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Reactor Technology

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POWER METALLURGY OF URANIUM
MONOCARBIDE (U)

C. R. Schmitt

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OAK RIDGE Y-12 PLANT

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Oak Ridge, Tennessee

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ABSTRACT

Uranium monocarbide has recently received considerable attention as a nuclear fuel because of its very desirable high-temperature properties, and it has good irradiation stability.

Several studies were conducted to determine ways of producing satisfactory pellets of uranium monocarbide. It was found that densification by cold pressing is dependent upon the powder particle size, oxygen content, sintering temperature and atmosphere, and the lubricant used in pressing.

Certain sintering promoters were investigated. The addition of approximately 0.5% nickel was found to enhance densification, and an average density of 97% of theoretical was obtained when 2 wt % uranium disilicide was used under the proper conditions.

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INTRODUCTION

Uranium monocarbide has recently received considerable attention as a nuclear fuel because of its very desirable high-temperature properties. Its melting point, uranium density, and thermal conductivity are high, and it has good thermal and irradiation stability.

Two routes for fabricating this refractory compound into solid bodies are most generally used: (1) melting and casting, and (2) powder ceramurgical techniques. Among the various powder ceramurgical techniques, hot-press and cold-press sintering are attractive for attaining high densities at moderate temperatures. For densification by conventional solid-state sintering, temperatures in excess of 1800° C are generally required. Liquid-phase sintering is also of importance since densification can be promoted at much lower temperatures.

The current objective is to investigate methods of producing high-density uranium monocarbide compacts by cold-pressing and sintering techniques. Research and development studies on various aspects of uranium monocarbide technology have been reported by the Atomic Energy Commission. (1 - 3)

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SUMMARY

Sintering studies on cold-pressed uranium monocarbide pellets showed that densification is dependent upon the powder particle size, oxygen content, temperature, sintering atmosphere, and the lubricants used in pressing.

The addition of approximately 0.5% nickel as a liquid-phase sintering promoter was more effective than copper, cobalt, or iron in enhancing densification at 1525° C.

The effectiveness of uranium disilicide (U_3Si_2) as a sintering aid was evaluated with cold-pressed uranium monocarbide pellets made from both relatively coarse and fine powders having high and low oxygen contents. It was found that an average density of 97% of theoretical was obtained when 2 wt % uranium disilicide was used after vacuum sintering for three hours at 1650° C using a uranium monocarbide powder having an average particle diameter of 5.6 microns.

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EXPERIMENTAL WORK

OVERALL RESULTS

The sintering characteristics of uranium monocarbide powder are greatly dependent upon the physical and chemical characteristics of the powder. For these studies, two batches of uranium monocarbide powder, as prepared by carbothermic reduction of uranium dioxide, were evaluated. A summary of the physical and chemical properties of these powders is given in Table 1 and particle-size distribution analyses obtained on a modified Micromerograph are indicated in Figure 1.

Table 1
PHYSICAL AND CHEMICAL CHARACTERISTICS OF URANIUM
MONOCARBIDE POWDERS USED IN SINTERING STUDIES

	Batch 10	Batch 20
Surface Area (m ² /gm)	0.59	0.17
Average Particle Size (μ)	5.4	12.0
Oxygen Content (%)	1.18	0.220
Carbon Content (%)	4.60	4.75
Uranium Content (%)	95.00	94.83
Helium Displacement Density (gms/cc)	12.2	-
Spectrographic Analysis (ppm)		
Ag	< 1	< 1
Al	< 7	< 7
B	< 1	< 1
Bu	< 10	< 10
Be	< 0.3	< 0.3
Ca	< 50	< 50
Cr	< 6	< 6
Cu	12	10
Fe	140	10
K	< 50	< 50
Li	< 2	< 2
Mg	< 5	< 5
Mn	< 5	< 5
Na	< 10	< 10
Ni	-	-30
P	< 100	< 100
Si	25	< 10
Sn	< 10	< 10

Difficulty was experienced in the initial attempts to die press uranium monocarbide powder at 30,000 psi using a 0.5-inch-ID steel die since the abrasive particles caused die seizure and galling. It was also found that the monocarbide powders were pyrophoric so that all handling and pressing operations had to be conducted in an argon-atmosphere glove box.

Use of a 3 wt % solution of cetyl alcohol in petroleum ether as a die lubricant and powder binder was found to be helpful in overcoming die-galling and pyrophoricity

Figure 1. PARTICLE SIZE DISTRIBUTION OF URANIUM MONOCARBIDE POWDER.

problems. By adding approximately one cubic centimeter of this solution to a 20-gram portion of monocarbide powder and stirring with a spatula, a thick paste resulted. The excess petroleum ether volatilized rapidly and die-pressing operations with the cetyl alcohol-coated powder could then be conducted in air.

The effects of various die and powder lubricants used in cold pressing uranium monocarbide pellets at 30,000 psi on the sintered density are compared by the graph in Figure 2. The use of cetyl alcohol or Carbowax binders had an adverse effect on density at sintering temperatures of 1600 and 1800° C despite prior vacuum treatment at $< 1 \mu$ Hg and 200° C for two hours to remove these organic binders before sintering. After obtaining sintering data at 1525° C, the pellets were resintered for 2.0 hours at 1600 and 1800° C under flowing helium. The same pellets were used so that additional variables associated with the pellet-fabrication procedure would not be introduced.

SPECIFIC STUDIES

Liquid-Phase Sintering Aids

To determine the effect of cobalt as a liquid-phase sintering promoter, five monocarbide pellets containing 0.05 - 2.0% cobalt were sintered for successive 2.0-hour

Figure 2. EFFECT OF LUBRICANTS AND BINDERS ON THE DENSITY OF SINTERED URANIUM MONOCARBIDE COMPACTS. (Two-Hour Soak Time at Temperature in Flowing Helium)

periods at 1525, 1600, and 1800° C under flowing helium. Results, plotted in Figure 3, show that cobalt additions up to 2.0% gave an increase in the density at 1525° C, but at 1800° C compacts containing greater than 1.0% cobalt showed a marked decrease in density.

