Depleted Uranium Dioxide Melting in Cold Crucible Melter and Production of Granules from the Melt for Use in Casks for Spent Nuclear Fuel and Radioactive Wastes

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ABSTRACT

This paper describes the results of a joint research program between the Russian Research Institute of Chemical Technology and Oak Ridge National Laboratory in the United States to develop new radiation shielding materials for use in the construction of casks for spent nuclear fuel (SNF) and radioactive wastes. Research and development is underway to develop SNF storage, transport, and disposal casks using shielding made with two new depleted uranium dioxide (DUO_2) materials: a DUO_2-steel cermet, and, DUCRETE with DUAGG (DUO_2 aggregate).

Melting the DUO_2 and allowing it to freeze will produce a near 100% theoretical density product and assures that the product produces no volatile materials upon subsequent heating. Induction cold-crucible melters (ICCM) are being developed for this specific application. An ICCM is, potentially, a high-throughput low-cost process. Schematics of a pilot facility were developed for the production of molten DUO_2 from DU_3O_8 to produce granules <1 mm in diameter in a continuous mode of operation.

Thermodynamic analysis was conducted for uranium–oxygen system in the temperature range from 300 to 4000 K in various gas mediums. Temperature limits of stability for various uranium oxides were determined. Experiments on melting DUO_2 were carried out in a high frequency ICCM in a cold crucible with a 120 mm in diameter. The microstructure of molten DUO_2 was studied and lattice parameters were determined.

It was experimentally proved, and validated by X-ray analysis, that an opportunity exists to produce molten DUO_2 from mixed oxides (primarily DU_3O_8) by reduction melting in ICCM. This will allow using DU_3O_8 directly to make DUO_2—a separate unit operation to produce UO_2 feed material is not needed.

Experiments were conducted concerning the addition of alloying components, gadolinium et al. oxides, into the DUO_2 melt while in the crucible. These additives improve neutron and gamma radiation-shielding and operation properties of the final solids. Cermet samples of 50 wt % DUO_2 were produced.

INTRODUCTION

Research and development (R&D) is underway to manufacture casks for spent nuclear fuel (SNF) and radioactive wastes (RW) storage, transport, and disposal using shielding materials made with depleted uranium dioxide (DUO_2) in a DUO_2-steel cermet, or, a DUCRETE with DUAGG (DUO_2 aggregate) with selective additives in cement matrix. Such casks would have superior performance (higher capacity for a

given weight, resistance against assault, improved repository performance) and the potential to use the entire inventory of excess DU in the United States and Russia.

The production of dense DUO_2 particles and aggregates with the appropriate properties is a significant cost in the production of these casks. The overall objective of this work is to develop very-low cost methods for production of dense DUO_2 particles and aggregations with tightly controlled particle-size distributions using cold-wall melters. One objective is to replace the DUAGG production process for DUCRETE.

The preparation of DUO_2 particles and aggregates for shielding could be produced from technologies that are extrapolated from the costly multi-step nuclear fuel pellet technologies. However, the DUO_2 product requirements for shielding applications are different than for nuclear fuel. Shielding applications require only modest purity and dimensional control. But, the particulates should approach the theoretical density of DUO_2.

DU oxide melting is a one step process that enables:

- approaching the theoretical density of DUO_2 in order to maximize shielding effectiveness;
- including additives in the DUO_2 to modify its chemical and nuclear properties (e.g. neutron absorbers) to improve cask performance;
- producing DUO_2 particles with given size by dispersing melt;
- assuring that the product generates no volatile materials upon subsequent heating.

The technical barrier to high-throughput melting is the ~2900°C melting point of DUO_2. Russia has developed cold-wall induction heated melters that have operated above 3000°C [1]. A cold crucible melter is an induction heated crucible where the furnace sides are actively cooled to create a frozen wall of the material being processed that provides insulation between the cooling coils and the melt. This allows operation at temperatures that exceed the capability of existing high-temperature materials. Solid DUO_2 and other additives will be added to the melter while liquid DUO_2 is withdrawn from the melter. The liquid DUO_2 will be drained into a special unit where the liquid stream is broken up and the droplets solidify as they drop to the bottom of the unit [2]. Droplet size will be controlled in the process.

