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THE COLD PRESSING BEHAVIOR OF URANIUM DIOXIDE AND TRIURANIUM OCTOXIDE MIXED POWDERS

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The main purpose of the experiment was to introduce uranium dioxide powder with the nonstoichiometric level between 0.6 and 0.7 in UO_{2+x} *powder for obtaining by cold pressing stable pellets in terms of geometric shape and green density more than 40% of the theoretical density of uranium dioxide (*ρ *= 10.96g/cm*^{3}*). Because the temperature evolution of uranium oxides is complex [1] [2] the temperature at which the highest amount of most stable oxide (triuranium octoxide) was determined. The* UO_{2+x} *powder was homogenized with different proportions of triuranium octoxide and led by cold pressing in a uniaxial press to achieve this goal. This article summarizes experiments for this purpose and is part of a larger work aimed to investigate the sintering behavior of powder mixtures of nonstoichiometric uranium dioxide and triuranium octoxide.*

Keywords: uranium dioxide, triuranium octoxide, powder, cold pressing

1. Introduction

O / U diagram is complex one [1]. According to interest zone can be distinguished at least 7 areas [2].

From UO, which existence at first was denied [3] to the UO_3. Extensive experiments were conducted in order to determine the laws that govern especially UO_2 oxidation [4, 5].

Explanations and complex computer simulations with dedicated programs [6] led to the conclusion that the oxidation of UO_2 obeys two laws: a linear one in temperature range of 25^0C - 350^0C and another sigmoidal Arrhenius type in the temperature range 350^0C - 900^0C [7]. Approaches were made by thermodynamic point of view of UO_2 oxidation [8] or by the point of view of the molecular dynamics of the surface uranium dioxide [9].

UO_2 is raw materials for CANDU power plants. Ways to reduce the cost of the fuel bundle were analyzed [10].

One way to reduce the costs of fuel bundles is the reuse of nonconforming material resulting from the production line of the UO_2 pellets (UO_2 powder, green pellets and sintered pellets).

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In this paper we pursue 3 goals; one was to determine the oxidation behavior of uranium dioxide industrial powder - non stoichiometric UO_{2+x} type - in the temperature range of 25^0C - 900^0C.

The other goal was to highlight the oxidation of non-stoichiometric uranium dioxide UO_{2+x} type occurs, assuming that it takes place through competition between two mechanisms: a main step by step oxidation ($UO_{2+x} \rightarrow U_3O_8$) and other cyclic secondary recovery oxidation ($U_3O_8 \rightarrow UO_{2+x}$).

The main purpose of the experiment was to introduce uranium dioxide powder with the nonstoichiometric level between 0.6 and 0.7 in UO_{2+x} powder for obtaining by cold pressing stable pellets in terms of geometric shape and green density more than 40% of the theoretical density of uranium dioxide (ρ = 10.96g/cm^3).

2. Experimental - Material - Apparatus and Procedure

The material has been provided by Nuclear Fuel Plant-Pitesti courtesy. The powder is the waste powder resulting from physicochemical analyses of the production line of the UO_2 pellets.

Uranium dioxide powder was passed through a three tower site and we keep only the powder that passed through a sieve of 125 μm. Sieving duration was 15 minutes. The resulting powder was manual passed three times through a sieve of 125 μm. The powder was analyzed in terms of density, O / U ratio, the average particle size and specific surface area.

By studying the phase diagram of O / U we chose nine (9) calcination temperatures of interest to illustrate the best possible hyperstoichiometrics the oxides population.

For calcination we used a Nabertherm laboratory furnace type with the possible control of temperature in a range from 300^0C to 1100^0C and an accuracy of ± 3^0C. To obtain the powder required for the analysis we calcined an amount of about 50g powder in porcelain crucibles.

The powders was calcined at a chosen temperature with a ramp rate of 5^0C/min, the residence time for 10h and free cooling to ambient temperature. The resulting powder was homogenized by tree manual 125 μM sieving.

Determination of bulk density was made using the Scott volumeter. We calculated the average diameter of particles by laser diffraction using a device made by Horiba.

