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Preparation of homogeneous $(Th_{0.8}U_{0.2})O_2$ pellets via coprecipitation of $(Th,U)(C_2O_4)_2 \cdot nH_2O$ powders

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Abstract

Thorium and uranium dioxides form a complete series of solid solutions. The formation from the individual oxides can be performed only by extensive co-milling and reaction at high temperatures. In this study, we prepared 80% ThO_2–20% UO_2 via coprecipitation of the mixed oxalates from nitrate solutions using an excess of oxalic acid. The parameters which may effect the powder properties were investigated, such as oxalic acid and thorium concentrations, temperature and type of agitation. The specific surface of the oxalates and their derived oxides were measured. Among the precipitation parameters, temperature of 10°C and mechanical stirring resulted in the highest surface area. The coprecipitated Th,U(IV) oxalate powders were decomposed at 350°C, calcinated at 900°C each for 24 h in air and were reduced during 2 h at 650°C in H_2 atmosphere. X-ray diffraction resulted in a single-phase mixed oxide solid solution. The green densities of pellets made from these mixed oxides varied between 36 and 38% TD. Pellets were sintered in flowing CO_2 at 1100°C for 30 min and achieved 81% TD. © 1997 Elsevier Science B.V.

1. Introduction

It is well known that Th^{4+} and U^{4+} have similar ionic radii [1] and ThO_2 and UO_2 have a similar crystallographic structure (CaF_2 type, cubic). They have very close lattice constants ($a_{UO_2} = 5.47$ Å, $a_{ThO_2} = 5.59$ Å) [2]. Therefore, mixed in any ratio, they can produce a $(Th,U)O_2$ solid solution having the same crystallographic structure. This system is expected to be used as a mixed oxide fuel for a thermal neutron breeder reactor and also for a high temperature gas cooled reactor. Mixed-oxide pellets are generally prepared by conventional metallurgical powder techniques. The method mentioned is based on obtaining high density pellets by compaction and subsequent sintering of powders, mixed at required ratios.

In this study, instead of conventional metallurgical preparation stages of individual oxides, we prepared the mixed oxide via coprecipitation of the mixed oxalates from nitrate solutions. The fact that the coprecipitated thorium and uranium (IV) oxalates can be decomposed and calcined in air and converted to a single-phase oxide solution makes this an excellent method of producing the mixed oxide fuel. Formation of a solid solution from the individual oxides can be accomplished only with extensive co-milling and reaction at 1700°C. The degree of homogeneity achieved with the coprecipitation undoubtedly would be superior to that achieved with the reaction of the separate oxides [3].

2. Experimental

The initial materials, ADU and commercial thorium nitrate salt are provided from Çekmece Nuclear Research and Training Center. The flow sheet of this process is shown in Fig. 1. As clearly seen in the flow sheet the

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process is based on two principal steps. The first step includes the preparation of the Th,U(IV) nitrate solution and coprecipitation of $(Th,U)(C_2O_4)_2 \cdot nH_2O$ powders. The second step consists of the preparation of $(Th,U)O_2$ pellets following decomposition, calcination and reduction operations of the $(Th,U)(C_2O_4)_2 \cdot nH_2O$ powders. The preparation of $(Th,U)(C_2O_4)_2 \cdot nH_2O$ powders was performed with addition of an excess amount of oxalic acid to the Th,U(IV) nitrate solutions. In spite of the oxidation stages the valency of Th is 4 + and U in general exists as 6 + in solution. For a homogeneous precipitation of two different ions their solubility product values must be similar. While the solubility product values of Th(IV) and U(IV) oxalates are similar, this value is considerably different for U(VI) oxalate. Therefore, uranium must be reduced in the initial stage. U(IV) sulphate is rather stable to oxidation due to the strong complex formation between U^{4+} and SO_4^{2-} [4]. For the preparation of the nitrate solution, sulfuric acid was chosen as a suitable medium for the reduction of the uranyl ion and the reduction was performed by using zinc. The parameters which effect the reduction of U(VI) to U(IV) such as acid concentration, the amount of zinc and reduction time were investigated. The $UO_2 \cdot 2H_2O$ was precipitated from sulfate solution

