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THE EFFECT OF ADDITIVES ON THE DENSIFICATION OF
URANIA-THORIA COMPOSITIONS

by

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Metallurgy Division

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FOREWORD

This investigation was done by J. A. Crookston, C. K. Russell, and J. D. Conley of A. P. Green Fire Brick Company at Mexico, Missouri, on Subcontract No. 31-109-38-721 from Argonne National Laboratory. The information in this report was condensed from "The Effects of Certain Additives on the Sintering Characteristics of Urania-Thoria Mixtures" written by the above investigators at the termination of their contract. Because of its length and detail, the report was condensed for publication as an Argonne National Laboratory Report.

THE EFFECT OF ADDITIVES ON THE DENSIFICATION OF URANIA-THORIA COMPOSITIONS

by

George D. White

ABSTRACT

An investigation is reported of the effect of several oxide additives on the densification of UO_2 - ThO_2 compositions in which U_3O_8 is the initial uranium oxide. The investigation also determined the effects on densification of variation of the compaction pressure and of the pretreatment of the oxide powders. The validity of results were checked by two forming techniques, dry pressing and extrusion. The results are indicated as follows:

1. Additives had an increasing effect on densification with decreasing ThO_2 content.
2. The oxides of transition elements were most effective as additives for improving the densification.
3. Varying the forming pressure had little effect on densification.
4. Precalcination of the initial powders was effective in improving densification.
5. Similar results as above can be achieved with extruded as well as dry-pressed specimens.

INTRODUCTION

The compounds UO_2 and ThO_2 form a continuous series of solid solutions⁽¹⁾ when protected from oxidation. Both compounds have the fluorite structure, but, unlike ThO_2 , UO_2 takes oxygen into solution and forms higher oxides. Because of the oxidation behavior of UO_2 with its accompanying volume expansion, UO_2 , or UO_2 -containing shapes, must be sintered in a protective atmosphere.

When heated in air, UO_2 oxidizes to U_3O_8 , which is stable to approximately 1150°C ^(2,3); with prolonged heating above this temperature, the U_3O_8 decomposes to lower oxides, ultimately to UO_2 . It has been demonstrated⁽⁴⁾ that shapes fabricated from mixtures of U_3O_8 - ThO_2 can be

sintered in air without disruptive physical effects. The resulting material is a solid solution of $\text{UO}_{2+x}\text{-ThO}_2$ with stoichiometry rich in oxygen but maintaining the fluorite crystal structure. To produce $\text{UO}_2\text{-ThO}_2$ shapes with the 2:1 ratio of oxygen to cation requires that the shapes be sintered in an inert atmosphere, a hydrogen atmosphere, or in vacuum. The air-sintered $\text{U}_3\text{O}_8\text{-ThO}_2$ shapes can be reduced to dioxide by refiring in H_2 .

Considerable effort has been devoted to the development of a $\text{UO}_2\text{-ThO}_2$ nuclear fuel using the molecular equivalent of U_3O_8 as the initial oxide of uranium.⁽⁴⁻⁶⁾ Resulting from this work was the manufacture of a fuel loading for Argonne's BORAX-IV Reactor.⁽⁵⁾ In view of the interest in the technique, it was thought desirable to investigate the possibility of improving the sinterability of the material by adding small amounts of different compounds, as has been done with ThO_2 ⁽⁷⁾ and other materials.

The main objective of this investigation was to determine the effects of several different additives on densification of $\text{U}_3\text{O}_8\text{-ThO}_2$ compositions. Additional objectives of this investigation were: (1) to establish the effect on densification of varying the pelletizing pressure, (2) to determine the effect of pretreatment of the oxide powders before forming into shapes, and (3) to establish if these effects would be valid when the forming technique was changed from dry pressing to extrusion.

PROCEDURES AND RESULTS

Effect of Additives on Densification of $\text{UO}_2\text{-ThO}_2$ Composition when the Initial Uranium Oxide is U_3O_8 .