THERMODYNAMICS OF THE URANIUM–OXYGEN SYSTEM

Thermodynamic analysis for the uranium – oxygen – inert gas (argon, helium) system in the temperature range 400–4000 K was performed by the total thermodynamic potential minimization method. In view of the fact that uranium nitrides are unstable compounds at high temperatures, its generation is ignored. From the presented data it follows that condensed (solid) uranium dioxide in inert gas atmosphere is the most stable phase at temperature below 2200 K (Fig.1). The concentration of uranium dioxide in gas phase rises as temperature increases to 2800 K. With further increase in temperature to 3200 K (UO_2 melting point), UO, UO_2 and UO_3 concentrations in the gas phase are raised up to 0.56; 0.055 and 0.065 mole/kg mix, accordingly.

Only gaseous uranium compounds - UO_2 and UO_3 (0.0179 and 0.3936 mole/kg mix) are generated at equilibrium conditions at a temperature of 3200 K, when oxygen concentration in air is large enough for UO_2 oxidation to UO_3. The smaller the oxygen needed for total oxidation, the greater is the probability to form condensed low valence uranium oxides. Concentration of gaseous UO, UO_2, and UO_3 are very small (0.0001, 0.05, and 0.043 mole/kg mix) at a 15% stoichiometric oxygen amount needed for the total UO_2 oxidation to UO_3 at temperatures 3200 K (Fig.2). At this condition, the condensed UO_2 is the bulk product.
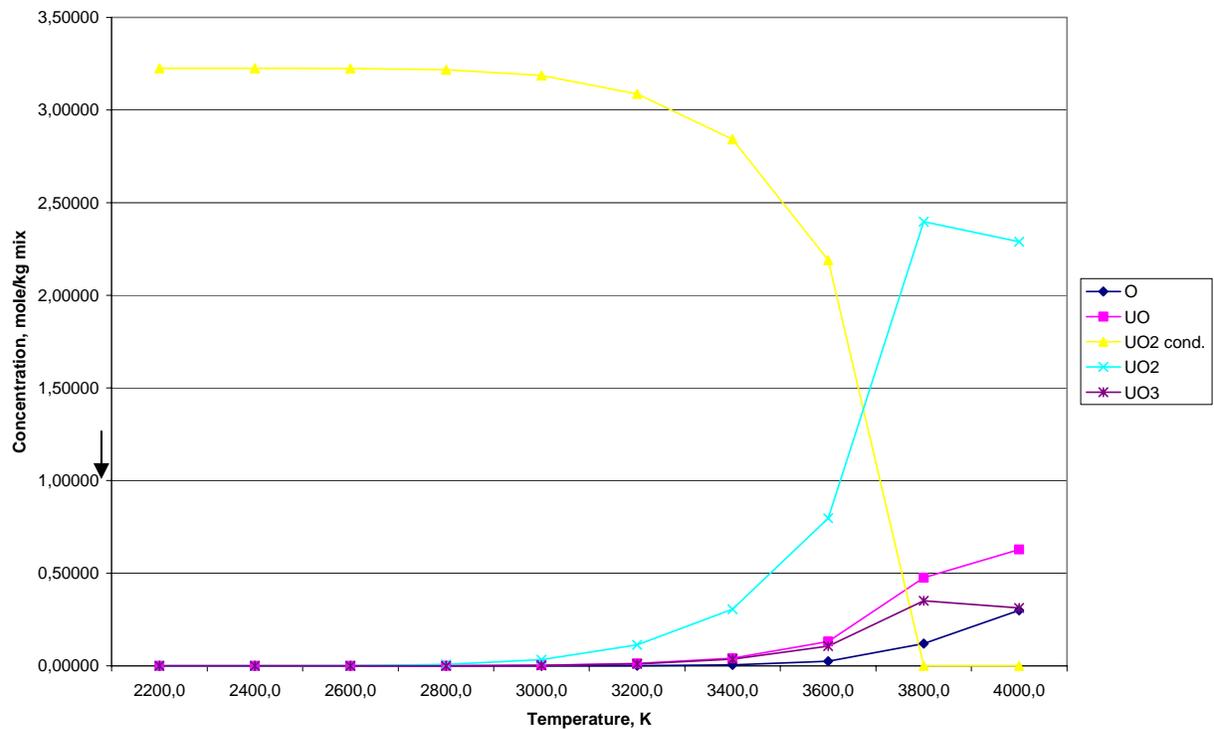
Fig. 1. Equilibrium concentration of compounds in uranium–oxygen system in inert gas atmosphere.
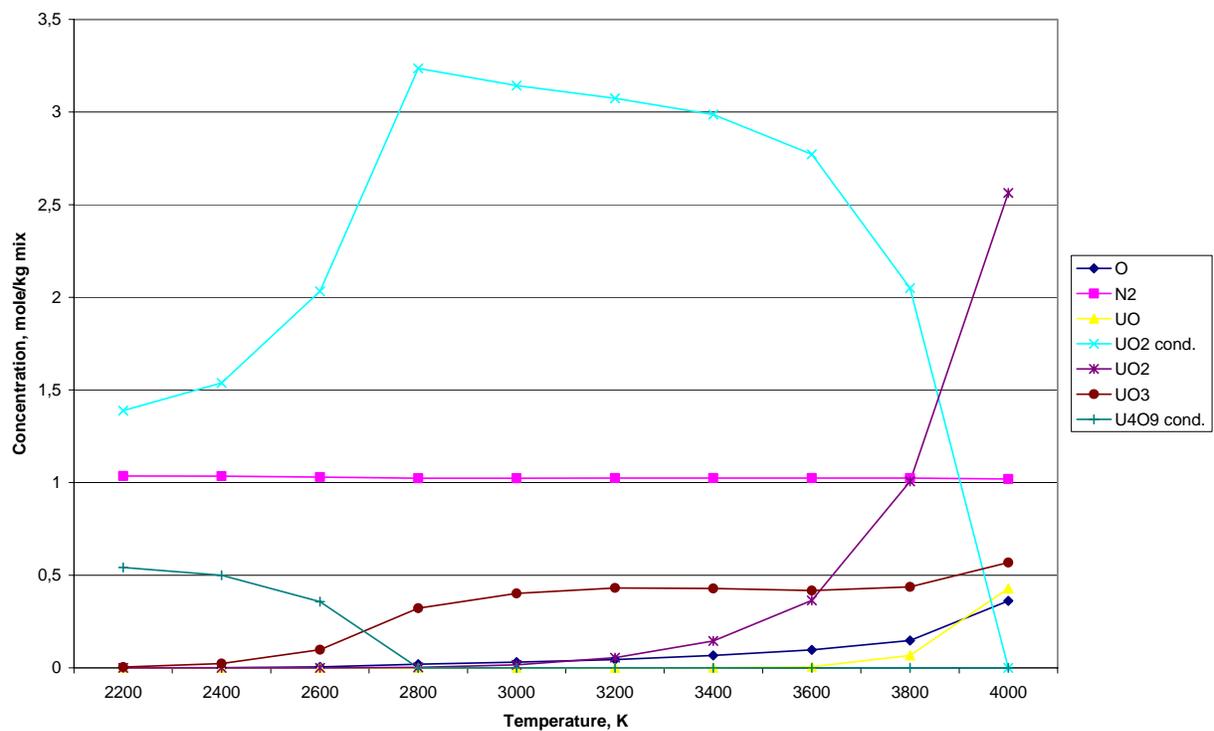
Fig. 2. Equilibrium concentration of compounds in uranium–oxygen system in air atmosphere (15% stoichiometric oxygen is needed for the total UO_2 oxidation to UO_3).

