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A GENERAL STUDY OF THE

DISTRIBUTION OF IMPURITIES IN LEAD URANATE CATAL

AND RELATED SUBJECTS

MCW Research Report No. 30

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A GENERAL STUDY OF THE
DISTRIBUTION OF IMPURITIES IN REMELTED URANIUM METAL
AND RELATED SUBJECTS

Introduction

During the production of extruded rods from uranium metal billets, it was found that some of the rods produced were pyrophoric. This problem, coupled with the need for basic knowledge of the distribution of impurities in remelted uranium metal, led to an extensive chemical and physical investigation of the different billets poured from the uranium metal melt.

Samples were taken from the three billets poured from a melt and tested both chemically and physically to see if any differences between billets could be found. Eggs cut from each billet were piled according to their respective pour positions and given a neutron absorption test to see if any differences were detectable in that manner.

Discussion

A list of seventy-eight billets which showed pyrophoricity in the extrusion operation was checked against existing records and gave the following results.

10% of the billets were from the first metal poured
from the melt.

14% of the billets were from the second portion of
the metal poured.

76% of the billets were from the last metal in the melt.

5% of the billets were produced from remelted pure metal.

25% of the billets were produced from slaggy crude metal.

70% of the billets were produced from clean crude metal.

This analysis showed two things, the first being that the last metal from the melt gave more trouble than the first or second portions poured. Also, billets produced from clean, crude metal gave more trouble than those poured from melts of remelted purified material or slaggy, crude metal.

The reasons why these two things gave trouble were readily apparent. When a load of crude uranium is melted under vacuum, there are a number of things which take place. As soon as the metal all melts, it begins to boil violently and a lot of the impurities rise to the top and boil out. The metal is agitated violently by its own boiling and the induction current produced by the coils which furnish heat, and this causes the impurities, which are lighter than the metal, to rise to the top. As the temperature of the metal rises to the pouring point, the melt becomes quiet. As soon as the melt reaches 2400°F, it is poured into the billet molds. The last billet poured contains the most impurities, as the top metal in the melt goes into that billet.

It also follows that the metal in the top of any one billet would contain more impurities than the metal in the bottom of that billet.

The metal could be left in the graphite crucible longer to boil out more of the impurities, but other factors enter in which make the practice undesirable. The remelt yield is decreased by leaving the metal in the crucible too long and other impurities start to form which are worse than the impurities which would be left in the metal under ordinary operating conditions.

An examination of the different types of metal from the reduction operation had shown the following things. The clean, shiny metal produced in reduction was very high in magnesium. This combination of uranium and magnesium made for very good metal-slag separation in the reduction vessel but gave crude metal which was very impure. The other type of crude metal which contained a visible slag coating on the top was in reality better material because it was purer throughout than the clean-looking metal. On melting the slaggy crude metal, the slag floated on top of the melt and stayed in the crucible and, because the crude metal was basically pure, the billets produced from it contained less impurities than those produced from clean metal.

Chemical analyses of the pyrophoric billets showed that magnesium and nitrogen tended to be higher in these billets than the regular run of material, but not all billets which were high in these impurities were pyrophoric. Therefore, it was assumed that the pyrophoricity could be blamed on some physical difference in the metal or possibly a combination of both of the above-mentioned things. Samples of pyrophoric and non-pyrophoric material were sent to the Metallographic Laboratory in Chicago for physical testing. Their reported conclusions are listed below.

1. "It is not likely that the relatively small differences in purity of these sets of samples would be the direct cause of marked differences in pyrophoricity."
2. "Microscopic porosity would seem to be the cause of the pyrophoric condition."

The second reported conclusion ties in with the available data in that billets which were high in nitrogen content, and very often gave pyrophoric rods, were low in density. This low density figure was attributed to microscopic porosity which was readily evident on etching low density samples with nitric acid.

Neutron absorption tests were run on the eggs from the first billet, the eggs from the second billet and the eggs from the third billet. The last metal in the crucible was also poured

into an egg mold and the neutron absorption test was run on this material. The results are listed below in Table 1.