Procedure:

The m/o compositions selected for investigation were as follows:

	Mole Per Cent					
UO_2 -	10	25	50	75	90	95
ThO_2 -	90	75	50	25	10	5

The UO_2 component was obtained by adding a molar equivalent of U_3O_8 , which reduced during sintering to the proper molar ratio of UO_2 . The U_3O_8 used in the compositions had a maximum grain size of 65 mesh, and the ThO_2 all passed through 325 mesh.

The oxide additives were added either as the oxide or as a compound which decomposes to the oxide when heated. All of the additives were reagent-grade chemicals. The additives used were: Li_2CO_3 ,

Na_2CO_3 , MgCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, SrCO_3 , BaCO_3 , TiO_2 , CeO_2 , V_2O_5 , Fe_2O_3 , CuO , ZnO , CaO , H_3BO_3 , Al_2O_3 , $\text{H}_2\text{SiO}_2 \cdot n\text{H}_2\text{O}$, and PbO_2 . In selecting these additives, the valence group and the thermal neutron cross section of the cation were the main considerations. Cations from a variety of the atomic groups and with low thermal neutron cross sections were desired. In some cases the cross section is low for only one isotope of the cation, i.e., boron.

The quantity of additives were calculated for the batch so that 5 and 10 m/o of the oxide would be present in the fired state. For each of the UO_2 - ThO_2 ratios both 5 and 10 m/o of additives were calculated. Batches of 300 g were compounded for each composition. In addition to the three oxide components, 0.25% CMC (carboxy-methyl-cellulose) was added as a temporary binder.

After weighing, the batch was transferred to a small sealed jar and tumbled on a roller mill for 10 min. The batch was then transferred to a kitchen-type mixer where it was tempered with water to bring the batch to a dry-press consistency. Pellets, 2.54 cm in diameter by about 1.27 cm long, were pressed from the batches on a small Denison press at 176 kg/cm^2 .

After pressing, the pellets were dried at room temperature in air for 24 hr, followed by drying at 100°C to 105°C in air for 24 hr. The dried pellets were measured with a micrometer for shrinkage calculations. Pellets were set on tabular alumina grains spread on an alumina setter plate and sintered. Five pellets were fired at 1700°C for one hour and one each at 1600, 1500, and 1400°C . All firings were done in a gas-fired kiln. The baffle walls of the kiln were arranged to prevent flame impingement on the specimens.

After sintering, the pellets were measured with a micrometer and weighed. The bulk density and firing shrinkage were calculated, and the apparent specific gravity and apparent porosities were determined on a Jolly balance.

Results and Discussion:

The pellets produced by means of this procedure were not the best in appearance. They had numerous cracks, and the best densities were only about 90% of theoretical. Pellets containing 95 and 90 m/o UO_2 were so soft and crumbly that these compositions are not included in the results. Owing to the poor condition of many of the pellets, bulk densities would not be meaningful as a measure of densification; therefore, the apparent specific gravity will be used as a means of comparing densification effects.

With increasing ThO₂ content, sintered compositions of UO₂-ThO₂ containing no additives had increasing densities. Since all of the compositions were fired and cooled with oxygen present, this result indicates an inverse relationship between the densification and the amount of oxygen retained in the solid solution.⁽⁸⁾ The complete deterioration on cooling of specimens containing 90 and 95 m/o UO₂ was due either to the oxidation of the very dilute ThO₂ solution or to the oxidation of free UO₂ which would be present if equilibrium was not attained. Anderson et al.,⁽⁹⁾ stated that a minimum of 22% ThO₂ is required to stabilize the UO₂ fluorite structure in air below 1400°C.

The effects of the various additives on the densification of the $\text{UO}_2\text{-ThO}_2$ compositions were so nearly the same for the 5 m/o and the 10 m/o additions that only the 5 m/o is considered here. Figures 1, 2, 3, and 4 show the effect on apparent specific gravity of the various additives for the several $\text{UO}_2\text{-ThO}_2$ compositions at the four sintering temperatures used.

Two generalizations can be inferred from these figures: with increasing ThO₂ content, the effect of the additives on the apparent specific gravity decreases, and among the additives investigated, the oxides of the transition elements had the largest positive effect on the apparent specific gravity.