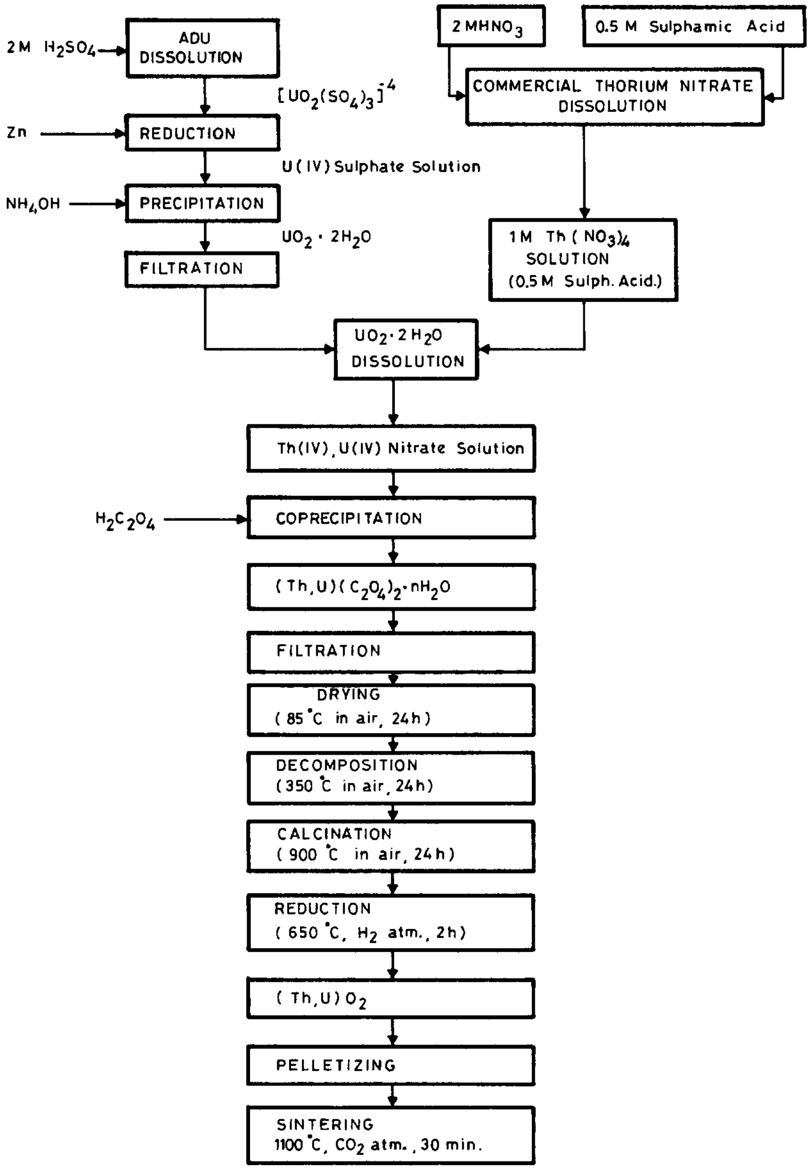

Fig. 1. Flow-sheet of the process.

with an excess amount of 3M ammonium hydroxide, therefore zinc was eliminated by forming the zinc–ammonia complex. The effect of nitric acid concentration such as 0.1, 0.3, 0.5 and 1.0 M was investigated for the determination of suitable acidity to dissolve $UO_2 \cdot 2H_2O$ precipitate. On the other hand, the necessary amount of sulphamic acid to prevent reoxidation of U(IV) was determined. Thorium stock solution which contains 2 M nitric acid and 0.5 M sulphamic acid as stabiliser was prepared from commercial thorium nitrate. The $UO_2 \cdot 2H_2O$ precipitate was rapidly dissolved with thorium stock solution and then the Th,U(IV) nitrate solution was prepared. The precipitation of mixed oxalates was performed from this solution by using an excess amount of oxalic acid. The parameters which may effect properties of the powder such as the oxalic acid and thorium concentration, the amount of oxalic acid, temperature and type of agitation were investigated. The behaviour of these powders, under the different decomposition and calcination conditions, was investigated. The specific surface area of the mixed oxalates and the derived oxides were also measured using a high speed surface area analyser (Micrometrics 2200 model). After the optimisation of the decomposition and calcination conditions, the oxalate powders were reduced in a hydrogen atmosphere for 2 h at 650°C. The degree of reduction was controlled by thermal analysis using a Shimadzu thermal analyser. Following the reduction, the produced mixed oxide powders blended with 0.5% zinc stearate were compacted without additional powder treatments. The pellets were sintered for 30 min at 1100°C in a CO_2 atmosphere, later replaced by CO_2 with H_2 and this operation was continued for 20 min. The green and sintered density of pellets was determined, based on weight and geometric measurements.