Hence, it follows that a considerable amount of uranium oxides may pass into the gas state when UO_2 is melting. Therefore, the melting process should be conducted in a inert gas atmosphere.

If the melting process is conducted in an air atmosphere, the following requirements must be met:

- melting chamber capacity should not be much more than the cold crucible capacity;
- melting process should be conducted under layer of non-melted uranium dioxide powder to prevent oxygen penetration in the melt and overheating melt surface and evaporation of gaseous uranium compounds; and the
- melting process duration should be reduced to minimum.

INITIAL EXPERIMENTAL STUDIES

Initial experimental studies were conducted to generate data on melting DUO_2 as input to a facility pre-conceptual design. Experiments on melting of 5 and 6 kg DUO_2 powder with a bulk density of 1.65 g/cm^3, an average specific particle diameter of 0.5 microns, and a uranium to oxygen ratio of 2.05 were carried out in an existing ICCM that has a cold crucible diameter of 120 mm, a 60 kw power supply, and a frequency of 1.76 MHz.

The melting process was conducted in an air atmosphere as follows: 1.2 kg of uranium dioxide powder was charged into a cold crucible with a graphite bottom. With the aim of producing a DUO_2 melt alloyed with a neutron absorber, gadolinium oxide (Gd_2O_3) was added to the source charge in the amount of 1.2 (wt. %) gadolinium contents. In the next experiment, chromium oxide (Cr_2O_3), which improves the wettability of ceramics by stainless steel [3], was added to the source charge in the amount of 1.4 (wt. %) chromium contents. To start the inductive heating process, a zirconium wire ring was placed in the powder at the top of the three-coil inductor. When power was supplied to the inductor, the zirconium ring and neighboring uranium dioxide powder particles were heated to the temperature at which the uranium dioxide becomes susceptible to electromagnetic energy—a frequency of 1.76 MHz. Uranium dioxide was then quickly heated and melted. During the melting process, 0.5 to 1 kg of uranium dioxide powder was periodically poured into the melt in the crucible. Then, the melting product was solidified by cooling the crucible with cooling water circulation through the section. A thin layer of non-melted uranium dioxide powder was on the molten uranium surface.

Melted uranium dioxide is very fragile and the samples cracked into separate segments while cooling in the crucible (see Fig.3).

Product samples were subjected to X-ray analysis by cobalt radiation with an iron filter. It was found that a thin layer of powdered particles, located on top and bottom parts of melted dioxide, are mixed uranium dioxide (U_3O_8). The lattice constant a varied between 5.438 and 5.469. The last value corresponds to the theoretical one for uranium dioxide. It is most likely that the decrease in value of a is caused by generation of uranium compounds with oxygen content more than UO_2 or the UO_2-U_4O_9 solution, and, by the inclusions of gadolinium and chromium oxides in structure [4].

From this it follows that, during preheating, uranium dioxide is oxidized to mixed oxides and then it is reduced to uranium dioxide at high temperatures (above 1450°C) with oxygen gas liberation. Uranium dioxide does not change during melting, the solidification of the melt, and the cooling of solidified product. This explains the dense monolith structure of DUO_2; there is also probably a protective outer layer of U_3O_8 powder which prevents oxygen penetration.

Fig.3. Samples of melted DUO_2.

From thermodynamic analysis and these facts, it is concluded that DU_3O_8 may be use as source material for melted and granulated DUO_2 production. This eliminates the very expensive step of converting DU_3O_8 to DUO_2 and makes this a low-cost process for dense DUO_2 production.

Analysis of gadolinium distribution in melted uranium dioxide was carried out in a microsound analyzer, model "Camebax MS46". Gadolinium and chromium contents at control points were: Gd: 1.26, 1.26, 1.20, 1.22, and 1.27; and Cr: 1.27, 1.31, 1.38, 1.25, 1.22, and 1.27 (wt %). It follows from this results that gadolinium and chromium are uniformly distributed in melted uranium dioxide.

The microstructure of melted DUO_2 is shown in Fig.4. The specific density of melted uranium dioxide was measured by the hydrostatic method and was in the range from 10.15 to 10.40 g/cm^3. Such a value is attributable to the presence of small gaseous pores (average diameter about 200 microns) in the DUO_2 that was adjacent to the cold crucible walls. They were formed when oxygen and volatile uranium oxides were liberated. Gaseous porosity may be eliminated by improving melting technology.