Fig. 1. Effect of Various 5 m/o Additions on Apparent Specific Gravity of UO_2 - ThO_2 Compositions Sintered at 1700°C . Initial Uranium Oxide was U_3O_8 . Additions were Oxides of Indicated Elements.

Fig. 2. Effect of Various 5 m/o Additions on Apparent Specific Gravity of UO_2 - ThO_2 Compositions Sintered at 1600°C . Initial Uranium Oxide was U_3O_8 . Additions were Oxides of Indicated Elements.

Fig. 3. Effect of Various 5 m/o Additions on Apparent Specific Gravity of UO_2 - ThO_2 Compositions Sintered at 1500°C . Initial Uranium Oxide was U_3O_8 . Additions were Oxides of Indicated Elements.

Fig. 4. Effect of Various 5 m/o Additions on Apparent Specific Gravity of UO_2 - ThO_2 Compositions Sintered at 1400°C . Initial Uranium Oxide was U_3O_8 . Additions were Oxides of Indicated Elements.

These effects undoubtedly cannot be considered as resulting from the production of defects as is the case when a minute addition is made to a pure oxide and enhances the sinterability. These compositions are ternary oxide systems with a variable oxygen content. In compositions which resulted in a sizable positive effect on the apparent specific gravity, the 5 m/o component most likely acted as a flux, producing a small amount of glassy phase during sintering.

The results indicate that the largest increases in apparent specific gravity effected by 5 m/o additions were with CuO , Fe_2O_3 , V_2O_5 , TiO_2 , Li_2O , and BaO .

Effect of Pelletizing Pressure on Densification in Air of Compositions of $\text{UO}_2 + \text{ThO}_2 + \text{R}_x\text{O}_y$ when the Initial Uranium Oxide Is U_3O_8 .

Procedure:

The object of this investigation was to determine what effect, if any, the forming pressure would have on the densification of the pellets. The same molar per cent ratios of UO_2 - ThO_2 were used as in the first section, with the exception of the 95 m/o and 90 m/o UO_2 compositions, which were omitted because of the inability to produce sound specimens

of these compositions. The additives included in these compositions were only those which were shown to be beneficial to densification in the first section. The UO_2 content of the compositions was again obtained by adding the molecular equivalent of U_3O_8 in the initial batch.

Compositions were made of each of the UO_2 - ThO_2 ratios without additives; the additives used were both 5 and 10 m/o of CuO , Fe_2O_3 , TiO_2 , V_2O_5 , BaO , Li_2O , B_2O_3 , and Na_2O . Again the additives were added either as the oxide or a compound which decomposes to an oxide when heated.

Pellets 0.635 cm in diameter by 0.635 cm long, were pressed from each composition at pressures of 176 kg/cm^2 , 634 kg/cm^2 , 915 kg/cm^2 , and 1,268 kg/cm^2 . The mixing, drying, and sintering procedures were the same as described in the first section.

After sintering, the bulk densities, apparent specific gravities, and apparent porosities of the pellets were determined.

Results and Discussion:

The effect of varying the forming pressure on the fired bulk densities of the compositions is shown in Tables I, II, III, and IV.

Table I

THE EFFECT OF FORMING PRESSURE ON THE DENSIFICATION
OF 75 m/o UO_2 -25 m/o ThO_2 WITH AND WITHOUT ADDITIVES,
USING U_3O_8 AS THE INITIAL URANIUM OXIDE