The effects of nickel and copper on the density of cold-pressed uranium monocarbide pellets were evaluated at 1525° C in flowing helium. Results, as summarized in Table 2, show that an appreciable increase in density was realized with nickel, but that additions of copper greater than 0.1% had a detrimental effect on the sintered density.

The effects of nickel and iron, separately and in combination, on the density of uranium monocarbide pellets sintered for 2.0 hours at 1800° C in flowing helium are shown in Figure 4. These data show nickel to have an increasingly beneficial effect

Figure 3. EFFECT OF COBALT ADDITIONS ON THE DENSITY OF SINTERED URANIUM MONOCARBIDE COMPACTS. (Two-Hour Soak Time at Temperature in Flowing Helium)

up to 0.5%. Some increase in density was shown with iron at 0.1%, but at 0.5 and 1.0% it had a detrimental effect. Although mixtures of nickel and iron showed an overall improvement in the density, the increase was not as great as that obtained by nickel alone.

The effect of the sintering temperature on densification in flowing helium is shown in Figures 2 and 3. The data in Figure 2 indicate that increasing the sintering temperature from 1525 to 1800° C in flowing helium increased the average density from about 86% to about 91% of the theoretical density. The beneficial effect of the temperature on density is also shown in Figure 3 for those monocarbide pellets not containing cobalt that were sintered in flowing helium. An increase in density from 85.8 to 90.6% of the theoretical density was realized by increasing the sintering temperature from 1525 to 1800° C. The density of these pellets sintered for 2.0 hours at 1525° C were considerably higher than those shown in Table 2 which

Table 2
EFFECT OF NICKEL AND COPPER ON THE DENSITY OF
URANIUM MONOCARBIDE
(Sintered at 1525° C for Two Hours Under Flowing Helium)

Additive	Heating Rate(1) (hrs)	Density (gms/cc)	Theoretical Density(2) (gms/cc)	Percent of Theoretical Density
None	1.0	10.31	13.63	75.6
None	1.0	10.08	13.63	74.0
None	1.0	10.74	13.63	78.8
None	1.0	10.82	13.63	79.4
0.1% Cu	1.0	11.35	13.62	83.3
0.5% Cu	1.0	9.33	13.59	68.7
1.0% Cu	1.0	9.14	13.55	67.5
0.05% Ni	1.0	11.42	13.63	83.8
0.05% Ni	1.0	11.37	13.63	83.4
0.1% Ni	1.0	11.60	13.62	85.2
0.5% Ni	1.0	12.23	13.59	90.0
1.0% Ni	1.0	12.15	13.55	89.7
5.0% Ni	1.0	11.65	13.27	87.8

(1) Time to attain the target sintering temperature.

(2) Theoretical density corrected for presence of metal additives.

were also sintered for 2.0 hours at 1525° C and had been prepared from the same monocarbide powder (Batch 10). Presumably, the higher densification values shown in Figure 3 resulted from the slower heating rate of 2.0 hours that was used to attain the target sintering temperature of 1525° C.

Pellets were cold pressed from relatively fine uranium monocarbide powder (Batch 10) and relatively coarse monocarbide powder (Batch 20) and vacuum sintered for 2.0 hours at 1800 and 2100° C at $< 1 \mu$ Hg to evaluate the effects of the powder particle size and sintering temperature on the density, and to compare sintering in vacuum and in helium. Results, reported in Table 3, indicate that the densities of the monocarbide pellets pressed from fine powder were not increased by increasing the temperature above 1800° C. The slight decrease shown in Table 3 for the average density at the two temperatures (93.9 to 93.2% of theoretical) may be due to the greater vaporization of uranium at the higher temperature. The average density of the monocarbide pellets pressed from coarse powder (Batch 20) increased from 75.9 to 84.5% of theoretical by increasing the sintering temperature from 1800 to 2100° C.

All uranium monocarbide pellets used for these studies were cold pressed at 30,000 psi. Except where indicated otherwise, both the steel die and pressing ram were lubricated with a solution of stearic acid in absolute ethyl alcohol applied by brushing.

The effect of nickel on the microstructure of uranium monocarbide after sintering for 2.0 hours at 1525° C in flowing helium is shown in Figure 5. The microstructures

Figure 4. EFFECTS OF NICKEL AND IRON ON THE SINTERED DENSITY OF URANIUM MONOCARBIDE. (Sintered for Two Hours at 1800° C. in Flowing Helium)

of those compacts containing nickel show grain growth with increasing additions of nickel. At greater than 0.5 wt % nickel, the monocarbide grains developed a distinct cubic symmetry, as can be seen in Figure 5(d), (e), and (f).

Extensive grain growth is evident in the microstructures of those compacts containing cobalt additions after successively sintering for 2.0 hours at 1525, 1600, and 1800° C in flowing helium (shown in Figure 6). The characteristic light Widmanstätten pattern⁽⁴⁾ is presumed to be a precipitate of uranium dicarbide.

The increasing degree of porosity shown in these photomicrographs was found to be in general agreement with the decreased density associated with increasing cobalt additions. The high degree of porosity shown by the monocarbide pellet containing 2 wt % cobalt is shown at low magnification in Figure 7.

It was also observed that some of the compacts containing a liquid-phase sintering aid exhibited segregation, or nonuniformity of the microstructure, over the entire

Table 3
DENSITY OF URANIUM MONOCARBIDE COMPACTS AFTER
VACUUM SINTERING AT 1800 AND 2100° C

Sinter Temperature (° C)	Heating Rate(1) (hrs)	Density (gms/cc)	Percent of Theoretical Density
<u>Batch 10 (Fine)</u>			
1800	2.0	12.83	94.1
1800	2.0	12.76	93.6
			(93.9)(2)
2100	2.0	12.74	93.5
2100	2.0	12.66	92.9
			(93.2)
<u>Batch 20 (Coarse)</u>			
1800	2.0	9.94	72.9
1800	2.0	10.35	75.9
1800	2.0	10.01	73.4
1800	2.0	10.67	78.3
1800	2.0	10.40	76.3
1800	2.0	11.04	80.6
			(75.9)
2100	2.0	11.50	84.4
2100	2.0	11.43	83.9
2100	2.0	11.59	85.0
			(84.5)

(1) Time to attain the target sintering temperature.