Determination of specific surface was achieved by N_2 adsorption at liquid nitrogen temperature of the sample using a 9600 series Qsurf ThermoQuest device. The method used was the Brunauer, Emmett and Teller (BET). In order to determine the grain forms, an analysis by scanning electron microscopy was made.

A SEM microscope Vega3 TESCAN type with a magnification 2kx and the scale of 20µm was used. For the identification of the powder calcined hyperstoichiometrics oxides, a X 'PERT PRO MEP diffractometer type for qualitative analysis of samples, equipped with two X-ray sources, a copper tube and anticathode of cobalt was used.

After identification of uranium oxides in the chosen temperature points we made a cumulative pie diagrams.

We cold pressed 35 pellets (five per mixed sample) in a uniaxial press at a pressure of 4MPa. The press was manually feeding with the wall lubrication. Anointing of the wall was made of zinc stearate in acetone.

3. Results

The results of physico-chemical analyses was done on the 9 samples for bulk density, O / U ratio, the average particle size (D_{50}), surface area and were systematized in Table 1. One can note that once the temperature increases the density of uranium oxides decreases reaching the minimum value of 1 g/cm^3 in the temperature range 350^{0}C - 650^{0}C and then grow again.

Table 1

Properties of uranium oxides at different temperatures

Temperatures [^{0}C]	Bulk density[g/cm$^{3]}$]	O/U	$D_{50[\mu m]}$	Surface area[m^2/g]
25	1.12	2.18	7.67	6.91
250	1.11	2.20	7.69	6.20
300	1.10	2.37	6.58	5.34
350	1.00	2.68	7.85	7.56
500	1.00	2.63	6.42	5.24
650	1.00	2.71	7.52	5.16
665	1.14	2.62	6.51	4.66
750	1.15	2.59	6.75	3.16
900	1.4	2.56	6.54	1.41

O / U ratio increases with the temperature until it stabilizes in the range of 650^{0}C - 750^{0}C temperature and then slowly decrease to 2.56. Specific area and D_{50} have a complicated evolution in the studied temperature range but global movement is to decrease while the temperature increases (see Fig.1).