m/o Additive	Firing Temp, °C	Apparent Specific Gravity (gm/cc) at Forming Pressures in kg/cm^2 of:			
		176	634	915	1268
0	1700	9.61	9.03	9.22	9.17
	1600	9.82	9.20	9.38	9.68
	1500	10.31	9.87	9.75	9.73
	1400	9.95	9.20	9.48	9.21
5 Li_2O	1700	9.33	9.37	9.28	9.60
	1600	10.15	10.50	10.72	10.72
	1500	10.48	10.52	10.30	10.15
	1400	9.58	9.00	9.00	9.42
5 CuO	1700	10.06	9.87	9.84	9.65
	1600	10.22	9.88	9.61	9.49
	1500	9.31	9.24	9.00	9.11
	1400	9.28	9.24	9.42	9.08
5 BaO	1700	9.19	9.02	8.96	9.01
	1600	9.21	9.34	9.07	9.38
	1500	9.38	9.22	9.17	8.81
	1400	9.07	8.74	8.84	8.56
5 Fe_2O_3	1700	9.24	8.88	8.78	8.31
	1600	10.51	9.93	9.96	9.64
	1500	9.27	9.24	9.57	9.34
	1400	9.24	9.07	8.90	8.52

Table II

THE EFFECT OF FORMING PRESSURE ON THE DENSIFICATION
OF 50 m/o UO_2 -50 m/o ThO_2 WITH AND WITHOUT ADDITIVES,
USING U_3O_8 AS THE INITIAL URANIUM OXIDE

m/o Additive	Firing Temp, °C	Apparent Specific Gravity (gm/cc) at Forming Pres- sures in kg/cm ² of:			
		176	634	915	1268
0	1700	8.46	8.28	8.43	8.34
	1600	9.43	9.10	9.42	9.37
	1500	9.14	8.90	9.03	9.10
	1400	8.94	8.74	8.67	9.07
5 Li_2O	1700	9.00	8.62	8.53	8.37
	1600	9.52	9.41	9.22	8.84
	1500	9.18	9.07	9.18	9.14
	1400	9.04	8.60	8.73	8.50
5 Fe_2O_3	1700	8.89	8.52	8.97	9.06
	1600	8.90	8.74	8.77	8.87
	1500	8.94	8.57	8.97	8.90
	1400	8.72	8.74	8.40	8.78
5 TiO_2	1700	9.12	8.84	8.51	8.56
	1600	9.43	9.42	9.15	9.21
	1500	9.25	9.09	8.93	8.93
	1400	9.00	9.00	8.98	8.63
5 V_2O_5	1700	8.94	8.87	8.92	8.85
	1600	8.87	8.78	9.36	9.36
	1500	8.61	8.61	8.47	8.97
	1400	8.74	8.48	8.37	8.78

Table III

THE EFFECT OF FORMING PRESSURE ON THE DENSIFICATION
OF 25 m/o UO_2 -75 m/o ThO_2 WITH AND WITHOUT ADDITIVES,
USING U_3O_8 AS THE INITIAL URANIUM OXIDE

m/o Additive	Firing Temp, °C	Apparent Specific Gravity (gm/cc) at Forming Pres- sures in kg/cm ² of:			
		176	634	915	1268
0	1700	8.81	8.69	9.07	9.04
	1600	9.29	9.70	9.08	9.03
	1500	9.28	8.93	9.14	9.08
	1400	9.08	9.28	9.58	9.41
5 Li_2O	1700	9.03	8.94	8.88	8.78
	1600	9.17	9.28	9.33	9.14
	1500	9.63	9.28	9.24	9.59
	1400	9.96	9.26	9.18	9.28
5 Fe_2O_3	1700	8.65	8.50	8.58	8.73
	1600	9.04	8.89	8.78	8.86
	1500	9.04	9.11	8.83	8.87
	1400	9.08	9.08	8.43	8.65
5 TiO_2	1700	8.64	8.44	8.27	8.25
	1600	8.82	9.23	9.00	9.00
	1500	8.86	8.57	8.58	8.78
	1400	8.58	8.69	8.58	8.78
5 V_2O_5	1700	8.35	8.23	8.15	8.35
	1600	9.20	8.96	8.99	8.62
	1500	8.56	8.70	8.89	8.52
	1400	8.61	8.42	8.05	8.24