In the second experiment, DUO_2 melt was drained through a hole in the bottom of the graphite crucible. Produced granules were pear-like in shape (Fig.5). This experiment proved that it is feasibility to produce granulated DUO_2 from the melt.
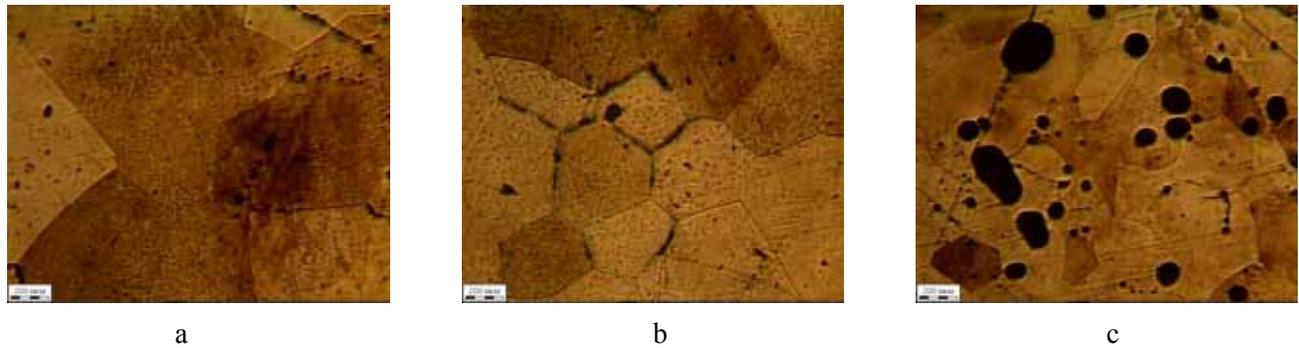
Fig. 4. Microstructure of melted DUO$_2$ samples taking from: a – the middle of the crucible; b – within 30 mm of the cold crucible wall; c – adjacent to the cold crucible wall.

Fig.5. DUO$_2$ granule produced by draining the melt through hole in graphite crucible bottom.

THE STUDY OF DUO$_2$–STEEL CAST CERMET PRODUCTION

The uranium dioxide–stainless steel system is one in which the solid surface of uranium dioxide is not "wetted" by molten steel. That is, the interfacial tension of uranium dioxide–stainless steel melt is very high and surface forces prevent impregnation of liquid into pores and capillaries. To resolve this problem, melted uranium dioxide was reduced to fine particles of 3–8 mm diameter (bulk density 4.7 g/cm^3), and 2 wt % chromium oxide was added in experiments. This particle size range was determined by the need of free space for molten steel penetration.

The experimental process was conducted as follows: uranium dioxide and steel were alternately charged with 150 and 170 grams, respectively, into aluminum oxide crucibles. The charge was heated to 1600°C in an argon atmosphere. Uranium dioxide pores were impregnated with molten stainless steel. Then, the sample was kept at temperature 1650–1700°C for 10 minutes. The excess molten stainless steel (needed for impregnation of crystalline powder DUO$_2$) was concentrated in the top of cermet ingot.

Samples of cast cermet with 1:1 mass proportion of DUO_2 and stainless steel 1:1 were produced. The ingot and hollow ingot cast metal matrix with impregnated uranium dioxide particles are shown in Fig.6. The specific density of the cast cermet samples was about 9.2 g/cm^3.

Fig. 6. Samples of cast cermet DUO_2–stainless steel.

The structure of the produced cermet was studied microscopically. Some of these photographs are shown in Fig.7. These photographs show that the stainless steel (black) is tightly adjacent to the DUO_2 (grey), therefore showing the elimination of pores.
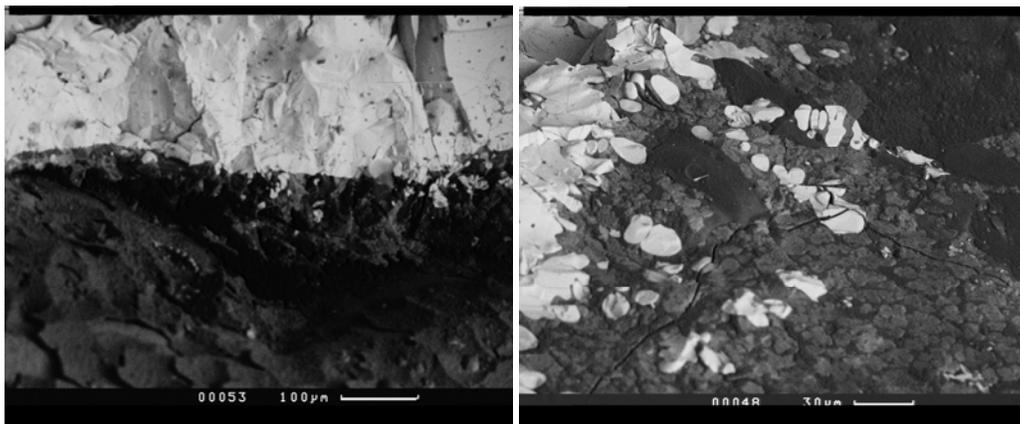
Fig.7. Structure of cast cermet DUO_2–stainless steel.