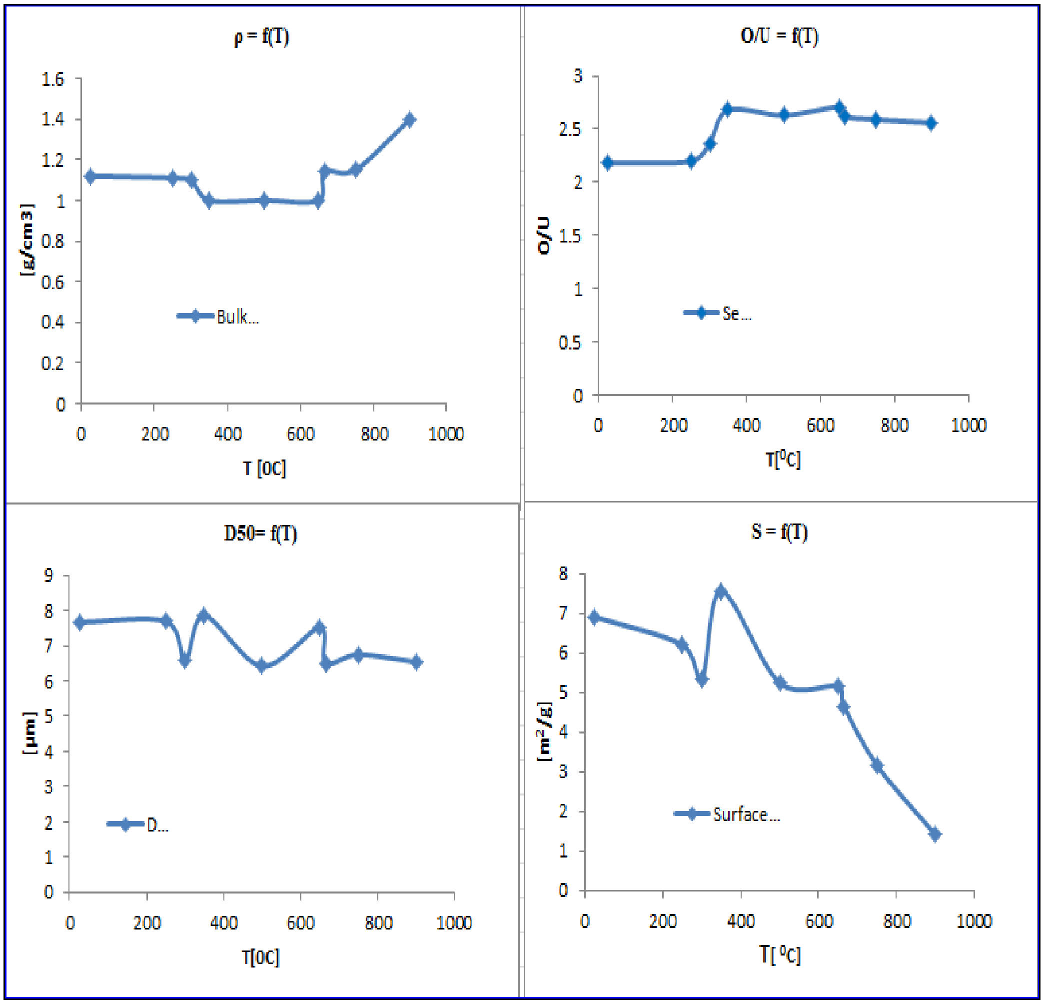


Fig.1. Bulk density, O/U, D_{50}, Surface area temperature depending

Analyzing cumulative chart obtained by laser diffraction we can conclude that the powder contains uranium oxides with bimodal repartition which may explain its behavior in the studied temperature range (see Fig.2). This conclusion proves to be accurate if we analyses the SEM microphotographs (see. Fig.3).