3. Results and discussion

Table 1
Decomposition, calcination and reduction conditions of oxalate powders

	Sample no.		
	I	II	III
Decomposition	350°C (24 h)	350°C (24 h)	350°C (24 h)
Calcination	–	900°C (24 h)	650°C (24 h)
Reduction	650°C (2 h), H_2 atm.	650°C (2 h), H_2 atm.	650°C (2 h), H_2 atm.

The uranium content of the first initial material ADU is determined as 77% (±1%) using potentiometric titration methods. The thorium content of commercial thorium nitrate is determined as 40.1% (±1%) by the EDTA titration method using pirocatehole violet indicator. During the reduction of U(VI) to U(IV) in sulphuric acid media, 1.5 M sulfuric acid, a 50% excess of a stoichiometric amount of zinc and 1 h reduction time were determined as optimum reduction conditions (Fig. 2a, b and c). During the precipitation of $UO_2 \cdot 2H_2O$ from the U(IV) sulphate solution, adjusting the pH to 9.5 using an excess amount of 3 M ammonium hydroxide, it was determined by AAS that zinc is completely removed by forming the complex. The suitable concentration of nitric acid and sulphamic acid, as stabiliser, were determined to be 1 and 0.5 M, respectively, to dissolve this precipitate.

The most important parameters related to the coprecipitation which effect the powder properties are temperature and type of agitation. The specific surface values of the coprecipitated powders which are 7.0 and 8.0 m^2/g at 10°C with magnetic and mechanical agitation, respectively, decrease to 2.0 and 2.1 m^2/g at 70°C under similar agitation conditions. When the precipitation is performed in a conical reactor agitated with argon from the bottom, the specific surface decreases to 5.4 m^2/g at 10°C and to 1.6 m^2/g at 70°C. These results indicate that the most suitable precipitation occurs at 10°C with mechanical agitation. The optimum parameters for preparing

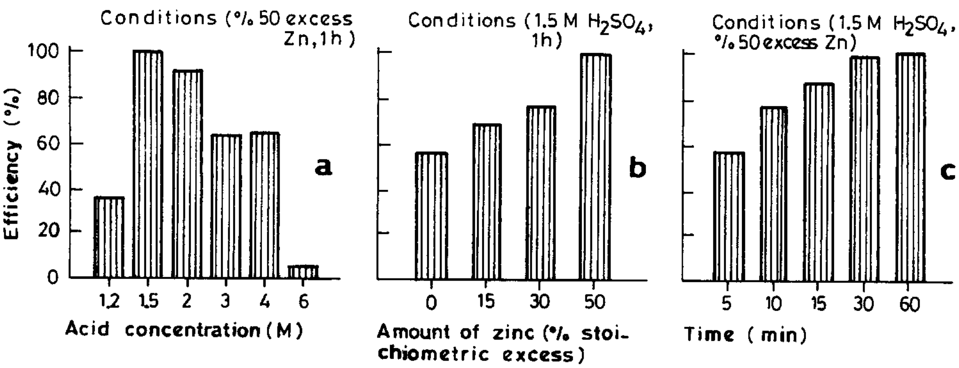

Fig. 2. Influence of acid concentration, amount of zinc and reduction time on U(IV) efficiency.

$(Th,U)(C_2O_4)_2 \cdot nH_2O$ powders from a Th,U(IV) nitrate solution with the addition of oxalic acid are: 1 M thorium and oxalic acid concentrations, 200% excess of a stoichiometric amount of oxalic acid, 10°C temperature, mechanical agitation and 1 h agitation time.

To investigate the effect of carbon content on the reduction and sintering, the powders which were coprecipitated using the optimum parameters, were calcined at different temperatures and then reduced (Table 1).

The reduced powders were oxidised in air at 900°C using a thermal analyser to control the degree of reduction. After examination of the TGA and TD curves of the samples I and III, it was seen that a lot of carbon was retained in these samples and that reduction was not achieved. From the TGA and TD curves of sample II, it was observed that the oxidation of carbon does not occur and the reduction was performed completely. The specific surface area values of the mixed oxalates and derived oxides are given in Table 2. These values also confirm the results of the thermal analysis.

