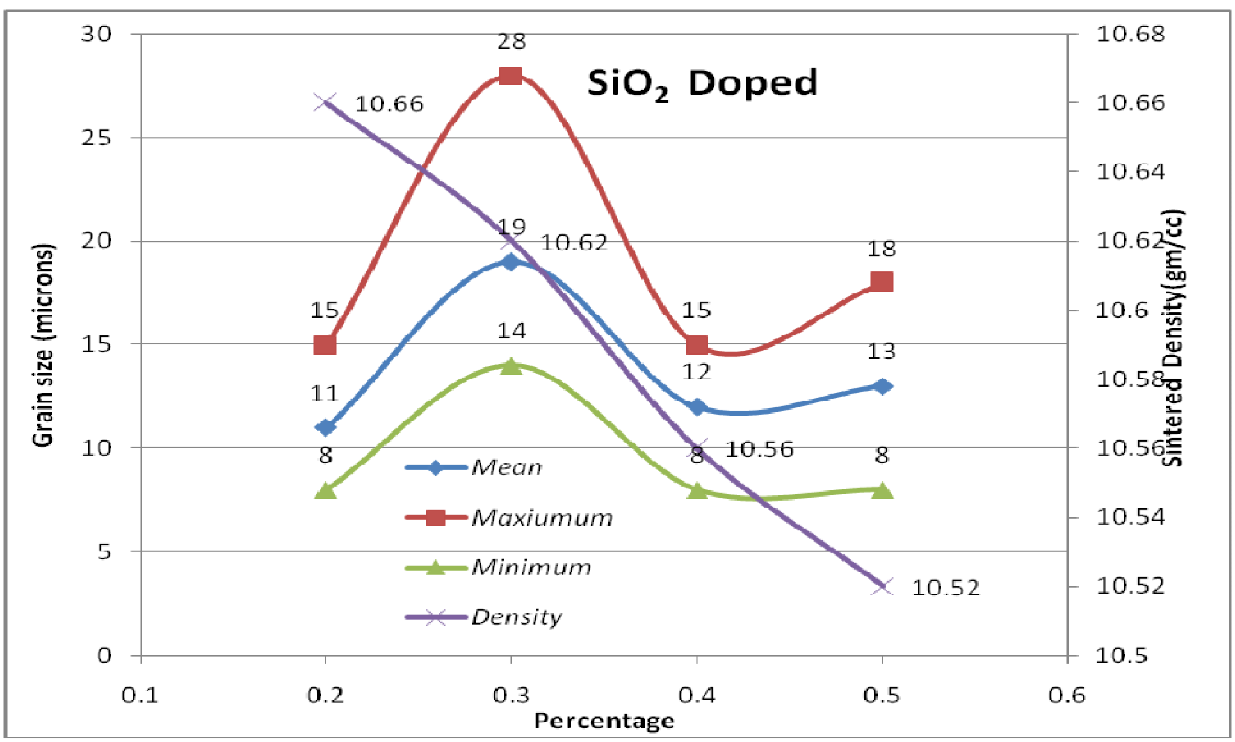
Graphs are prepared taking maximum, minimum and mean grain size values with the quantity of dopant and superimposing the sintered density values on same plot for every dopant.