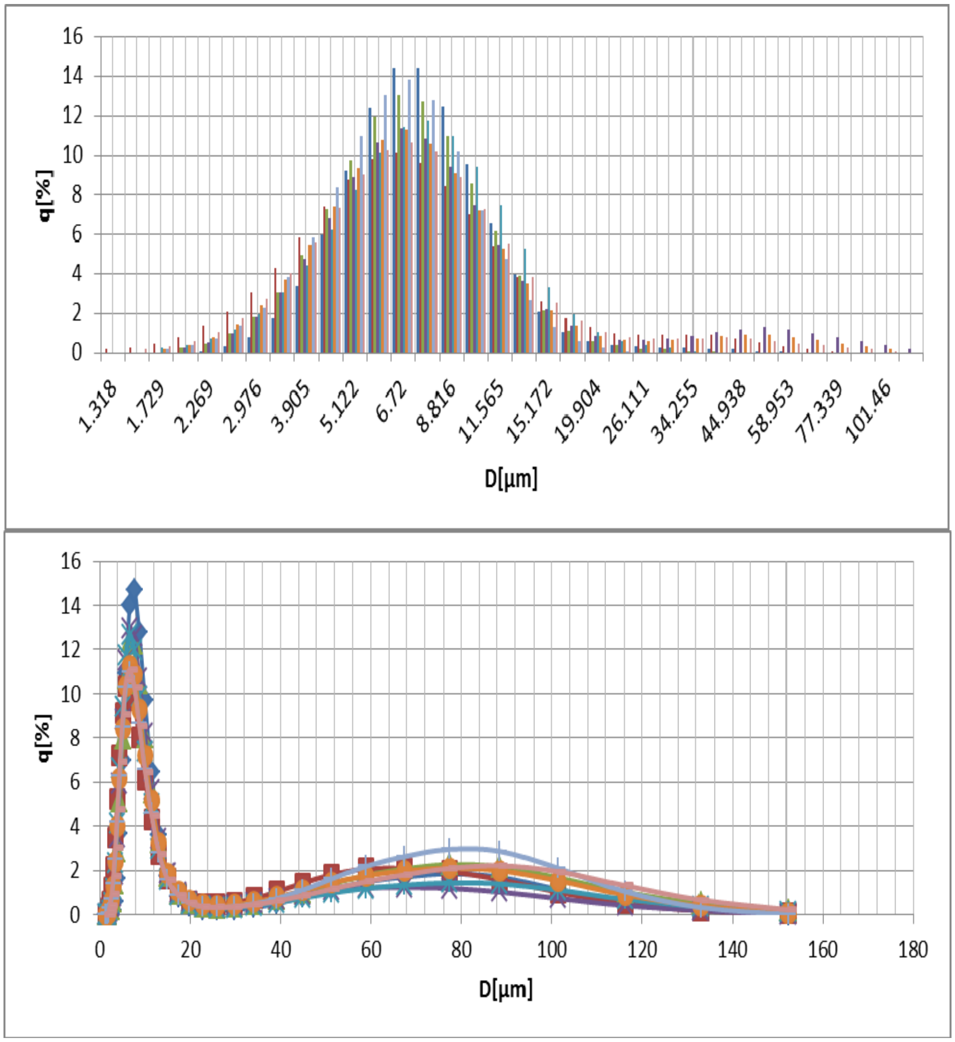
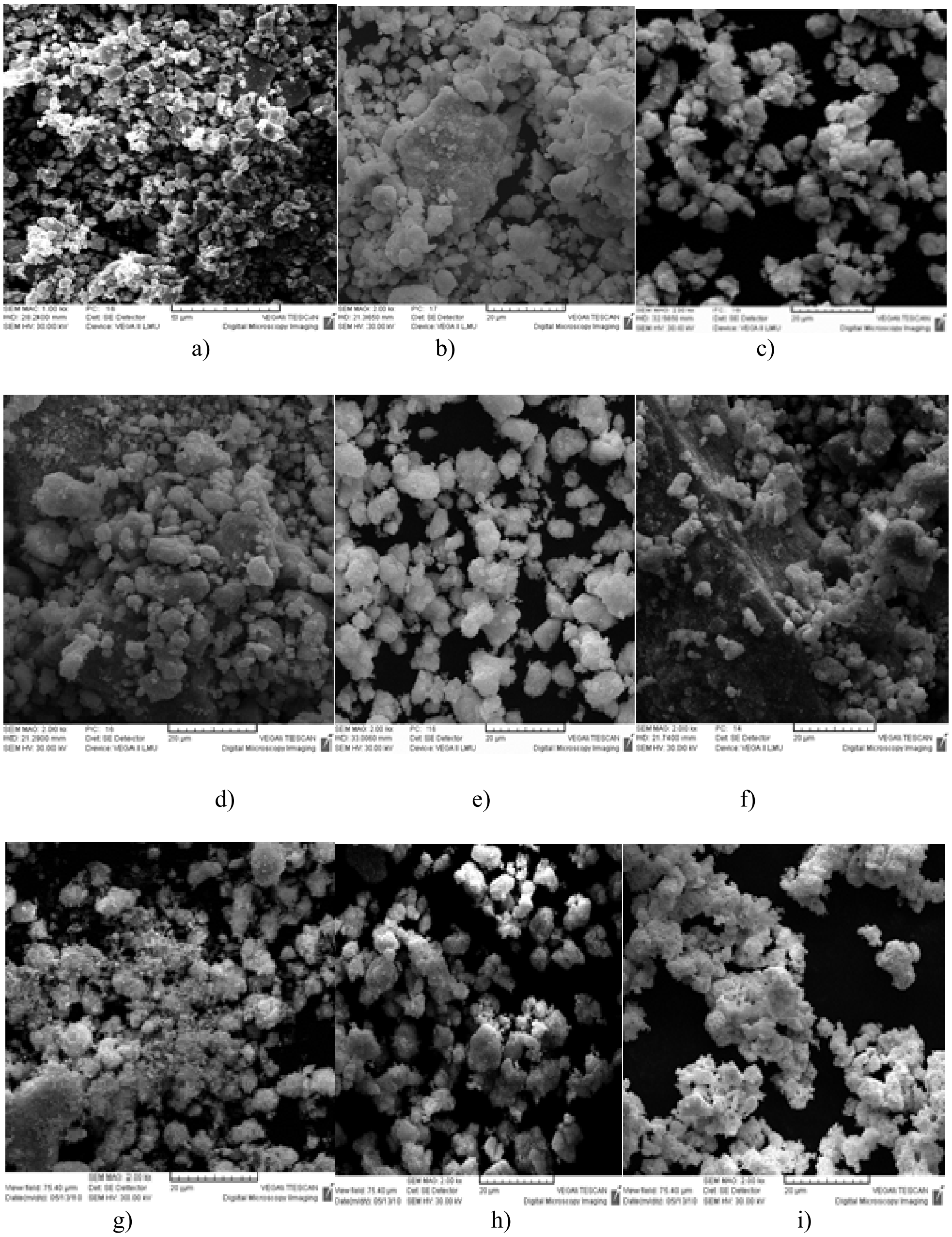