The specific surface area of the oxide powders derived from oxalate samples I and III were considerably high because of their high carbon content depending on low calcination temperatures. These experiments show that the decomposition and calcination processes of the powders must be performed under the conditions of sample II. The powders were decomposed and calcined as previously determined and reduction was performed in a hydrogen atmosphere for 2 h at 650°C. The green densities of the pellets made from these mixed oxides were found to be in the order of 37% TD. The green pellets were sintered in a program controlled furnace. The sintering was carried out at 1100°C for 30 min under a CO_2 atmosphere, H_2 was then introduced to replace the CO_2 and the operation was continued for 20 min. The densities of the sintered pellets were found to be 81% TD. Higher densities are expected with high temperature sintering. The influence of previous conditioning (granulation or precompaction) is also very important in reaching higher densities. This pre-conditioning may include blending additives for further processing such as lubricants and binders for modifying the final pellet structure [5,6]. Many authors stressed that the key step in the development of thorium–uranium fuel is the preparation of homogeneous oxide mixtures [7]. The X-ray diffraction diagram of the mixed oxide powder which was produced using the optimum conditions is illustrated in Fig. 3. The data are in good agreement with the ASTM data and it is clearly seen that a single-phase solid solution was formed.

Table 2
BET surface area of oxalates and derived oxides

Sample No.	BET surface area (m^2/g)	
	Th–U(IV) oxalate	mixed oxide
I	7.6	24.0
II	4.7	4.4
III	9.6	22.5

It is well known that coprecipitation can occur in different forms (inclusion, occlusion, isomorph, chemical, etc.). Th^{4+} and U^{4+} having similar ionic radii and electronic configurations have also very close chemical properties. On the other hand the solubility product constants of thorium oxalate and uranium (IV) oxalate are very close. In this case, the coprecipitation is very homogeneous and it is expected that the form of coprecipitation is isomorphous. In the crystal lattice, both U and Th are capable of mutual replacement and this capability strongly depends on their formation of the same type of chemical bond and their ability of crystallisation in the same system. The formation of a continuous series of mixed crystals at the

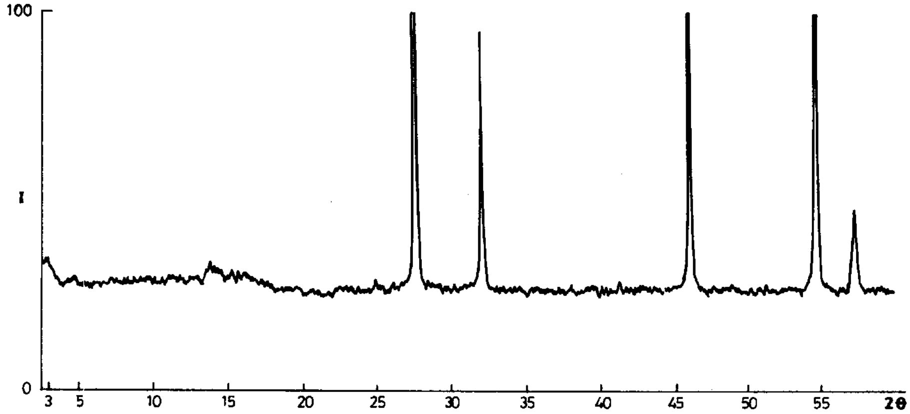

Fig. 3. XRD diagram of the mixed oxide powder produced via coprecipitation.

Table 3
Lattice spacings d_{hkl} and 2θ data of the oxalate samples

$Th(C_2O_4)_2 \cdot 6H_2O$		$U(C_2O_4)_2 \cdot 6H_2O$		$(Th,U)(C_2O_4)_2 \cdot 6H_2O$	
d (Å)	2θ	d (Å)	2θ	d (Å)	2θ
7.82	11.30	6.34	13.95	7.82	11.30
6.41	13.80	5.37	16.50	6.43	13.75
4.98	17.80	3.41	26.10	5.43	16.30
4.56	19.50	3.17	28.10	5.26	16.85
3.91	22.70	3.07	29.10	3.20	27.90
3.24	27.50	2.72	32.95	3.07	29.10
2.99	29.90	2.07	43.70	2.88	31.00
2.89	30.90			2.73	32.80
2.68	33.40			2.09	43.30