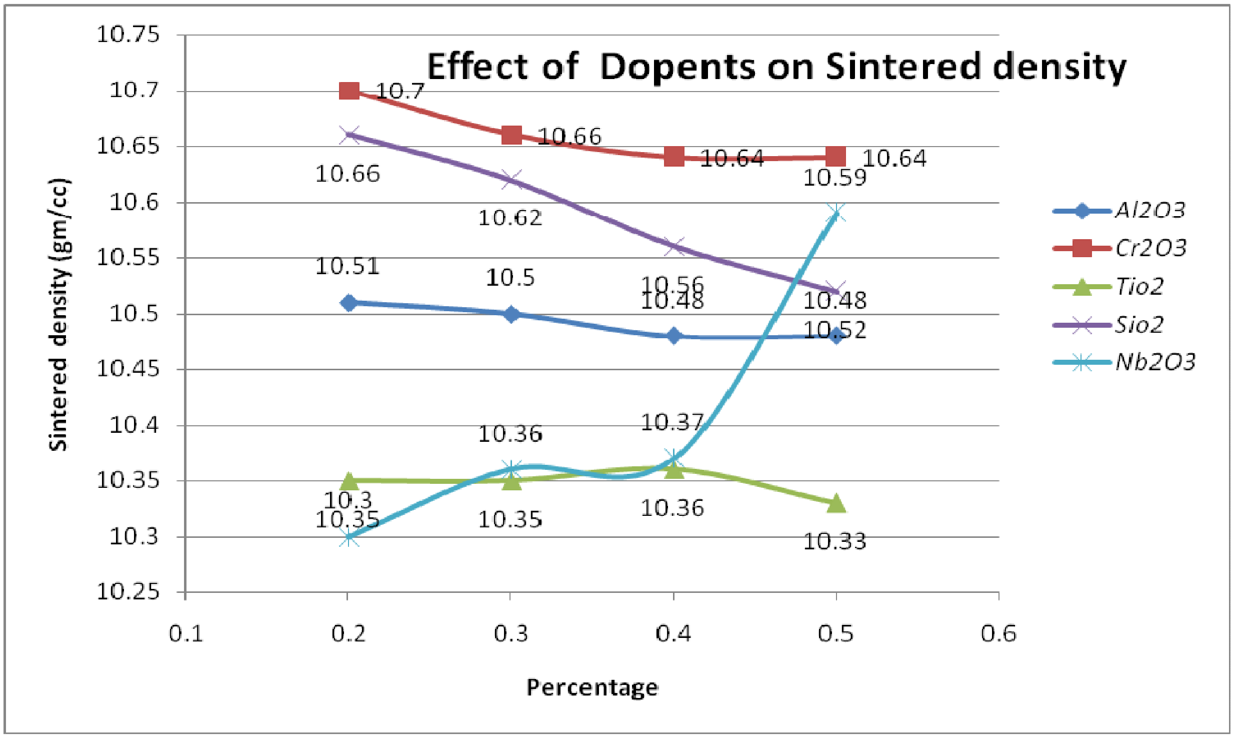


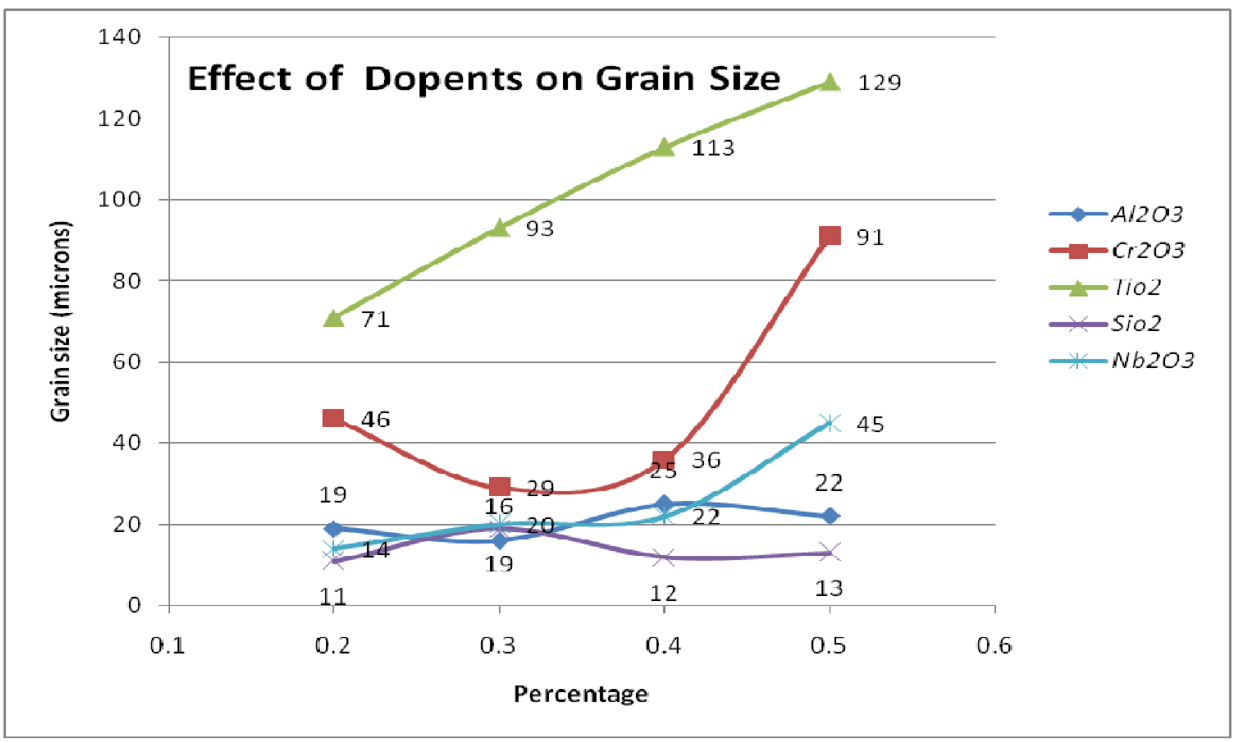

TiO_2 Doped
Mean
Maxiumu m
Minimum
Grain size (microns)
Sintered Density(gm/cc)
Percentage
189
141
136
91
129
113
93
71
90
56
55
43
10.36
10.35
10.35
10.33
200
180
160
140
120
100
80
60
40
20
0
10.37
10.36
10.36
10.35
10.35
10.34
10.34
10.33
10.33
0.1
0.2
0.3
0.4
0.5
0.6


Nb_2O_5 Doped
Mean
Maxiumu m
Minimum
Grain size (microns)
Sintered Density(gm/cc)
Percentage
76
10.59
45
30
25
32
10.37
10.36
17
22
20
16
15
14
10.3
9
80
70
60
50
40
30
20
10
0
10.65
10.6
10.55
10.5
10.45
10.4
10.35
10.3
10.25
0.1
0.2
0.3
0.4
0.5
0.6


Al2O3 Doped
Grain size (microns)
Sintered Density(gm/cc)
Percentage
Mean
Maxiumum
Minimum
density
40
35
30
25
20
15
10
5
0
10.52
10.51
10.51
10.50
10.50
10.49
10.49
10.48
10.48
0.1
0.2
0.3
0.4
0.5
0.6
38
30
