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THE EFFECT OF INNOCULATION OF URANIUM AND
URANIUM-6 WEIGHT PERCENT NIOBIUM WITH 0.01 TO 1.0
WEIGHT PERCENT TITANIUM ON IMPURITY LEVELS

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Research and Ecology
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THE EFFECT OF INNOCULATION OF URANIUM AND URANIUM-6 WEIGHT PERCENT NIOBIUM WITH 0.01 TO 1.0 WEIGHT PERCENT TITANIUM ON IMPURITY LEVELS

John G. Avery

Abstract. Titanium in the range 0.01 to 1.0 wt % was added to uranium and uranium-6 wt % niobium. Some titanium additions were made during arc melting followed by induction remelting; other titanium additions were made directly to the induction melt.

Chemical analyses and metallographic examination determined that significant cleaning of the impurities carbon and nitrogen occurs in uranium with titanium additions above 0.5 wt %. When the added titanium level is on the order of the impurities present, no significant removal of carbon, nitrogen, or oxygen occurs. In uranium-6 wt % niobium alloy, no level of titanium addition examined resulted in a significant reduction in carbon, nitrogen, or oxygen levels.

INTRODUCTION

Uranium and uranium-6 wt % niobium alloy are used to fabricate a wide variety of shapes at Rocky Flats. Many of these shapes are produced from induction-cast material. In addition, scrap generated during fabrication is consolidated for reuse by induction melting.

Induction melting increases the carbon, oxygen, and nitrogen levels of Derby uranium (Table I).

Table 1. Typical Impurity Levels in Derby and Induction-Cast Uranium.

Derby Uranium (ppm*)	Induction-Cast Uranium
C 15 - 40	C 100 - 200
N 20 - 25	N 100 - 120
O 20 - 25	O 50 - 70

*weight percent

(Derby is uranium resulting from the reduction of UF_4 .) Additional cycles of induction melting increase the levels further. This contamination is caused by a variety of factors including (a) use of graphite crucibles and molds, (b) use of "felt" (graphite cloth) to insulate certain areas of the furnace, (c) the long melting times inherent in induction melting large charges, which allow more metal-gas interaction, and (d) the poorer vacuum levels obtainable in induction furnaces as compared to arc-melt furnaces. The tendency of oxygen, nitrogen, and carbon to form compounds with uranium and niobium ensures the formation of inclusions during induction melting.

Inclusions, especially niobium carbides, have proved detrimental to fabrication for several reasons. First, hot workability is decreased compared to higher purity material. Drawing operations require more stages to produce a given part, and scrap rates caused by forming failures are higher. A second problem is encountered in machining where hard NbC and Nb_2C inclusions dull the cutting tool and cause excessive cold work during machining.¹ This excessive cold work can cause severe dimensional changes with changing temperatures.² Close tolerances cannot be held consistently and finish-machined parts may have to be scrapped.

Development efforts on uranium-0.75 wt % titanium revealed that after induction melting, carbon levels stayed at or below the carbon levels found in the Derby uranium feed.³ Further investigations showed that high (>200 ppm) levels of carbon were reduced to approximately 50 ppm by titanium additions of 7500 ppm (0.75 wt %). This carbon reduction was accompanied by a titanium loss of a magnitude that made it appear TiC was forming and floating out of the melt.

Figure 1. Location of Chemistry Samples from Cast Ingots.
Turnings were used for carbon, niobium, and titanium. Solid chunks were used for oxygen and nitrogen.

It seemed reasonable to see if titanium additions of less than 0.75 wt % in uranium would combine with carbon and result in flotation of most of the carbon and titanium from the melt. A similar plan was pursued on uranium-niobium alloy to see if titanium would exhibit a cleaning effect in this alloy.