(2) Average density is shown by parentheses.

length of the pellet. A typical example of a segregated area is shown in Figure 8. Segregation probably resulted from the use of sintering additives that were considerably coarser than the uranium monocarbide powder so that a homogeneous blend of the mixed powders used for pressing the pellets was probably not attained. A summary of the powder characteristics of the sintering additives used, showing the coarseness of these powders, is given in Table 4.

The microstructure of a typical low-density pellet, sintered at 1525° C in the absence of any metal additive, shown in Figure 5(a), consists of relatively small carbide grains and large pores which lie along the grain boundaries. A typical high-density pellet sintered at 1800° C in the absence of any metal additive is shown in Figure 9(a). This view shows a large grain size, no apparent voids, and the presence of considerable uranium at the grain boundaries.

It is believed that the formation of uranium metal at the monocarbide grain boundaries resulted from the reaction of oxygen impurities (as UO_2) with uranium monocarbide at high temperatures according to the reaction:

Nickel Content (%)	Density	
	(gms/cc)	(% of Theoretical)

None	10.08	74.0
------	-------	------

0.05	11.42	83.8
------	-------	------

0.1	11.60	85.2
-----	-------	------

0.5	12.23	90.0
-----	-------	------

1.0	12.15	89.7
-----	-------	------

5.0	11.65	87.8
-----	-------	------

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Figure 5. EFFECT OF NICKEL ON THE MICROSTRUCTURE OF URANIUM MONOCARBIDE THAT WAS COLD PRESSED AT 30,000 PSI AND SINTERED FOR TWO HOURS AT 1525°C IN FLOWING HELIUM. (Etchant: $\text{HNO}_3\text{-CH}_3\text{COOH-H}_2\text{O}$; 1000X)

	Cobalt Content (%)	Density	
		(gms/cc)	(% of Theoretical)
(a)	None	12.54	92.0
(b)	0.1	12.25	90.0
(c)	1.0	11.88	87.7
(d)	2.0	11.33	84.1

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Figure 6. EFFECT OF COBALT ON THE MICROSTRUCTURE OF URANIUM MONOCARBIDE THAT WAS COLD PRESSED AT 30,000 PSI AND SINTERED FOR TWO HOURS AT 1525, 1600, AND 1800° C IN FLOWING HELIUM. (Etchant: $\text{HNO}_3\text{-CH}_3\text{COOH-H}_2\text{O}$; 1000X)

Batch 10 had an oxygen content of 1.18%, which is equivalent to a uranium dioxide content of 9.9%. The extensive grain growth shown in Figures 5(a) and 9(a) suggest that liquid-phase sintering by uranium metal may be a major mode of densification. Both compacts shown in Figures 5(a) and 9(a) were made from Batch 10.

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Figure 7. MICROSTRUCTURE OF SINTERED URANIUM MONOCARBIDE CONTAINING TWO WEIGHT PERCENT COBALT SHOWING LARGE INTERNAL CAVITIES (Bright Field Illumination; 25X)

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Figure 8. SEGREGATION IN A SINTERED URANIUM MONOCARBIDE COMPACT CONTAINING 0.1 WEIGHT PERCENT COBALT (90.0% OF THE THEORETICAL DENSITY). (Bright Field Illumination; Etchant: $\text{HNO}_3\text{-CH}_3\text{COOH-H}_2\text{O}$; 1000X)

Table 4
CHARACTERISTICS OF METAL POWDERS USED FOR
LIQUID-PHASE URANIUM MONOCARBIDE
SINTERING STUDIES

Metal	Melting Point (° C)	Boiling Point (° C)	Surface Area (m ² /gm)	Oxygen Content (%)	Average Particle Diameter ⁽¹⁾ (μ)	Particle Size Range ⁽¹⁾ (μ)
Copper	1083	2582	0.13	0.284	—	—
Cobalt	1492	3100	0.40	0.408	23	10.0 - 40
Iron	1535	2800	0.29	3.480	26	1.8 - 43
Nickel	1453	2800	0.25	0.636	32	1.3 - 62

(1) Determined by Micromerograph analysis.

(a)

(b)

12.83	Sintered Density (gms/cc)	10.33
94.1	Sintered Density (% TD)	75.9
5.5	Average UC Powder Size (μ)	12
1.18	Oxygen Content (%)	0.22

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Figure 9. MICROSTRUCTURE OF URANIUM MONOCARBIDE AFTER COLD PRESSING AT 30,000 PSI AND SINTERING FOR TWO HOURS AT 1800°C IN VACUUM. (Etchant: HNO₃-CH₃COOH-H₂O; 1000X)

In contrast, only traces of free uranium metal are present in the microstructure of a compact sintered under equivalent conditions from Batch 20 containing only 0.2% oxygen, as shown in Figure 9(b).

Dry-Milling Studies

Previous sintering studies (see Table 3) using a batch of fine uranium monocarbide powder (average particle diameter of $5.4\ \mu$) had shown that densities greater than 94% of theoretical could not be attained even at sintering temperatures of 2100°C because of the high oxygen content of this powder. Grinding studies were made on the batch of relatively coarse (Batch 20) stoichiometric monocarbide powder, having a low oxygen content, in an attempt to make it more sinterable.

The powder was milled in a sealed seven-inch-OD uranium-lined stainless steel cylinder rotating at 45 rpm, using 1/2-inch-diameter by 1-inch-long uranium pellets for grinding. The mill had been charged with monocarbide powder until it was approximately 1/2 to 2/3 full and contained five pounds of uranium pellets. Periodic withdrawal of the powder samples during the initial 96-hour milling period showed very little reduction in the particle size, from an average particle diameter of 12 microns before milling to 10 microns after milling, and indicated that the mill had been charged with too much powder and too few pellets.