TABLE 1
Neutron Absorption Values

<u>Egg Position</u>	<u>Neutron Absorption Value</u>	<u>Average</u>
1	0.14	0.16
1	0.18	
2	0.14	0.16
2	0.18	
3	0.14	0.165
3	0.19	
4	0.80	0.755
4	0.71	

As can be seen, the neutron absorption value for the fourth egg was very high, showing that the impurities in this egg were very concentrated. As this test was a statistical one, the results from two runs were not too conclusive, but good order of magnitude results were obtained. A great number of runs would probably show the neutron absorption value to be lowest for the first egg, a little higher for the second, a little higher yet for the third and very high for the fourth egg.

Experimental

Chemical analyses were run on samples from the first and third billets. These samples were tested for silver, chromium, nickel, boron, nitrogen, iron, manganese, magnesium, carbon, hydrogen, chloride and silica. In general, the only impurities which were higher in the third billet than the first were nitrogen and magnesium. The rest of the impurities were fairly evenly distributed throughout the melt.

The third and fourth eggs from the neutron absorption tests were tested chemically. Slices from these eggs were also tested for pyrophoricity in the following manner. A muffle with a stainless steel coffin was so set up that a steady flow of argon gas could be run through the coffin. The muffle was heated to 1650°F and flushed with argon. The sample was then inserted into the coffin and left there for fifteen minutes in an atmosphere of argon. At the end of this time, the sample was up to the temperature of the muffle. The sample was then removed and allowed to cool down to room temperature in air. If the material was pyrophoric, it was readily noticeable as the sample remained red for some time and then began to burn to U_3O_8 with some sparking. If the sample was all right, it cooled down rapidly with a light surface coating of the oxide remaining on it.

The results of the pyrophoricity tests are shown in Table 2.

Column one gives the run number of the egg tested. Column two gives the position of the egg in the pour. Column three gives the results of the pyrophoricity tests.

TABLE 2
Pyrophoricity Tests

<u>Egg Number</u>	<u>Egg Position</u>	<u>Remarks</u>
9906	No. 3	O.K. to Fair
09	No. 3	O.K.
19	No. 3	O.K.
24	No. 3	O.K.
9930	No. 3	O.K.
33	No. 3	O.K.
45	No. 3	O.K.
48	No. 3	O.K.
9951	No. 3	Poor to pyrophoric
54	No. 3	Poor to pyrophoric
57	No. 3	Poor to pyrophoric
60	No. 3	O.K.
9964	No. 3	O.K.
70	No. 3	O.K. to Fair
73	No. 3	O.K. to Fair
76	No. 3	O.K.
9904-05-06	No. 4	Pyrophoric
9907-08-09	No. 4	Pyrophoric
9917-18-19	No. 4	Pyrophoric
9922-23-24	No. 4	Pyrophoric
9928-24-30	No. 4	Pyrophoric
9931-32-33	No. 4	Pyrophoric
9943-44-45	No. 4	Pyrophoric
9946-47-48	No. 4	Pyrophoric
9949-50-51	No. 4	Pyrophoric
9952-53-54	No. 4	Pyrophoric
9955-56-57	No. 4	Pyrophoric
9958-59-60	No. 4	Pyrophoric
9962-63-64	No. 4	Pyrophoric
9968-69-70	No. 4	Pyrophoric
9971-72-73	No. 4	Pyrophoric
9974-75-76	No. 4	Pyrophoric

As can be seen from the table, all the slices from the number four eggs were pyrophoric. These samples all turned to U_3O_8 with some sparking. The slices from the number three egg were all good with sparking. The slices from the number three egg were all good with the exception of six samples which showed some tendencies to be pyrophoric. These samples were not nearly as bad as the fourth egg slices.

The chemical analyses of the third and fourth eggs are listed in Tables 3 and 4. Table 3, which contains the analyses for the third eggs, shows nothing out of the ordinary with the exception of egg number 9970, which was high nitrogen. The sample from this billet showed some tendency to be pyrophoric.