Table IV

THE EFFECT OF FORMING PRESSURE ON THE DENSIFICATION
OF 10 m/o UO_2 -90 m/o ThO_2 WITH AND WITHOUT ADDITIVES,
USING U_3O_8 AS THE INITIAL URANIUM OXIDE

m/o Additives	Firing Temp, °C	Apparent Specific Gravity (gm/cc) at Forming Pres- sures in kg/cm ² of:			
		176	634	915	1268
0	1700	9.60	9.63	9.27	9.35
	1600	9.68	9.58	9.39	9.23
	1500	9.27	9.68	9.73	9.43
	1400	9.58	9.72	9.79	9.57
5 Li_2O	1700	9.51	9.25	9.33	9.49
	1600	9.30	9.43	9.47	9.35
	1500	9.78	9.38	9.32	9.73
	1400	9.68	9.74	9.32	9.54
5 Fe_2O_3	1700	9.26	9.15	9.16	9.13
	1600	9.13	9.27	9.01	8.97
	1500	8.74	9.08	9.21	8.69
	1400	9.08	9.00	9.14	9.10

Again only the results for compositions with the 5 m/o additive are shown, since the data for the 10 m/o additive were similar. Outside of a very slight effect on densification of compositions containing no additive, the variation of forming pressure had no effect on the densification. The variations in density were small and were not consistent; they were probably within the limits of accuracy of the method used in measuring the densities of the pellets.

Effect of Precalcining and Particle Size Reduction on the Densification of $\text{UO}_2 + \text{ThO}_2 + \text{R}_x\text{O}_y$ when the Initial Uranium Oxide is U_3O_8 .

Procedure:

Using a 50 m/o UO_2 -50 m/o ThO_2 base composition, the UO_2 added as a molecular equivalent of U_3O_8 , with and without 5 and 10 m/o additions of Li_2O , CuO , and Fe_2O_3 , the following procedures were followed in preparing the powder mixes for pressing:

Series A. The materials, as received, were dry-mixed as in the previous sections.

Series B. The U_3O_8 was ball milled to pass a 325 mesh sieve before combining with the other components which were already -325 mesh.

Series C. The U_3O_8 and ThO_2 were dry-mixed and calcined at 1200°C for 5 hr in loose form, and then ball milled to pass a 325 mesh sieve. The additions were added to this material and dry-mixed.

Series D. The U_3O_8 , ThO_2 , and additive were dry-mixed and calcined at $1200^\circ C$ for 5 hr, after which the material was ball milled to pass 325 mesh sieve.

Series E. The U_3O_8 and ThO_2 were dry-mixed, pressed into 2.54-cm-dia pellets, and calcined at $1200^\circ C$ for 5 hr. The calcined pellets were crushed and ball milled to pass a 325 mesh sieve.

Series F. The U_3O_8 , ThO_2 , and additive were dry-mixed, pressed into 2.54-cm-dia pellets, and calcined at $1200^\circ C$ for 5 hr. The calcined pellets were crushed and ball milled to pass a 325 mesh sieve.

In addition to the 50 m/o UO_2 -50 m/o ThO_2 composition series, compositions of 75 m/o UO_2 -25 m/o ThO_2 with and without 5 and 10 m/o additions of Li_2O , CuO , BaO , and Fe_2O_3 , and of 25 m/o UO_2 -75 m/o ThO_2 with and without 5 and 10 m/o additions of Li_2O , CuO , Fe_2O_3 , TiO_2 , and V_2O_5 were made. These two composition series were prepared for pressing as in Series A, B, and D above.

Pellets were pressed at $1,268 \text{ kg/cm}^2$ and five of each composition and treatment were fired at 1400, 1500, 1600, and $1700^\circ C$. Again, the bulk density, apparent specific gravity, and apparent porosity for each of the pellets were determined.

Results and Discussion:

The pellets prepared in this part of the investigation were in good condition. Except for those of Series A which were prepared in the same manner as those in the first section, the pellets were relatively free from cracks and gross defects. Since the physical condition of the pellets was good, the bulk or geometric density is used as a means of comparing the densification for the different series and additives. The relative densification of the various series and compositions is shown in Tables V, VI, and VII. Each table contains the data for one base composition with 5 m/o additives, 4 firing temperatures, and for each of the pretreatments as indicated. Each density value is the average of 5 pellets.