Some uranium monocarbide powder was then removed from the mill so that the powder charge only occupied approximately 25% of the cylinder volume, and some additional uranium pellets were added. After an additional 24 hours of milling, a considerable improvement in particle-size reduction was realized. Particle-size distribution analyses obtained on a modified Micromerograph, showing the extent of particle size reduction obtained after various milling times, are given in Figure 10. No significant reduction in the particle size resulted after milling for another 24 hours (an increase from 120 to 144 hours total time) and it was observed that the monocarbide powder had become partially agglomerated and compacted against the walls of the cylinder.

The effect of uranium pellet milling on the properties of the monocarbide powder after various milling periods is reported in Tables 5 and 6. These values indicate that no significant change in the uranium content or pickup of extraneous metallic impurities occurred after dry milling with all-uranium metal components. Although the milling vessel had been loaded in an argon atmosphere and was sealed by a rubber gasket, the milling operation had been conducted in air and appreciable oxygen pickup occurred. As shown in Table 5, a significant increase in the oxygen content resulted after the average particle diameter had been reduced to below approximately 9 microns.

To reduce the possibility of penetration of the mill by air and moisture, additional dry-milling studies were conducted entirely within an argon-atmosphere glove box using a four-inch-diameter rubber-lined or polyvinylplastisol-lined vessel and 5/8-inch-diameter cobalt-bonded tungsten carbide balls. Results, given in Table 7, indicate that the use of tungsten carbide balls resulted in a high contamination of the monocarbide powder with tungsten and cobalt. A photograph showing the seven-inch-diameter uranium-cladded milling vessel with all-uranium components and the four-inch-diameter rubber-lined milling vessel is given in Figure 11.

Figure 10. PARTICLE-SIZE DISTRIBUTION OF URANIUM MONOCARBIDE POWDER THAT HAD BEEN MILLED WITH URANIUM PELLETS.

Table 5
PROPERTIES OF URANIUM MONOCARBIDE POWDER BEFORE AND
AFTER DRY MILLING WITH URANIUM PELLETS

Milling Time (hrs)	Uranium (%)	Carbon (%)	Oxygen (%)	Particle Size ⁽¹⁾ (microns)	
				Average Diameter	Range
0 ⁽²⁾	94.83 ⁽³⁾ 94.38 ⁽³⁾	4.75 ⁽³⁾ 4.79 ⁽³⁾	0.220 -	12 -	0.8 - 40 -
8	95.05	4.90	-	-	-
24	94.34	4.93	0.148	11	0.8 - 33
48	95.11	4.80	0.245	11	0.8 - 33
96	94.84	4.81	0.278	9.5	0.8 - 25
120	94.44	4.82	0.689	5.8	0.7 - 20
144	94.90 -	5.03 ⁽³⁾ 4.86 ⁽³⁾	0.946 ⁽³⁾ 0.634 ⁽³⁾	5.6 -	0.7 - 20 -

(1) Determined by modified Micromerograph analysis.

(2) Minus 400 mesh, Batch 20.

(3) Duplicate determinations on separate samples.

Wet-Milling Studies

A photograph of four vacuum-sintered ($< 1 \mu \text{Hg}$ at 1650°C) pellets is shown in Figure 12. These pellets represent batch portions of uranium monocarbide powder

Table 6

SPECTROGRAPHIC ANALYSES OF URANIUM MONOCARBIDE POWDER
BEFORE AND AFTER DRY MILLING WITH URANIUM PELLETS

Impurity(1)	Unmilled(2)	Milling Time (hrs)		
		8	96	120
Ag	< 1	< 1	< 1	< 1
Al	< 7	< 7	8	< 7
B	< 1	< 1	< 1	< 1
Ba	< 10	< 10	< 10	< 10
Be	< 0.3	< 0.3	< 1	< 0.4
Ca	< 50	< 50	< 50	< 50
Cr	< 6	< 6	< 6	< 6
Cu	10	10	< 2	< 2
Fe	10	20	< 10	< 10
K	< 50	< 50	< 50	< 50
Li	< 2	< 2	< 2	< 2
Mg	< 5	< 5	< 5	< 5
Mn	< 5	< 5	< 5	< 5
Na	< 10	< 10	< 10	< 10
Ni	30	30	< 25	< 25
P	< 100	< 100	< 100	< 100
Si	< 10	< 10	31	< 10
Sn	< 10	< 10	< 10	< 10

(1) All values in parts per million.

(2) Minus 400 mesh, Batch 20.

Table 7

SPECTROGRAPHIC ANALYSES OF URANIUM MONOCARBIDE
POWDER BEFORE AND AFTER DRY MILLING WITH
TUNGSTEN CARBIDE BALLS

Impurity(1)	Batch 20		Batch 22	
	Before Milling(2)	After Milling(3)	Before Milling(4)	After Milling(5)
Al	10	8	3	60
B	< 0.1	< 0.1	< 0.1	< 0.1
Ba	< 2	< 2	6	8
Be	0.4	0.6	< 0.01	< 0.01
Ca	< 10	35	< 10	15
Co	10	400	2	20
Cr	< 2	2	2	4
Cu	25	5	20	35
Fe	30	35	750	1000
K	< 6	< 6	< 6	< 6
Li	< 0.2	< 0.2	< 0.2	< 0.2
Mg	< 2	6	40	50
Mn	< 1	1	15	20
Mo	4	< 4	12	< 4
Na	8	< 1	< 1	2
Ni	35	20	600	1200
P	< 100	< 100	< 100	< 100
Si	10	30	18	35
W	< 100	> 1000	< 100	300

(1) All values in parts per million.

(2) This powder had been milled previously for 134 hours with all uranium components as an oversized batch, but milling time had been insufficient to effect any appreciable particle-size reduction.

(3) Uranium monocarbide powder (390 gms) milled with 48 tungsten carbide balls for 55 hours at 35 rpm.