Fig.2. Bimodal size of uranium oxides samples

SEM micrographs shown that bimodal appearance is preserved. However there is a tendency of wafers to agglomerate function of temperature. In turn smaller wafers tend to sinter when the temperature rich the 900^{0}C (Fig.3).



a) b) c)

d) e) f)

g) h) i)

Fig.3. S.E.M. images for powders calcined in the range of 100^{0}C – 900^{0}C.UO_{2+x} powder at 25^{0}C (a); uranium oxides produced at 250^{0}C(b);uranium oxides produced at 300^{0}C(c);uranium oxides produced at 350^{0}C(d); uranium oxides produced at 500^{0}C(e); uranium oxides produced at 650^{0}C(f);uranium oxides produced at 665^{0}C(g);uranium oxides produced at 750^{0}C(h);uranium oxides produces at 900^{0}C(i)

Identification of higher oxides by XRD in the temperature range studied 25^0C – 900^0C (see Table 2), has led to a graphic representing explicitly the evolution, emergence and complex transformation of higher oxides of uranium (see Fig. 4).

Table 2

X.R.D. Identification analysis and semi quantitative per cents of uranium oxides in the range of 100^0C - 900^0C

T [^{0}C]	$UO_{1,75}$	$UO_{1,96}$	UO_2	$UO_{2,11}$	$UO_{2,13}$	$UO_{2,25}$ (U_4O_9)	$UO_{2,33}$ (U_3O_7)	$UO_{2,5}$ (U_2O_5)	$UO_{2,61}$ ($U_{13}O_{34}$)	$UO_{2,66}$ (U_3O_8)	UO_3
25	0	19	24	0	37	20	0	0	0	0	0
250	24	0	11	7	13	19	25	0	0	1	0
300	30	0	8	0	0	58	0	2	0	2	0
350	0	0	0	0	0	0	0	14	14	24	48
500	0	0	0	0	0	0	0	0	0	86	14
650	0	0	0	0	0	0	0	8	20	58	14
665	0	0	0	0	0	0	0	0	0	90	10
750	0	0	0	0	0	0	0	0	0	88	12
900	1	0	0	0	0	0	0	25	26	45	3

Hypostoichiometric uranium oxides are observed in the temperature range of 250^0C - 300^0C.