The most significant improvement in densification resulted from precalcination of the mixture of the components. It made little difference whether the mixture was pelletized before calcining or whether the additive was calcined along with the base mixture. In all compositions there was a significant improvement in density when the mixture was precalcined.

To a much less degree, there appeared to be an improvement in density when the U_3O_8 was ground to pass a 325 mesh sieve before mixing with the other components (Series B).

Table V

EFFECT ON DENSIFICATION OF PRETREATMENTS OF
OXIDE POWDERS: 50 m/o UO_2 -50 m/o ThO_2

m/o Additive	Firing Temp, °C	Bulk Density (gm/cc) for Series:					
		A	B	C	D	E	F
0	1700	5.63	5.74	8.72	-	8.75	-
	1600	5.50	5.69	8.67	-	8.61	-
	1500	5.53	5.54	8.49	-	8.66	-
	1400	5.29	5.39	7.97	-	8.05	-
5 Li_2O	1700	6.81	7.35	9.85	9.80	9.68	9.78
	1600	6.83	7.42	9.90	9.78	9.79	9.84
	1500	6.80	7.35	9.98	9.83	9.79	9.84
	1400	6.61	7.21	9.49	9.55	9.30	9.61
5 CuO	1700	7.37	7.99	9.49	9.76	9.62	9.86
	1600	7.33	8.02	9.49	9.72	9.65	9.92
	1500	7.46	8.12	9.64	9.76	9.79	9.92
	1400	7.57	8.20	9.77	9.91	9.86	10.05
5 Fe_2O_3	1700	7.09	7.80	9.63	9.32	9.52	9.40
	1600	6.96	7.60	9.70	9.31	9.56	9.40
	1500	6.85	7.42	9.73	9.19	9.57	9.24
	1400	5.98	6.41	9.61	9.23	9.62	9.37

Table VI

EFFECT ON DENSIFICATION OF PRETREATMENTS OF
OXIDE POWDERS: 75 m/o UO_2 -25 m/o ThO_2

m/o Additive	Firing Temp, °C	Bulk Density (gm/cc) for Series:		
		A	B	D
0	1700	3.91	4.48	6.75
	1600	3.88	4.42	6.65
	1500	3.84	4.42	6.64
	1400	3.90	4.41	6.90
5 Li_2O	1700	5.86	6.88	8.19
	1600	5.65	6.94	8.19
	1500	5.71	6.73	8.18
	1400	5.53	6.44	8.08
5 CuO	1700	6.79	9.39	9.50
	1600	7.20	9.30	9.46
	1500	8.39	9.44	9.55
	1400	8.51	9.39	9.57
5 BaO	1700	6.07	7.02	7.73
	1600	5.73	6.82	7.60
	1500	4.37	5.19	6.64
	1400	3.86	4.47	6.49
5 Fe_2O_3	1700	7.93	8.50	8.87
	1600	7.12	7.97	8.96
	1500	7.15	7.94	9.05
	1400	6.66	7.69	9.01

Table VII

EFFECT ON DENSIFICATION OF PRETREATMENTS OF
OXIDE POWDERS: 25 m/o UO_2 -75 m/o ThO_2

m/o Additive	Firing Temp, °C	Bulk Density (gm/cc) for Series:		
		A	B	D
0	1700	7.53	7.78	9.05
	1600	7.34	7.59	8.70
	1500	7.15	7.33	8.10
	1400	6.86	6.92	7.41
5 Li_2O	1700	7.80	9.13	9.17
	1600	6.55	9.05	9.19
	1500	7.62	9.08	9.11
	1400	7.13	8.59	9.06
5 CuO	1700	8.12	8.67	8.98
	1600	7.53	8.54	8.84
	1500	8.14	8.44	8.82
	1400	7.73	8.52	8.87
5 Fe_2O_3	1700	8.01	8.69	9.36
	1600	8.00	8.70	9.08
	1500	7.67	8.20	8.66
	1400	7.61	7.62	8.02
5 TiO_2	1700	8.13	8.92	9.50
	1600	8.13	9.17	9.74
	1500	7.46	8.12	8.82
	1400	7.13	7.56	7.44
5 V_2O_5	1700	8.02	8.06	9.00
	1600	8.13	8.24	8.93
	1500	8.11	8.48	9.13
	1400	8.20	8.39	9.22

Again, as in the first section, it is very apparent that the improvement in densification due to additives increases with increasing UO_2 content of the base mixture. The only additive which did not improve densification to any large extent was BaO ; however, there was some increase in density even with BaO .