(4) This powder was -200 mesh and high in iron and nickel content. This contamination resulted from hammer-mill treatment of uranium dioxide prior to carbothermic reduction with graphite to form uranium monocarbide.

(5) Uranium monocarbide powder (800 gms) milled with tungsten carbide balls for three days at 35 rpm.

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Figure 11. RUBBER-LINED AND URANIUM-LINED TUMBLERS USED FOR MILLING URANIUM MONOCARBIDE POWDERS.

that had been wet milled with trichloroethylene in a planetary ball mill for various periods of time. This photograph shows severe surface blistering and deformation for Pellets 38E and 38G, which were made from relatively fine powders having a low oxygen content. The deformation and the relatively low sintered densities shown by these compacts were suspected to have been caused by the presence of high metallic impurities (eg, iron and nickel) in the ball-milled powder. Volatilization of these elements probably formed vapor pockets. Spectrographic analyses of the pellets after sintering are reported in Table 8.

Also presented in Table 8 is a spectrographic analysis showing > 1000 ppm iron and nickel for a small fragment of another pellet identical to Pellet 38A-1. The metallic impurities associated with this pellet fragment, however, were not present in such large amounts in the green monocarbide powder compact, and it is believed that they were picked up inadvertently by direct contact with a contaminated area on the tungsten setter plate during vacuum sintering. The sintered density of this

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Figure 12. URANIUM MONOCARBIDE PELLETS AFTER VACUUM SINTERING FOR 1.5 HOURS AT 1650°C. (Cold Pressed from Planetary Ball-Milled Powder; 1.5X)

Table 8
SPECTROCHEMICAL ANALYSES OF SINTERED URANIUM
MONOCARBIDE PELLETS

Element(1)	Pellet Number			
	38A-1(2)	38E(3)	38G(4)	38A-2(5) Fragment
Al	5	1	1	1
B	< 0.1	0.6	0.4	1.5
Co	6	35	30	40
Cr	< 2	20	10	8
Cu	1	< 1	2	20
Fe	75	> 1000	> 1000	> 1000
Li	< 0.2	< 0.2	< 0.2	25.0
Mg	1	4	< 2	2
Mn	< 1	15	10	15
Ni	400	> 1000	> 1000	> 1000
Si	300	200	200	500
Sn	< 1	< 1	4	< 1
V	3	4	4	< 1
W	> 1000	> 1000	> 1000	> 1000

(1) All values in parts per million.

(2) Pellet made from -230 mesh powder, Batch 38.

(3) Pellet made from Batch 38 powder that was wet milled for 45 minutes in a planetary ball mill.

(4) Pellet made from Batch 38 powder that was wet milled for 90 minutes in a planetary ball mill.

(5) High-density fragment of a pellet made identical to Pellet 38A-1.

pellet fragment was 12.90 gms/cc or 94.5% of the theoretical density. Since this pellet fragment represents the same extremely coarse uranium monocarbide powder used for making Pellet 38A-1, which only densified to 9.02 gms/cc or 67% of the theoretical density, it is suspected that a vapor-diffusion or capillary-diffusion mechanism involving a sintering aid (eg, Fe, Ni, W, or Li) from the contaminated setter plate is involved. The high density obtained on this pellet fragment was confirmed by an examination of its microstructure which revealed the presence of large monocarbide grains and an absence of voids.

Particle Shape

Particle shape is an important factor influencing the compactibility of a powder by cold pressing. Generally, irregularly shaped particles are best for forming strong, green compacts because of a greater amount of interlocking between the particles. Photomicrographs showing the general particle shape of two batches of uranium monocarbide powder used for sintering are presented in Figure 13. One batch was dry milled for 144 hours with uranium pellets and the other was wet milled under trichloroethylene in a Steele and Cowlshaw planetary ball mill for 45 minutes. Both powders exhibit considerable shape irregularity and appear to be agglomerated.

(a) Dry Milled for 144 Hours
with Uranium Pellets

(b) Wet Milled for 45 Minutes
in a Planetary Ball Mill with
Trichloroethylene 111827(U)

Figure 13. PARTICLE SHAPE OF MILLED URANIUM MONOCARBIDE POWDERS. (Bright Field Illumination; 500X)

Effect of Pressure

A study was made of the suitability of various uranium monocarbide powders for isostatic compaction. It was found that these carbide powders, representing a wide range of particle sizes and distributions, could be satisfactorily pressed isostatically at 30,000 psi without the use of any binder. Table 9 lists some characteristics of those monocarbide powder batches which produced pellets with sufficient green strength to permit normal handling. These powders were originally prepared by reacting uranium dioxide and graphite and were milled by various methods.

Table 9
PROPERTIES OF URANIUM MONOCARBIDE POWDERS AMENABLE
TO ISOSTATIC COMPACTION AT 30,000 PSI

Powder Batch Number	Milling Method(2)	Particle Size Range (μ)	Particle Size Distribution ⁽¹⁾			Oxygen (%)
			Percent ≤ Diameter			
			95 Wt % ⁽³⁾ (μ)	50 Wt % (μ)	5 Wt % (μ)	
38G	b	0.7 - 20	9.5	3.5	1.1	0.33
38E	b	0.7 - 18	10.0	4.0	1.2	0.44
10	a	0.7 - 24	16.0	5.3	1.2	1.18
20UC55	a - c	0.7 - 20	16.0	5.4	1.0	0.86
20UC144	a	0.7 - 20	15.0	5.6	1.1	0.63
38B	b	0.8 - 33	24.0	10.5	1.8	0.30
22UC3D	c	0.8 - 33	26.5	12.0	1.5	0.47
38B50	b - c	0.8 - 33	27.0	14.5	1.6	0.58
20UC134	c	0.7 - 33	29.0	17.0	1.3	0.33

(1) Particle diameters were interpolated at 95, 50, and 5 wt % levels from the distribution curves obtained with a modified Micromerograph.

(2) a. Dry milled with uranium pellets in a seven-inch-diameter uranium-lined vessel.

b. Wet milled under trichloroethylene in a Steele and Cowlishaw planetary ball mill with 5/8-inch-diameter tungsten carbide balls.

c. Dry milled with tungsten carbide balls in a four-inch-diameter brass vessel lined with polyvinyl plastisol.