29
31
25
22
19
16
16
14
13
8
10.51
10.5
10.48
10.48


SiO2 Doped
Grain size (microns)
Sintered Density(gm/cc)
Percentage
Mean
Maxiumum
Minimum
Density
30
25
20
15
10
5
0
10.68
10.66
10.64
10.62
10.6
10.58
10.56
10.54
10.52
10.5
0.1
0.2
0.3
0.4
0.5
0.6
28
19
18
15
15
14
13
12
11
8
8
8
10.66
10.62
10.56
10.52


Effect of Dopents on Sintered density
Sintered density (gm/cc)
Percentage
10.75
10.7
10.65
10.6
10.55
10.5
10.45
10.4
10.35
10.3
10.25
0.1
0.2
0.3
0.4
0.5
0.6
10.7
10.66
10.64
10.64
10.66
10.59
10.62
10.51
10.5
10.56
10.48
10.48
10.52
10.36
10.37
10.3
10.35
10.35
10.36
10.33
Al2O3
Cr2O3
Tio2
Sio2
Nb2O3


Effect of Dopents on Grain Size
Grain size (microns)
Percentage
140
120
100
80
60
40
20
0
0.1
0.2
0.3
0.4
0.5
0.6
129
113
93
91
71
46
45
36
29
25
22
19
16
20
22
14
19
11
12
13
Al2O3
Cr2O3
Tio2
Sio2
Nb2O3