Free space between metal and ceramics phases was not detected. Strong cohesive forces between phases are proved since microbreaks do not go through ceramic and metal phases and are not interrupted and shifted.

DETERMINATION OF BASIC PARAMETERS FOR GRANULATOR DESIGN APPLIED FOR PRODUCTION OF DUO$_2$ GRANULES

The cooling rate and path length of particle in different gas medium were computed using the assumption that spherical droplets move and lose heat as a result of heat transfer by convection and radiation. The heat transfer equation is given by

$$\frac{dq}{dt} = \left(\alpha_{conv} + \alpha_{rad}\right)\left(T_{surf} - T_g\right) \tag{1}$$

where: α_{conv} and α_{rad} are convection and radiation heat transfer coefficients, and
T_{surf} and T_g are temperatures of particle surface and gas medium.

Particles dropped into a gas atmosphere lose heat at the expense of heat transfer by convection:

$$dH = -\alpha_{conv}S(T - T_g)\,dt, \tag{2}$$

where S – particle surface.

The convection heat transfer coefficient is determined by the well known criteria dependence for case "particle in gas flow":

$$Nu = 2 + 0.033Pr^{0.33}\,Re^{0.54} + 0.35Pr^{0.356}\,Re^{0.58} \tag{3}$$

$$Re = \frac{vd}{v_\text{г}} \;;\;\; Nu = \frac{d\alpha_{конв}}{\lambda_\text{г}} \;;\; Pr = \frac{\mu c_\text{г}}{\lambda_\text{г}} \tag{4}$$

Heat transfer by radiation is described by:

$$dH = \varepsilon C_0 S\left[\left(\frac{T_{surf}}{100}\right)^4 - \left(\frac{T_g}{100}\right)^4\right]dt \tag{5}$$

Particle trajectory and rate is determined from equations of moving spherical particle in gas medium of given density:

$$\frac{dv_{hor}}{dt} = g\,\frac{\rho - \rho_g}{\rho} - \frac{3f\rho_g v}{4d\rho}\,v_{hor} \;\;\; ; \tag{6}$$

$$\frac{dv_{vert}}{dt} = -\frac{3f\rho_\text{г} v}{4d\rho}\,v_{vert}\,, \text{ and } v = \sqrt{v_{hor}^2 + v_{vert}^2}\,. \tag{7}$$

where, $f = 24/Re$, if $Re < 2$;

$f = 18.5\ Re^{-0.5}$, if $Re = 2 - 500$;

$f = 0.44$, if $Re = 500 - 2*10^5$

The cooling of liquid spherical particle is described by the differential equation

$$\frac{\lambda_l}{r^2}\frac{d}{dr}\left(r^2\frac{dT}{dr}\right) = c_l\rho_l\frac{dT}{dt} \tag{8}$$

with initial condition $T(r, 0) = T_0$ and boundary condition

$\lambda_l\dfrac{dT(R,t)}{dt} = f(\upsilon, T_{surf})$, where $f(\upsilon, T_{surf})$ is the given function determined from heat transfer by convection.

Cooling two-phase spherical particle of radius R (at $0 < r < r_f$ – liquid phase, $r_f < r < R$ - solid phase) is described by the following equations:

$$0 < r < r_f \qquad \frac{\lambda_l}{r^2}\frac{d}{dr}\left(r^2\frac{dT}{dr}\right) = \lambda_l\rho_l\frac{dT}{dt} \tag{9}$$

$$r_f < r < R \qquad \frac{\lambda_s}{r^2}\frac{d}{dr}\left(r^2\frac{dT}{dr}\right) = \lambda_s\rho_s\frac{dT}{dt} \tag{10}$$

with joining condition

$T(r_f - 0) = T(r_f + 0) = T_{mp}$

and boundary condition

$\lambda_s\dfrac{dT(R,t)}{dt} = f(\upsilon, T_{surf})$

and condition determining change of position of solidifying front

$$\lambda_l\frac{dT(r_f - 0, r)}{dr} - \lambda_s\frac{dT(r_f + 0, r)}{dr} = L\rho\frac{dr_f}{dr}$$