Probably most significant in these results is that with some of the additives the density apparently reaches a peak below 1700°C and falls off with higher firing temperatures. This is especially true with additions of CuO and Fe_2O_3 to the high UO_2 content base composition. Maximum densification of high UO_2 content compositions at low peak temperatures would apparently be possible using small additions of these oxides.

Fabrication of UO_2 - ThO_2 Tubing by Extrusion Using U_3O_8 as the Initial Uranium Oxide.

Procedure:

The object of this part of the investigation was to establish the applicability of the results of the previous sections to a different and a more flexible technique of fabrication. Two compositions were selected for extrusion: the 50 m/o UO_2 -50 m/o ThO_2 base composition, both without an additive and with 5 m/o CuO .

The base mixture, with the molecular equivalent of U_3O_8 added for the UO_2 content, was mixed in a ball mill and calcined at 1200°C for 5 hr. The calcined material was crushed and ball milled to pass a 325 mesh sieve. In a ball mill 5 m/o CuO was mixed with half the material.

To the two mixtures 0.33% CMC was added as plasticizer and binder along with 10% water. Initially, the binder and water were incorporated by means of a kitchen-type mixer, and the mixture was then hand kneaded until the material exhibited the proper plasticity for extrusion. Tubes, 0.635 cm in ID x 0.953 cm in OD x 15.24 cm long, were extruded on a ram-type extruder. The load for the extruder was furnished by a hand-operated hydraulic jack.

The tubes were extruded onto central rods to facilitate handling. They were dried without support for 24 hr in air at 100 - 105°C . Some slumping was evident before drying progressed sufficiently to give the pieces strength. Tubes were set on pure alumina in a horizontal position and fired in a gas kiln for one hour at 1400°C and 1700°C .

Out-of-roundness was determined before and after firing. Bulk density, firing shrinkage, apparent porosity, and apparent specific gravity were also determined.

Results and Discussion:

Table VIII lists the properties of the extruded specimens. Tubes containing the CuO additive had considerably higher densities than the tubes without an additive. Again, the density of the specimens with the additive was higher when fired at a lower temperature than at 1700°C . The appearance of the specimens was excellent, and they suffered no deformation during sintering. The results of the previous sections appear to be applicable to extruded as well as dry-pressed specimens.

Table VIII

PROPERTIES OF EXTRUDED 50 m/o UO_2 -50 m/o ThO_2 SPECIMENS
USING U_3O_8 AS THE INITIAL URANIUM OXIDE

m/o Additive	Firing Temp, °C	Per Cent Firing Shrinkage	Bulk Density, gm/cc	Per Cent Apparent Porosity
0	1700	7.8	7.36	28.5
0	1400	3.6	6.25	38.5
5.0 CuO	1700	15.7	8.24	15.1
5.0 CuO	1400	16.3	8.89	7.4

CONCLUSIONS

The effect of 5 m/o additions on apparent specific gravity of sintered UO_2 - ThO_2 shapes formed with a molecular equivalent of U_3O_8 as the uranium oxide increased with decreasing ThO_2 content.

Among the additives investigated, the oxides of the transition elements had the largest positive effect on the apparent specific gravity.

Within the limits of this investigation, there was no apparent effect on densification of variation of the forming pressure.

A substantial increase in densification can be achieved by precalcining the mixture of U_3O_8 and ThO_2 before forming the shapes.

The effects due to additions and pretreatment of starting materials are valid for extruded as well as pressed shapes.

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