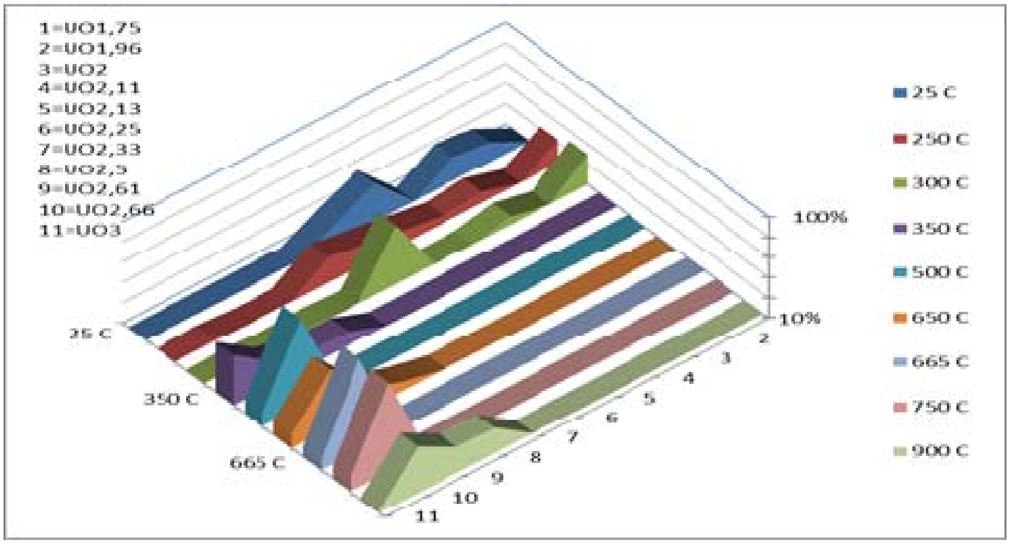


Fig.4. 3D diagram of semi quantitative per cents of uranium oxides in the range of 25^0C - 900^0C

The powder obtained at the temperature of 665^{0}C (having the highest content of triuranium oxide) was mixed in a proportion of 50%, 40%, 30%, 20%, 10%, 5% with UO_2 powder.

Table 3.

Compressibilityaccording to% U_3O_8 content

[%]U_3O_8 in UO_2	Compressibility(ρ_{exp}./ρ_t)•100
50	49.64
40	50.18
30	52.37
20	52.92
10	52.92
5	53.83
0	52.65

The pressing was made in a cylindrical mold of tungsten carbide in two stages. A 2MPa pressing with 15 seconds keeping followed by a final pressing at 4MPa with 20 seconds maintenance. The resulted pellets were free of surface defects. The graph shown in Figure 5 was plotted with the data from Table 3.

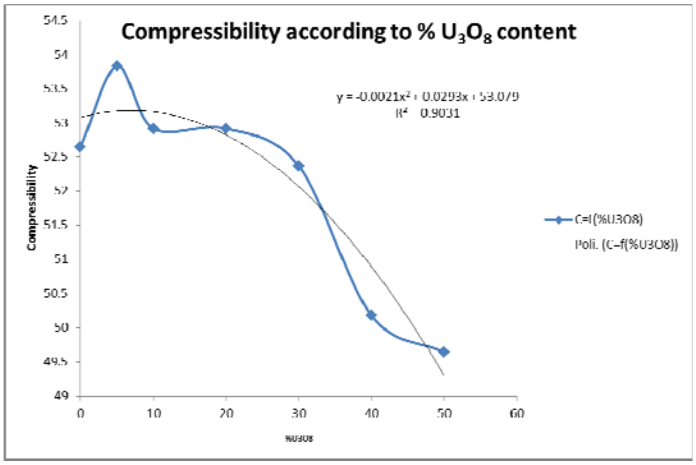


Fig.5 Compressibility according to% U_3O_8 content

Analyzing the graph, one can observe that when increasing the content of triuranium oxide the compressibility decreases. The values remain approximately constant for the values of 30%, 20%, 10% U_3O_8.

4. Discussion

Comparing the data of Table 1 (Properties of uranium oxides at different temperatures) with those of Table 2 (Identification and semi-quantitative analysis per cents of uranium oxides in the range of 25^0C - 900^0C) we can deduce that we cannot explain the complexity of uranium oxides obtained by linear progression from UO_2 to UO_3. One can note that the temperature about 670^0C - 680^0C to obtain the largest amount of U_3O_8 in normal atmosphere. To support this claim come the O / U ratio whose value of 2.62 corroborates the percentage of 90% of XRD diffraction.

Taking into account that the overall rate of these reactions is Arrhenius-type, the formation of uranium oxides are function of the temperature at which the transformation take place and stabilizes in normal atmosphere if the temperature does not rise. Inside contraction coupled with expansion of the outer layer leads to oxidation and exfoliation of the latter and the oxidation reaction keep up if the temperature continues to rise.