(3) This signifies that 95% of the powder for each batch has a particle diameter equal to or smaller than the number shown in this column.

In order to determine the effect of the compacting pressure on the green density and compressive strength, uranium monocarbide pellets were cold pressed in an argon-atmosphere glove box using a 0.5-inch-ID steel die. For these studies the 144-hour dry-milled powder was used. Compressive-strength values were determined by slow crushing of the pellets (contained in sealed polyethylene bags with entrapped argon) at a constant speed of 0.05 inch per minute. Green densities were calculated from the weight and dimensions of each pellet.

Results, presented in Table 10, show that the green densities increased with the compacting pressure over the range from 5000 to 25,000 psi. At higher compacting pressures, excessive fragility (ie, lamination, chipping, and breakage) of the pellet was experienced, which precluded a reliable determination of the green densities. The relatively low compressive strengths (ranging from 20 to 128 psi) indicate the general fragile nature of the monocarbide pellets. Although fairly uniform pellets

Table 10
EFFECT OF THE COMPACTING PRESSURE ON THE GREEN DENSITY
AND COMPRESSIVE STRENGTH OF URANIUM MONOCARBIDE

Compacting Pressure (psi)	Green Density ⁽¹⁾ (gms/cc)	Compressive Strength (psi)
<u>With 0.15% Cetyl Alcohol Binder in the Pellet⁽²⁾</u>		
5,000	9.70	77
10,000	9.72	43
15,000	9.76	59
20,000	9.85	128
25,000	9.88	20
30,000	9.26 ⁽³⁾	46
40,000	9.62 ⁽³⁾	31
50,000	9.87 ⁽³⁾	79
75,000	9.15 ⁽³⁾	94
<u>Without Binder⁽²⁾</u>		
12,500	8.25	90
25,000	8.45	49
37,500	8.98	30
50,000	9.22	33

(1) Dry-milled powder used; Batch 20UC144.

(2) Stearic acid lubricant was applied to the die ram and walls by brushing.

(3) Erratic values because of pellet deformation.

having parallel ends were obtained over the range from 5000 to 25,000 psi, no correlation between the strength and compacting pressure is indicated. At compacting pressures greater than 30,000 psi, nonparallelity and deformation of the pellet ends precluded reliable compressive-strength values.

For cold pressing uranium monocarbide powder, the relationship between compacting pressure and pellet fragility could be roughly evaluated by using a constant weight of monocarbide powder (approximately 20 gms) and gauging the size or weight of the pellet after ejection from the die. At compacting pressures below 30,000 psi, the pellets exhibited good physical integrity; whereas, at 30,000 psi some chipping and breakage occurred upon gentle handling with the loss of approximately 10% of the main pellet body. At 60,000 psi, several small laminated pieces equivalent to approximately 40% of the main pellet body usually broke away; at 90,000 psi, usually less than 50% of the main pellet body remained as a unit.

To determine the effect of the compacting pressure on the compressive strength, uranium monocarbide pellets (1/2" D x 1/2" L) were isostatically pressed at 30,000 psi using Batch 20UC144 powder (see Table 9). Compressive-strength measurements were made by crushing the pellets (contained in argon-filled, sealed polyethylene bags) at a constant speed of 0.05 inch per minute. Results, reported in Table 11 and Figure 14, indicate that the compressive strength increased linearly with the forming pressure over the range from 5000 to 30,000 psi. The highest compressive strength was obtained with the batch of monocarbide powder which had the finest

Table 11
EFFECT OF ISOSTATIC FORMING PRESSURE ON THE COMPRESSIVE
STRENGTH OF URANIUM MONOCARBIDE PELLETS

UC Powder Batch Number	Average Particle Diameter (μ)	Isostatic Forming Pressure (μ)	Compressive Strength ⁽¹⁾ (psi)
20UC48	11.0	20,000 ⁽²⁾	-
38B	10.5	30,000	37 ⁽³⁾
20UC144	5.6	5,000	100
20UC144	5.6	10,000	117
20UC144	5.6	15,000	175
20UC144	5.6	20,000	178
20UC144	5.6	25,000	242
20UC144	5.6	30,000	263
20UC144	5.6	30,000 ⁽⁴⁾	302
10	5.3	30,000 ⁽⁴⁾	315
38E	4.0	30,000	276
38G	3.5	30,000	417

- (1) Crosshead speed of 0.05 inches/minute.
 (2) Failed to produce a pellet.
 (3) Value may be higher than shown because of nonparallelity of pellet ends.
 (4) Pressure maintained for an extra 30 seconds.

Figure 14. EFFECT OF ISOSTATIC FORMING PRESSURE ON THE
COMPRESSIVE STRENGTH OF URANIUM MONOCARBIDE PELLETS.
(Batch 20UC144)

average particle size (ie, 3.5 μ). The compressive strengths of isostatically pressed pellets from Batch 20UC144 are approximately double the highest value obtained previously on pellets die pressed from this same batch of powder.

The feasibility of using the isostatic-pressing technique for making larger uranium monocarbide compacts was demonstrated by the compaction of a 1 1/4-inch-diameter by 1 1/2-inch-long monocarbide compact weighing over 3/4 pound. This pellet was isostatically pressed at 30,000 psi from a rather coarse powder having an average particle diameter of 10.5 microns. The compact was sintered for 2.0 hours at 1800° C in vacuum using a 3.0-hour heat-up period to attain the sinter temperature and a 3.0-hour cooling period to minimize the possibility of cracking by thermal stresses. The sintered compact showed no visible cracks, and had a density of 11.8 gms/cc (87% of theoretical) as obtained by kerosene-displacement weighing.

Uranium Disilicide as a Sintering Aid

Recent development studies by Hammond and Sease⁽⁵⁾ indicated that densities as high as 97% of theoretical could be attained at 1650° C using uranium disilicide as a sintering aid. Studies of various interrelated parameters concerning the consolidation of uranium monocarbide powder by cold pressing and sintering and to evaluate the effectiveness of the disilicide as a sintering aid were continued.