Computations for uranium dioxide particles of diameter from 0.6 up to 1.4 mm were performed. Initial temperature of uranium dioxide melt was assumed 10 degrees above melting point. Initial velocities of dropping uranium dioxide particles were 6.3 and 10.5 m/sec. These velocities are characteristic for a dispergator diameter of 40 mm and a maximum rotation speed 5000 in minute. The distances covered by particles, up to complete solidifying (it is taken as radius of designed granulator) in nitrogen and helium atmospheres, were computed. It follows from computations that a granulator with a rather large diameter of $7.1 \times 2 = 14.2$ meters is required for completely solidifying molten droplets of minimum diameter (0.6 mm) in helium atmosphere, when the best heat transfer regime is realized. It is evident that such a large granulator is not acceptable for pilot facility.

In order to decrease the size of the facility, the special case of a molten droplet being only partially solidified is considered. It follows from calculations that 27% of total mass will be localized in solidified layer with thickness (S) of 0.1 radiuses and at increasing thickness up to 0.2 and 0.33 radiuses – 49% and 70%, accordingly. Computed path lengths traversed by dioxide droplets of different diameters are presented in Table I.

Table I. Distances Covered by Molten Droplets up to Partial Solidification

Atmosphere	Initial velocity m/sec	Particle diameter mm	Distances covered by particle			
			S = 0.33R	S = 0.2 R	S = 0.15R	S = 0.1R
Nitrogen	6.3	0.6	2.02	1.1	0.9	0.6
		0.8	3.1	1.47	0.92	0.48
		1	4.3	2.1	1.1	0.67
		1.2	5.6	3.1	1.7	0.99
		1.4	6.9	3.5	1.9	1.1
Nitrogen	10.5	0.6	3.2	1.77	1.24	0.83
		0.8	4.2	2	1.3	0.89
		1	5.1	2.53	1.45	0.93
		1.2	6.2	2.9	1.9	1
		1.4	7.2	3.2	2.1	1.1
Helium	6.3	0.6	0.9	0.49	0.35	0.23
		0.8	1.6	1	0.7	0.39
		1	2.2	1.2	0.83	0.55
		1.2	2.85	1.4	0.93	0.74
		1.4	3.5	2	1.2	0.9
Helium	10.5	0.6	1.6	0.9	0.6	0.4
		0.8	2.8	1.75	1.15	0.85
		1	4	2.24	1.3	0.9
		1.2	5.2	2.34	1.52	0.94
		1.4	6.5	3	2	1.1

It is assumed that, when solidified, the granule thickness will be more than 1/5 radius (half mass of particle solidified) and the dropping granules will not be crushed in receiver. It follows from Table I that the diameter of designed granulator will be 2.2 m. Therefore, it is feasible to obtain DUO_2 granules with diameters 0.8 and 0.6 mm at initial velocities 6.3 and 10.5 m/sec in a helium atmosphere. DUO_2 production with a 0.6 mm in diameter orifice, at initial velocities 6.3 m/sec, will be possible in nitrogen atmosphere.

It should be noted that the melt inside the cold wall crucible will solidify when it collides against intensive cooling walls of the granulator and when dropping into the receiver. Therefore, the above mentioned diameters of granules are minimum values, and in actual practice, it is expected to produce granules that are larger than that computed.

The designed receiver will be equipped with intensively cooled walls, vibrator, and screw conveyer to prevent the accumulation of hot granules. Such a granulator design prevents particles from sticking together and the sintering processes.

DESIGNING OF INDUCTION MELTER WITH COLD CRUCIBLE FOR STUDY DUO_2 MELTING AND GRANULATION

Conducted experiments strengthen our hypothesis about the feasibility of producing melted DUO_2 in ICCM with a cold crucible diameter of 120 mm at a frequency of 1.76 MHz. A standard high frequency power supply, with output power 100 Kw, was chosen for the pilot facility for DUO_2 granules production. Based on computation of cooling rate and drop path length in different gas medium, the pilot facility will be equipped with a granulator of 2.2 m in diameter. An overview schematic of pilot facility for production of DUO_2 granules is shown in Fig. 8.

CONCLUSIONS

1. The feasibility of producing molten DUO_2 from mixed oxides in an induction cold crucible melter at a frequency of 1.76 MHz was thermodynamically confirmed and experimentally proven.