EXPERIMENTAL PROCEDURE

A series of alloys, shown in Table 2, was used in this study. They were designed to vary several parameters that might influence the cleaning effect of titanium on carbon in uranium alloys. Among these parameters were:

- (1) Casting Geometry. To determine the effect of directional solidification, two mold geometries were used: one where solidification would proceed upwards from the bottom,

and one where solidification would proceed in from the walls.

- (2) Method of Addition. Titanium was added during arc melting followed by induction remelting, or added directly to the induction melt.
- (3) Titanium Level. Titanium additions ranged from 1,000 to 10,000 ppm.

All alloys were induction melted in coated* graphite crucibles and poured into coated graphite molds. The ingots were then analyzed chemically at the locations shown in Figure 1. The microstructure was also examined to determine the level of inclusions present. Identification of the exact type of inclusions present, whether a carbide, carbonitride or whatever, was not the purpose of this study. The purpose was to determine the overall level of inclusions and whether titanium reduced this level in uranium and uranium-6 wt % niobium.

RESULTS AND DISCUSSION

Table 3 shows the chemical analyses of the 15 ingots.

Examination of Table 3 shows that in the case of depleted uranium (alloys 5 through 8, and 11 through 15), 0.5 wt % of titanium and above produced significant cleaning of carbon. At a lower level of titanium addition, the 0.1 wt % used in alloys 5 through 8, carbon levels were equal to that in Table 1 for induction-melted uranium with no titanium additions. In all the inoculated uranium alloys, a high percentage of titanium remained in the casting after induction melting. At the titanium levels that resulted in a cleaning effect, the residual titanium level was high enough to result in the heat-treatable uranium-titanium binary.

Figure 2 shows various titanium levels used in the depleted uranium and the effectiveness of those levels in removing impurities.

*The coating consisted of a zirconium oxide slurry.

Table 2. Alloys Used in Investigation.

Alloy No.	Composition (Nominal)		Mold Size (in.)	Feed Material	Method of Titanium Addition
	Ti* (ppm)	Nb (wt %)			
1	1,000	6	1.625 dia. x 22.5 high	Virgin Arc** Melt	Elemental Ti added to induction charge
2	1,000	6	3 dia. x 9 high	Virgin Arc Melt	Elemental Ti added to induction charge
3	10,000	6	1.625 dia. x 22.5 high	Virgin Arc Melt	Elemental Ti added to induction charge
4	10,000	6	3 dia. x 9 high	Virgin Arc Melt	Elemental Ti added to induction charge
5	1,000	0	1.625 dia. x 22.5 high	Virgin Derby Scrap	Arc cast U-Ti alloy added to induction charge
6	1,000	0	3 dia. x 9 high	Virgin Derby Scrap	Arc cast U-Ti alloy added to induction charge
7	1,000	0	1.625 dia. x 22.5 high	Virgin Derby Scrap	Elemental Ti added to induction charge
8	1,000	0	3 dia. x 9 high	Virgin Derby Scrap	Elemental Ti added to induction charge
9	1,000	6	3 dia. x 9 high	Virgin Arc Melt	Elemental Ti added during arc casting
10	10,000	6	3 dia. x 9 high	Virgin Arc Melt	Elemental Ti added during arc casting
11	6,000	0	3 dia. x 9 high	Virgin Derby Scrap	Arc cast U-Ti alloy added to induction charge
12	9,000	0	3 dia. x 9 high	Virgin Derby Scrap	Arc cast U-Ti alloy added to induction charge
13	6,000	0	3 dia. x 9 high	High Carbon† and High Gas Feed††	Arc cast U-Ti alloy added to induction charge
14	9,000	0	3 dia. x 9 high	High Carbon and High Gas Feed	Arc cast U-Ti alloy added to induction charge
15	5,000	0	3 dia. x 9 high	Virgin Derby Scrap	Arc cast U-Ti alloy added to induction charge

*Added as weight percent i.e. 0.01 wt % = 1000 ppm.