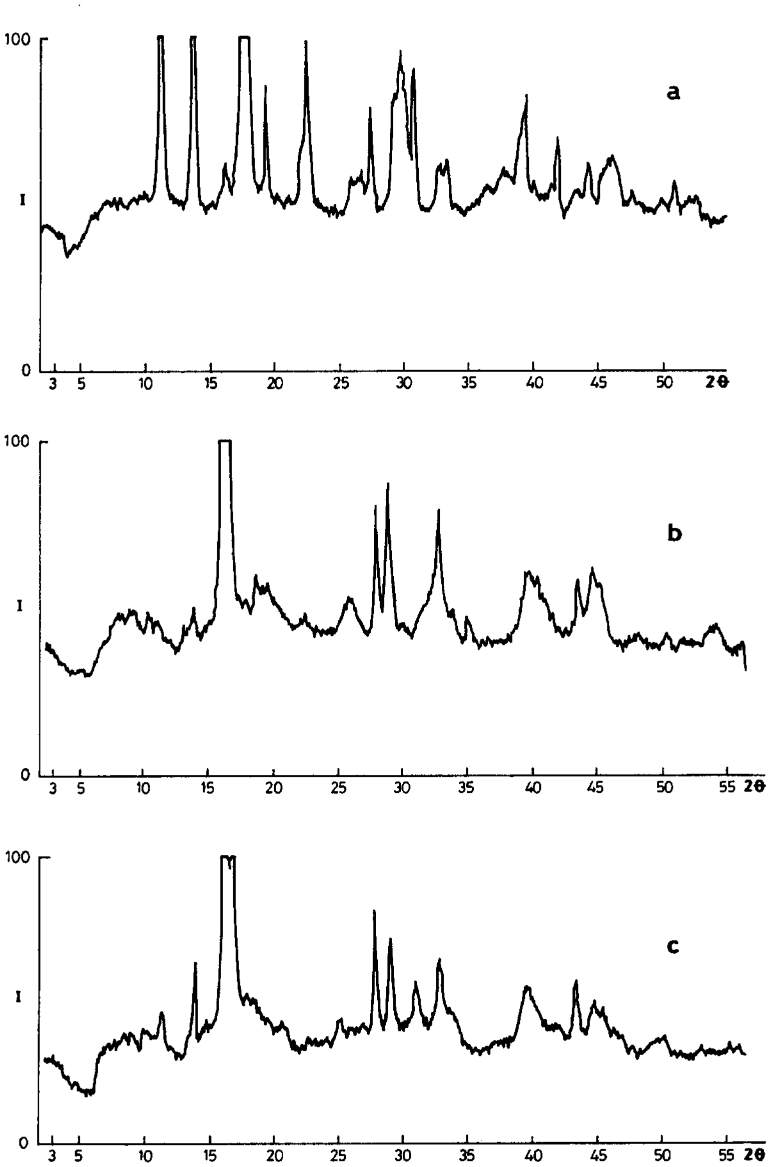

Fig. 4. XRD diagrams of oxalate powders. (a) Thorium oxalate, (b) uranium (IV) oxalate and (c) coprecipitated (Th,U) oxalate

isomorph replacement is widely known as a form of solid solution. To have an idea on the coprecipitation form of mixed oxalates, the X-ray diffraction diagrams of the individually precipitated uranium and thorium oxalates and the coprecipitated oxalate are taken. The d_{hkl} and 2θ data and X-ray diffraction diagrams related with these samples are given in Table 3 and Fig. 4.

These results reinforce our previous impression that the coprecipitation is generally isomorphous and this occurrence facilitates the formation of solid solutions at a relatively low sintering temperature, even in this study the formation of the solid solution is realised after the reduction step following calcination at 900°C before sintering. In comparison with conventional powder techniques where the solid solution formation is not complete at 1100°C during the first-stage sintering, this method provides considerable advantage from homogenisation and the formation of the solid solution [8]. In this study suitable powder properties, high homogeneity and the formation of a solid solution are achieved. It is necessary to investigate the optimisation of different parameters of pre-conditioning, pelletizing and sintering conditions in order to reach high densities.

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