4. Results analysis and conclusions

In case of Cr_2O_3 doped pellets, the average grain size is increasing with the quantity of Cr_2O_3 above 0.3% but the sintered density of the pellet decreases with increasing percentage but maintaining higher values. For TiO_2, the grain size is increasing steadily with the percentage increases but the sintered density values are low compare to other additives and hence not acceptable. In case of Nb_2O_5, the grain size is remarkably enlarged from 22μ to 45μ when the quantity increases from 0.4% to 0.5% but the density increases modestly from 10.37 to 10.59 gm/cc. The optimum quantity for Al_2O_3 is 0.4%.The density decreases with increasing quantity. In case of SiO_2, the graph looks like Al_2O_3 except the optimum quantity here is 0.3%.The density decreases when quantity increased but maintaining reasonably higher density values. Any dopant acts as an impurity in the reactor especially in PHWR is concerned w.r.t neutron absorption point of view. Therefore reasonably good results at lowest quantity addition is always expected during reactor operation. In summary, the grain size effectively increases with TiO_2 and Cr_2O_3 at lower quantity addition. Cr_2O_3 and SiO_2 are giving reasonably good sintered densities among all other dopants at lower percentage. It appears from the trials that the dopant Cr_2O_3 with 0.2 wt% is the most suitable choice for increasing the grain size and sintered density both in UO_2. The experimental condition needs to be checked number of times in order to obtain reproducible results.

5. Discussion and future scope

The high temperature sintering of reactor grade ADU-ex UO_2 pellet in reducing atmosphere gives grain size of about 10-25μ without addition of any sintering aid. The UO_2 grain size of about 70-80μ is achieved with addition of 0.2 wt% Cr_2O_3 as an external doping agent. Some additives like Al_2O_3, SiO_2 might appear in the form of a liquid glassy phases along the grain boundaries at high temperature and thus increases the diffusion rate by the mechanism of liquid phase sintering. Other soluble aliovalent dopant probably goes into the solid solution, creates vacancies or interstitials depending upon the oxidation states of dopant cations $Nb^{4+, 5+}$, $Cr^{3+, 4+}$, $Ti^{3+, 4+}$ etc and thus change the defect chemistry of UO_2 lattice during solid state sintering [1][2]. Any defects inside UO_2 lattice lower the activation energy and enhance the diffusion rate. In case of TiO_2, some of Ti^{4+} ions substitute U^{4+} ions but few Ti^{3+} ions may form interstitial solid solution with UO_2 [3]. Diffusion of slow moving U^{4+} ion is activated by interstitial mechanism of diffusion. Segregation of dopant can alter the structure and composition of surfaces thereby influence the thermodynamic factors by modifying the interfaces and grain boundary energy during sintering [4]. It has been observed that the solubility limit for Cr_2O_3 dopant in UO_2 is about 0.07% at 1700ºC. The excess dopant above solubility limit generally acts as inclusion and thus inhibit grain growth [1] by pinning the grain boundaries through Zener mechanism. The grain growth at 0.2wt% Cr_2O_3 may indicate formation of low melting eutectic (Cr-CrO) at temperature of about 1500-1660°C in Cr-Cr_2O_3-UO_2 system in presence of SiO_2 [1]. It is therefore assumed the dissolution and precipitation of UO_2 takes place through liquid secondary phase [1]. Although, exact mechanism of grain growth in UO_2 is not clear yet, but it is apparently understood that the combination of one with the others are mostly responsible for microstructure modification of UO_2. Additional information about the effect of dopant in reactor operating condition like irradiation behavior, coefficient of reactivity, neutron absorption, thermal conductivity, induced radioactivity etc are necessary before final conclusion for the selection of dopant to promote grain growth of UO_2.

6. Acknowledgement

The work was made possible thanks to Shri D.Pramanik, NFC for facilitating various powder dopants from in and outside of NFC. He gave valuable guidance for carry out the experimental trials along with regular plant production. The authors wish to thank Shri S.V.Ramana Rao, NFC for his scientific contribution during metallographic sample preparation and SEM analysis at their laboratory. He gave valuable comments during preparation of this report.

7. References

[1] L. Bourgeois, Ph. Dehaudt, C. Lemaignan, A. Hammou " Factors governing microstructure development of Cr_2O_3- doped UO_2 during sintering"- *journal of nuclear materials* 297 (2001)313-326

[2] Y. Harada, "Sintering behavior of niobia-doped large grain UO_2 pellet"- *journal of nuclear materials* 238 (1996) 237-243

[3] Hj. Matzke, "On the effect of TiO_2 addition on sintering of UO_2"- *journal of nuclear materials* 20 (1966) 328-331

[4] M. N. Rahaman, "Ceramic processing and sintering", Department of Ceramic Engineering, University of Missouri-Rolla Rolla, Missouri, Marcel Dekker, Inc.