Cold-pressed uranium monocarbide pellets made from both relatively coarse and fine powders, with high and low oxygen contents, were sintered under various conditions. A summary of the powder characteristics, sintering conditions, and densities is given in Table 12.

Table 12
DENSITIES OF URANIUM MONOCARBIDE PELLETS SINTERED UNDER VARIOUS CONDITIONS

Batch Number	UC Powder Average		U ₃ Si ₂ Added(1) (wt %)	Sintering Conditions			Number of Pellets	Theoretical Density (%)	
	Diameter (μ)	O ₂ (%)		Temperature (° C)	Time (hrs)	Atmosphere		Range	Average
20-48	11.0	0.25	None	1550	3.0	Argon	2	78.7 - 79.6	79.2
20-48	11.0	0.25	2	1550	3.0	Argon	2	84.7 - 86.9	85.8
20-48	11.0	0.25	None	1550	3.0	Vacuum(5)	4	69.3 - 74.2	72.1
20-48	11.0	0.25	2	1550	3.0	Vacuum(5)	4	78.4 - 81.8	80.1
10	5.0	1.18	None	1550	3.0	Vacuum(5)	4	83.8 - 88.3	86.0
10	5.0	1.18	2	1550	3.0	Vacuum(5)	3	81.3 - 89.0	84.9
20-48	11.0	0.25	None	1650	3.0	Vacuum(5)	11	76.5 - 79.8	79.0
20-48	11.0	0.25	2	1650	3.0	Vacuum(5)	5	82.9 - 88.6	86.2
20-96	9.5	0.28(2)	None	1800	3.0	Argon	5	88.5 - 92.6	91.9
20-96	9.5	0.28(2)	2	1800	3.0	Argon	10	92.1 - 95.5	93.6
20-144	5.6	0.63	None	1650	3.0	Vacuum(5)	2	86.4 - 88.2	87.8
20-144	5.6	0.63	2	1650	3.0	Vacuum(5)	9	94.0 - 99.9	97.2
20-144	5.6	0.63(2)	None	1650	3.0	Helium	4	89.8 - 92.1	90.8
20-144	5.6	0.63(2)	2	1650	3.0	Helium	7	90.0 - 92.8	91.8
38A	39.0	0.235	None	1650	1.5	Vacuum(5)	2	66.2 - 67.9	67.1
38B(4)	10.5	0.30	None	1650	1.5	Vacuum(5)	2	79.3 - 80.8	80.1
38E(4)	4.0	0.44	None	1650	1.5	Vacuum(5)	1	69.7(3)	69.7(3)
38G(4)	3.5	0.33	None	1650	1.5	Vacuum(5)	1	79.4(3)	79.4(3)

(1) Added as a -300 mesh powder and blended with uranium monocarbide by tumbling.

(2) Pellets exposed to air upon loading into furnace; suspect oxygen content considerably higher than shown.

(3) Low density attributed to high metallic impurities in powder.

(4) Wet milled in planetary ball mill.

(5) Less than 1 μ Hg.

These data show that uranium disilicide is very effective in enhancing the densification of uranium monocarbide powders having a relatively low oxygen content (ie, $< 0.5\%$), but that it is relatively ineffective in the presence of a high oxygen content. It is also significant that in the presence of 2 wt % disilicide, an average density of 97% of theoretical was obtained with a monocarbide powder (Batch 20-144) of only medium fineness (average particle diameter of 5.6μ) and relatively high oxygen content (0.6%). In the absence of uranium disilicide, this powder only sintered to an average density of 88% of theoretical under equivalent conditions.

Pellet Handling

Pyrophoricity is a major problem associated with cold pressing and sintering uranium monocarbide. For the vacuum-sintering runs shown in Table 12, monocarbide pellets were die pressed in an argon-atmosphere glove box. The pellets were then placed in a one-quart polyethylene bag and the end of the bag sealed with plastic tape. The pellet in its sealed polyethylene envelope could then be safely removed from the glove box and transported in air. By folding over the taped end of the bag, creasing, and resealing with a heat sealer, the size of the polyethylene envelope could be reduced to approximately 2 by 2 inches by trimming off the excess at the sealed edges. The enclosed pellet was then loaded directly into the vacuum furnace and sintered, vaporizing the polyethylene bag during the heat up.

A thermogravimetric analysis of a polyethylene bag (one-quart size) having a thickness of 1.5 mil is presented in Figure 15. These data show that the polyethylene decomposed rapidly under vacuum between 360 and 500°C , leaving a final residue of less than 0.1 milligram.

All sintered densities shown in Tables 2, 3, and 12 were determined by displacement weighing in dry^(a) kerosene after vacuum impregnation with dry kerosene to close any open porosity. As indicated in Table 12, some of the monocarbide pellets may have become partially oxidized upon making a rapid transfer from the sealed polyethylene bags to the sintering furnace. In the sintering runs made with argon or helium, and in one run under vacuum, the pellets were never removed from their polyethylene envelopes. Examination of the tungsten susceptor used for these vacuum-sintering studies showed that it had experienced severe deterioration, possibly from an interaction with the carbonaceous gases formed by decomposition of the polyethylene envelopes, or with carbon monoxide gas evolved from the monocarbide pellets. Thus, other methods were investigated for rendering the green uranium monocarbide pellets nonpyrophoric.

(a) Dried with Linde 4A Molecular Sieves.

Figure 15. THERMOGRAVIMETRIC ANALYSIS OF A POLYETHYLENE BAG AS A FUNCTION OF TIME AND TEMPERATURE.

It was found that presintering for one hour at 1500° C in flowing argon in a tube furnace heated by silicon carbide elements was effective in rendering the pellets nonpyrophoric. All powder and pellet-handling operations were conducted in an argon-atmosphere glove box. The green pellets were loaded into Alundum boats, the boats positioned in Alundum tubes, and both ends of the tubes sealed with rubber stoppers fitted with glass stopcocks. The sealed Alundum tubes could then be transported safely to the furnace for presintering under flowing argon. Using this same furnace-loading technique, it was found that a presintering temperature of 975° C for one hour in flowing argon was ineffective in rendering the pellets nonpyrophoric upon subsequent exposure to air after cooling.