2. Depleted U_3O_8 (generated from direct conversion of DUF_6) may be used as the source material for melting and granulated DUO_2 particulate production. This enables efficient, high-throughput production of granulated DUO_2 from melts.

3. A uniform distribution of additives in the DUO_2, to modify its chemical and nuclear properties and to improve cask performance, was attained.

4. It was experimentally proven that it is feasible to produce cast cermets from the melted DUO_2 and stainless steel, including the production of the cermet in a hollow ingot shape.

5. Thermal computations were done to establish the characteristic dimensions for melting and granulating chambers. A melting chamber with a power supply (frequency 1.76 MHz, output power 100 kw) was designed. A pilot facility, including melting and granulating chambers, was designed. The fabrication of the melting and granulating chambers is underway now.
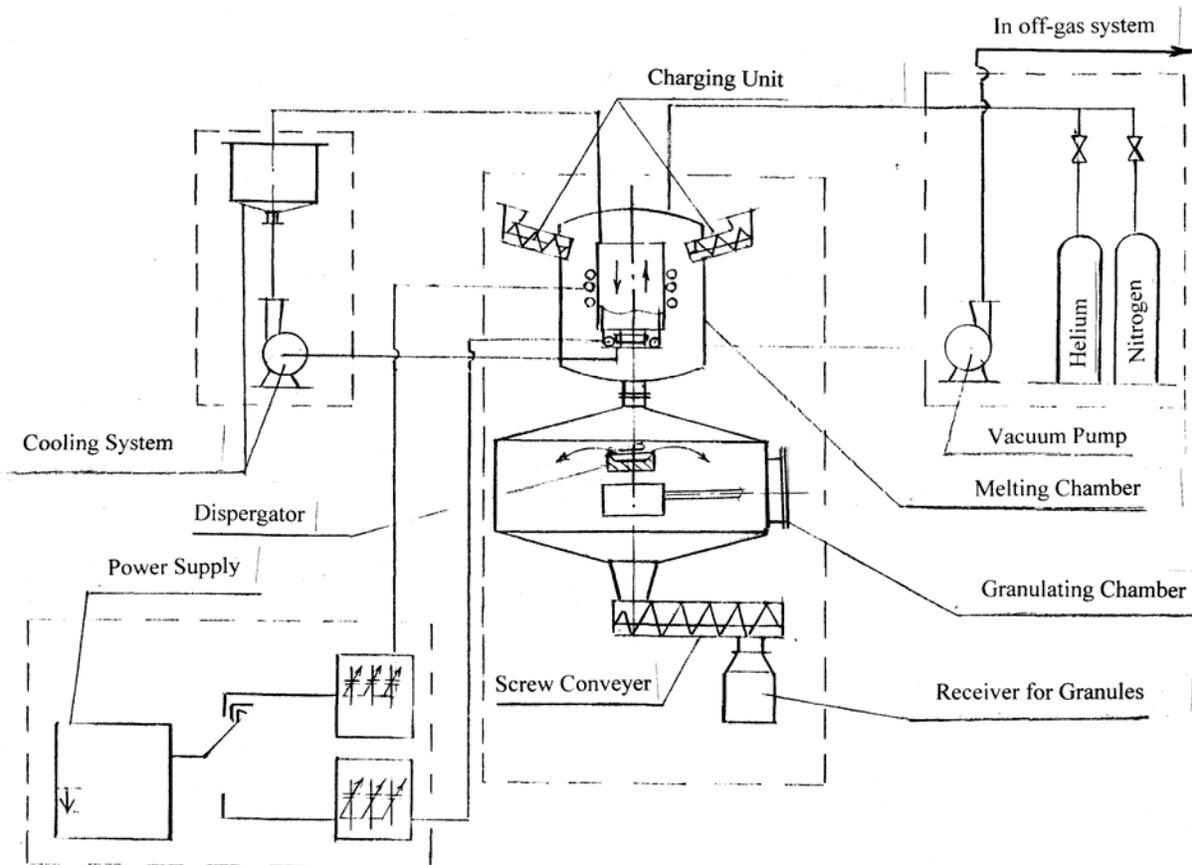
Fig.8. Principal scheme of pilot facility for melting and granulation of DUO$_2$.

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