The phenomenon is complex because the submicron particles tend to oxidize quickly and commits violent, additional temperature generating the formation of uranium hyperstoichiometric oxides where bimodal size distribution is present.

The formation of uranium oxides is competitive. Oxygen diffuses out by the grain boundary and tends to sinter the particles to give hypostoichiometric interior oxides while external oxygen diffuses towards the inside interstitial space leading to an oxide as hyperstoichiometric (see Fig.6).

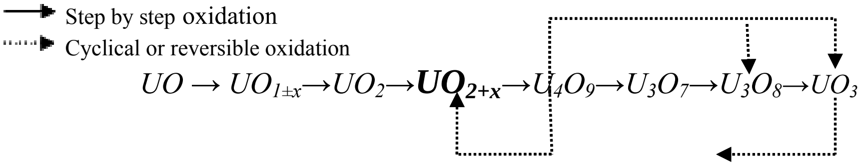


Fig.6. Competitive and cyclical oxidation scheme of UO_{2+x}

Studying Table 3 and the compressibility curve in Figure 5, one can observe that the degree of compressibility has a stabilizing plateau in 10÷30% range of U_3O_8 in UO_2.

5. Conclusion

Our results are consistent with those in the literature. Oxides formation depends on the temperature, the specific surface area, particle shape - in this case the wafer shape.

Hypothesis by which we proposed that the mechanism of oxidation of UO_{2+x} is composed by two mechanisms - one step by step oxidation and other by cyclic oxidation - is confirmed.

This qualitative study approach will be followed by an exhaustive quantitative research.

The main purpose of the experiment was successfully accomplished. By introducing in uranium dioxide powder the nonstoichiometric oxides with level between 0.6 and 0.7 in UO_{2+x} powder we have obtained by cold pressing stable pellets in terms of geometric shape and green density more than 40% of the theoretical density of uranium dioxide ($\rho = 10.96 g/cm^3$).

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REFERENCES

[1] *Gmelin Handbuch der Anorganischen Chemie*, C1, Das system U-O, p.94-206, Springer – Verlag Berlin-Heidelberg-New York 1977.

[2] *Belle J.,* Proprieties of Uranium dioxide, Washington 25, 1961, 750p

[3] *Pascal, P. (dir.), Caillat,R., Salesse, M.* et al., Combinaisons de l'Uranium, Nouveau traité de chimie minérale: Uranium et transuraniens, tome XV, deuxième fascicule, Paris, Masson et Cie Editeurs, 1961, 810 p.

[4] *McEachern R. J., Taylor P.*, A review of the oxidation of uranium dioxide at temperatures below 4000C, Journal of Nuclear Materials 254 (1998) p. 87–121.

[5] *Jae Ho Yang, Young Woo Rhee, Ki Won Kang, et. al.,* Formation of columnar and equiaxed grains by the reduction of U_3O_8 pellets to UO_{2+x}, Journal of Nuclear Materials 360 (2007) p.208–213.

[6] *Rousseau G., Desgranges L., Charlot F. et al.,* A detailed study of UO_2 to U_3O_8 oxidation phases and the associated rate-limiting steps, Journal of Nuclear Materials 355 (2006) p.10–20.

[7] *Barbu A., Cojocaru M.*, Influence of 1% higher oxides on the UO_2 powders sintering(I), Metalurgia International, Special Issue vol.XVIII, no.1, 2013, ISSN 1582 – 2214.

[8] *Hiroshi Ohashi, Etsuzo Noda, Takashi Morozumi*, Oxidation of Uranium Dioxide, Journal of Nuclear Science and Tehnology, II(10), p.445-451,October 1974

[9] *Boyarchenkov A.S., Potashnikov S.I., Nekrasov K. A., Kupryazhkin A.Ya.*, Molecular dynamics simulation of UO2 nanocrystals surface, Journal of Nuclear Materials 421 (2012) 1–8.

[10] *Alfredson,* P. G. Report, Pilot plant development of processes for production of nuclear grade uranium oxide, AAEC/E245, Lucas Heights, 1972, 16p.