**Virgin Derby depleted uranium, alloyed with commercially pure niobium by vacuum consumable electrode arc melting.

†High carbon scrap refers to uranium with 150 to 200 ppm carbon.

††High gas scrap refers to uranium with >300 ppm oxygen + nitrogen.

Table 3. Chemical Analyses of Experimental Ingots.

Alloy No.	C (ppm)		Nb (wt %)		N (ppm)		O (ppm)		Ti (wt %)	
	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom
1	100	80	6.35	6.10	25	15	122	143	0.140	0.135
2	130	120	5.45	5.58	18	21	141	99	0.118	0.123
3	100	115	6.11	5.89	22	30	129	159	0.984	0.908
4	100	90	5.75	5.63	18	29	111	130	0.962	0.963
5	125	100	—	—	20	16	136	242	0.151	0.077
6	170	150	—	—	20	17	168	221	0.097	0.082
7	190	180	—	—	10	9	160	171	0.084	0.082
8	175	140	—	—	15	20	82	151	0.101	0.082
9	90	120	5.74	5.93	30	20	149	131	0.101	0.097
10	100	115	5.71	5.68	19	23	157	118	0.940	0.917
11	25	25	—	—	15	14	60	50	0.580	0.600
12	20	25	—	—	13	9	60	60	0.800	0.800
13	60	40	—	—	10	15	55	50	0.500	0.510
14	32	17	—	—	15	5	40	60	0.790	0.790
15	40	40	—	—	14	12	60	40	0.480	0.480

Figure 2. Final Carbon Content in Induction-Cast Depleted Uranium as a Function of the Amount of Titanium Added.

Based on limited data, it appears that more titanium is required to clean a melt where the feed is initially higher in impurities than one having a lower initial impurity level.

The effect of ingot geometry on impurity removal could not be determined because the melts where levels of titanium additions were sufficiently large to result in cleaning were all poured into 3-in. diameter by 9-in. high molds.

The uranium-6 wt % niobium with titanium additions (alloys 1 through 4 and 9 and 10) showed no tendency toward removal of carbon. The carbon levels of all uranium-niobium alloys inoculated with titanium were in the range expected in induction melted uranium-niobium that was not inoculated.

Figure 3. Induction Melted Uranium Inclusions that are Primarily Uranium Carbides. 100X. Unetched.

Metallographic examination of the experimental alloys was conducted. In all cases, the carbide-inclusion contents correlated with chemical analyses results.

Figure 3 shows the microstructure of induction-melted uranium, Figure 4 illustrates induction-melted uranium with 0.5 wt % of titanium added, while Figure 5 shows the microstructure of induction-melted uranium with 1.0 wt % titanium added.

Figure 6 displays the microstructure of uranium-6 wt % niobium melted by vacuum-consumable arc melting. During the short time the metal was molten, lack of a carbon source and the good vacuum ($<20\mu$) prevented the pickup of any significant amount of impurities. In Figure 7, this arc-cast feed has been induction melted and large inclusions, probably niobium carbon and Nb_2C are present. Figure 8 illustrates uranium-6 wt % niobium with 0.1 wt % titanium, and

Figure 4. Induction Melted Uranium with 0.5 Wt % Titanium. Small inclusions, mostly oxides, are present. 100X. Unetched.

Figure 5. Induction Melted Uranium with 1 Wt % Titanium. Oxide inclusions are still present. 100X. Unetched.

Figure 6. Vacuum Arc Melted Uranium-6 Wt % Niobium.
Note lack of carbide inclusions. 100X. Unetched.

Figure 7. Induction Melted Uranium-6 Wt % Niobium.
Note large inclusions which are either Nb_2C or NbC . 100X. Unetched.

Figure 8. Induction Melted Uranium-6 Wt % Niobium with 0.1 Wt % Titanium.
Carbide inclusions are still present, 100X. Unetched.

Figure 9. Induction Melted Uranium-6 Wt % Niobium with 1.0 Wt % Titanium. Inclusions are still present. 100X. Unetched.