Other methods found suitable for rendering the green pellets nonpyrophoric were: (1) spray coating the pellets with a clear acrylic lacquer; (2) brush coating the pellets with a 6 - 12% solution of Dylene^(b) in benzene; and (3) dip coating the

(b) A powdered polystyrene manufactured by Koppers Company, Inc.

pellets with molten paraffin. Although these three methods would still cause carbonaceous attack of the tungsten heating elements in high-temperature vacuum-sintering furnaces, they may be suitable for other types of furnaces operating in an inert atmosphere. In this regard, monocarbide pellets that were considered pyrophoric and had been Dylene and paraffin coated were still intact after exposure to ambient air for over two months.

Isostatic pressing of uranium monocarbide powder would have a definite advantage over die pressing since larger and more complex shapes could be pressed by this method than could be compressed in, or ejected from, a die. In addition, isostatic pressing produces more uniform densities than die pressing.

Although the sintered density of the largest uranium monocarbide compact (3/4 lb) made by isostatic pressing was rather low (87% of theoretical), this result was according to expectation since a relatively coarse powder had been used. The coarse powder enabled the green compact to be loaded quickly into the vacuum sintering furnace with minimum danger of loss by pyrophoricity. Also, it was not necessary to use a protective polyethylene envelope. The dimensions of this compact (1 1/4" x 1 1/2") represented the maximum size that the available high-temperature vacuum sintering furnace would accommodate, but it is believed that larger monocarbide compacts could be pressed isostatically and sintered without difficulty if a larger furnace were available.

Isostatic compaction of uranium monocarbide powder was accomplished by loading the powder into a five-mil-walled latex sheath in an argon-atmosphere glove box and pressing at 30,000 psi in a pressure vessel filled with mineral oil. Because of the extreme reactivity of the finely divided monocarbide powders with air or moisture, the latex sheaths were sealed inside of a second latex sheath to provide containment in case the inner sheath was ruptured by the abrasive carbide particles. In addition, the mineral oil used as the hydraulic medium was always kept dry because of the danger of a violent reaction between the monocarbide particles and the moisture in the event of sheath rupture.

The blending of as much as 4 wt % uranium disilide powder (-300 mesh) with relatively coarse uranium monocarbide powders presented no difficulty in isostatic pressing.

Post-Sintering Analyses

Post-sintering analyses of uranium monocarbide pellets representing various types of monocarbide powders and various sintering conditions are summarized in Table 13.

Table 13
POST-SINTERING ANALYSES OF URANIUM MONOCARBIDE PELLETS

UC Powder		2% U ₃ Si ₂ Present	Sintering Conditions	Time (hrs)	Carbon (%)	Uranium (%)	Oxygen (%)	Total (%)
Batch Number	O ₂ (%)							
10	1.18	No	1525, 1600, 1800° C in Helium	6(1)	4.54	92.77	0.270	97.58
10	1.18	No	1525, 1600, 1800° C in Helium	6(1)	4.47	92.75	0.204	97.42
10	1.18	No	1800° C in Vacuum	2	4.45	94.51	0.130	99.09
10	1.18	No	1800° C in Vacuum	2	4.55	94.27	0.165	98.99
10	1.18	No	1800° C in Vacuum	2	4.41	93.93	0.116	98.46
10	1.18	No	1800° C in Helium	2	4.80	93.58	0.519	98.90
10	1.18	No	2100° C in Vacuum ⁽²⁾	2	4.57	93.65	0.212	98.43
20-0	0.22	No	2100° C in Vacuum	2	5.13	93.82	0.176	99.13
20-144	0.63	No	1650° C in Helium	3	4.20	95.15	0.360	99.71
20-144	0.63	No	1650° C in Helium	3	4.34	95.01	0.346	99.70
20-144	0.63	Yes	1650° C in Vacuum	3	4.60	(3)	0.351	-
20-144	0.63	Yes	1800° C in Argon	3	4.41	(3)	0.350	-
20-48	0.245	No	1650° C in Vacuum	3	4.55	94.82	0.761	100.13
20-48	0.245	No	1650° C in Argon	3	4.76	94.95	0.412	100.12

(1) Sintered for two hours at each temperature.

(2) One pellet became welded to the tungsten setter plate during this run.

(3) Uranium content varied from 92 - 96%.

These data show that the oxygen content of the pellets made from Batch 10 powder, having rather high oxygen, was reduced considerably by sintering. After sintering Batch 20-0 powder in vacuum at 2100° C, an increase in the carbon content from 4.80 to 5.13% was found which may be due to the volatilization of the uranium at high temperatures. A decrease in the carbon content shown by many of the pellets might be attributed to the reaction of carbon or uranium monocarbide with the oxygen present (as UO₂) and the evolution of carbon monoxide. Unfortunately, analytical material balances do not permit any positive conclusions to be made.

The microstructures of various sintered uranium monocarbide pellets were also studied. It was observed that those pellets that had been vacuum sintered while contained in polyethylene envelopes developed a skin approximately three microns thick which may be carbon or uranium dicarbide. A cross section of the edge of such a monocarbide pellet, containing two percent uranium disilicide, showing this skin and associated segregated zones is presented in Figure 16. The microstructure of the

(a) Edge; 100X

(b) Center; 1000X

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Figure 16. CROSS SECTIONS OF A URANIUM MONOCARBIDE PELLET CONTAINING TWO PERCENT URANIUM DISILICIDE THAT WAS SINTERED FOR 3.0 HOURS AT 1650°C IN VACUUM. (Bright Field Illumination; Etchant: $\text{HNO}_3\text{-CH}_3\text{COOH-H}_2\text{O}$)

center or core of this pellet, which exhibited very large monocarbide grains, is also shown.

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