Figure 9 shows uranium-6 wt % niobium with 1.0 wt % titanium. Both titanium-innoculated alloys contain carbide particles.

THERMODYNAMIC CONSIDERATIONS

Figure 10 relates the free energies of formation (ΔG_T) of Nb_2C , NbC , TiC , TiN , and UC as calculated by R. W. Krenzer. At the melting temperatures employed in induction casting, and neglecting reaction kinetics, one would expect a uranium-niobium-titanium alloy with less than a few hundred ppm carbon to form Nb_2C rather than TiC . In a uranium-titanium alloy with less than a few hundred ppm of carbon, one would expect TiC to form preferentially to UC . Both predictions are in agreement with experimental results. Also in agreement are the low residual levels of nitrogen, reflecting the favorable free energy of formation of TiN .

Figure 10. Free Energies of Various Compounds of Uranium, Niobium, Titanium, and Carbon as a Function of Temperature.

In addition one would expect, disregarding the reaction kinetics, that 0.02 wt % of titanium would displace about 0.1 wt % uranium from UC .* This is not the case; in fact, 0.1 wt % of titanium did not remove significant amounts of carbon from depleted uranium. There are several factors that could explain the lack of cleaning predicted by free energies of the compounds involved. First, for 0.02 wt % of titanium to remove 0.1 wt % of carbon, no titanium could be lost to reactions with other impurities such as nitrogen or oxygen.

*0.02 wt % of titanium, having an atomic weight of 47.9, contains five times as many atoms as 0.02 wt % of depleted uranium with an atomic weight of 238.07.

A second factor is the kinetics of the reaction. After the titanium dissolves in the molten uranium, it is transported through the melt in some manner. Statistically, the number of titanium atoms that will come in contact with a UC particle in a given time period is proportional to the number of titanium atoms and UC particles. If the time period is long enough (and assuming additional titanium is added to make up for the losses already described), 0.02 wt % of titanium should remove 0.1 wt % of carbon. In actual practice, the time during which the metal is molten is held to a minimum, only enough to allow the melt to reach the pouring temperature. This is done to minimize impurity pickup which becomes greater with increasing time. With the hold time used in the experimental runs of this investigation (approximately 20 minutes), the amount of titanium sufficient to accomplish a significant amount of reaction with UC was between 0.1 and 0.5 wt %.

The use of longer holding times could result in gettering of carbon with lower amounts of titanium, if additional pickup of carbon could be avoided. Elimination or reduction of carbon pickup would require extensive modification of the current melting practice, especially elimination of graphite crucibles and molds. This approach warrants investigation. Another possible answer to impurity removal is the use of an inoculant that would break down Nb_2C and NbC . This area will also be investigated.

CONCLUSIONS

1. Addition of titanium to depleted uranium will remove carbon. With current melting practice, about 0.5 wt % of titanium is required to lower carbon from 0.020 to 0.005 wt %.
2. Addition of titanium to uranium-niobium alloys does not result in carbon removal.

REFERENCES

1. R. J. Jackson, "Properties of Uranium-6.3 wt % Niobium Alloy," USAEC RFP-1613, Rocky Flats Division, Dow Chemical U.S.A., Golden, Colorado, October, 1971.
2. R. J. Jackson and W. L. Johns, "Temperature Induced Shape Memory in Polycrystalline Uranium Base Nb Alloys—Characterization," USAEC RFP-996, Rocky Flats Division, The Dow Chemical Company, Golden, Colorado, September 23, 1970.
3. J. G. Avery, "The Effect of Alloy Content, Carbon, Oxygen and Nitrogen on the Mechanical Properties of U-2.2 wt % Nb and U-0.75 wt % Ti Wrought Heat Treated Alloys," USAEC RFP-1950, Rocky Flats Division, Dow Chemical U.S.A., Golden, Colorado, March 1, 1973.