Table 4 shows the chemical analyses of the fourth egg. The results on silver, chromium, nickel, boron and iron were no different than those for the third egg. That gives a good indication that these impurities are well distributed throughout the melt as was mentioned before.

Some of the samples, when dissolved for the nitrogen test, gave off phosphine. Also, when a sample was burned for the carbon-hydrogen analysis, a yellow speck was discovered and tested and found to be phosphorous. Most of the samples were then analyzed for phosphorous, but the results are all low, as can be seen in column six of Table 4. Therefore, the phosphorous in the metal must be segregated and a sample cut from a slice might not hit it.

Column seven shows a few cobalt analyses around the ten ppm range, which is a little higher than they usually run. The manganese analyses in column eight are not consistently higher than the third egg analyses and none of them are very bad. The magnesium analyses in column nine are all very high, as are the nitrogen results in column ten. The density results were very low as can be seen from column eleven. The three abovementioned things tie together well in that when the nitrogen is high in the metal, the magnesium will be high and the density low. All the samples when etched for the density test showed microscopic porosity.

The carbon and hydrogen results were also quite a bit higher than the run of regular metal as can be seen from columns twelve and thirteen. This shows that these two impurities are well distributed throughout the main mass of the melt but are very high in the last portion of the metal. Only a few chlorides were run and they were consistent with regular metal analyses. The silica results were somewhat lower than the regular run of material. Some of the silica analyses were obtained from testing composites and the rest were run individually.

A literature search was made to make use of any available information on pyrophoric uranium compounds. Several references were made to an article by M. A. Colani (1) which stated that

(1) "Researches on Uranous Compounds" by M. A. Colani, Annales de Chimie et de Physique, [8] , 12 (1907), pp.59-144.

uranium phosphide burned when heated in air. The sulfide of uranium was also pyrophoric when heated in air and would spark when thrown into a flame. The article also mentioned that the selenide of uranium was pyrophoric.

As was stated above, the phosphorous in the metal was probably segregated and it is doubtful if this would cause pyrophoricity. The metal was analyzed for selenium and sulfur and none was detected. However, it is feasible that sulfur could be in the metal as there is sulfide in the liner of the reduction vessel. This could possibly be reduced to sulfide by the molten uranium and carried over into the billets.

Summary and Conclusions

1. Most of the impurities in remelted uranium metal are evenly distributed throughout the melt. These impurities include silver, chromium, nickel, boron, cobalt, iron, manganese, chloride and silica. The other impurities, which include magnesium, nitrogen, carbon and hydrogen are much higher in the top portion of the melt.
2. The neutron absorption test showed the last metal in the crucible to be very impure, as the neutron absorption coefficient for this material was very high.
3. All samples cut from the number four egg, or the last material in the melt, were extremely pyrophoric. Samples from other eggs were all right with a few exceptions. These exceptions only showed tendencies toward pyrophoricity but could not be compared with the fourth egg samples along this line.
4. Phosphides, sulfides and selenides of uranium are pyrophoric. The last two impurities were not detected in the material at all and the amount of phosphorous present probably is not enough to cause pyrophoricity.
5. A metallographic examination of pyrophoric and non-pyrophoric metal samples showed that "microscopic porosity would seem to be the cause of the pyrophoric condition."

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TABLE 3

Chemical and Physical Analyses of the Third Egg

K number of 3rd egg	Ag	Cr	Ni	Boron	Nitrogen	Density	Fe	Mn	Mg	Lot
9906	L 2.0	L 10	L 10	L 0.2	68	18.93	26	5.8	15	EC39
09	"	"	"	"	59	18.95	24	4.5	L 2.0	"
19	"	"	"	"	60	18.94	32	6.2	14	"
24	"	"	"	"	50	18.95	28	6.5	6.6	EC40
30	"	"	"	"	65	18.93	17	4.1	16	"
33	"	"	"	"	49	18.93	21	5.3	19	"
45	"	"	"	"	37	18.96	30	-	5.7	EE41
48	"	"	"	"	46	18.96	34	-	13	"
51	"	"	"	"	42	18.93	30	6.5	9.0	EG42
54	"	"	"	"	56	18.92	29	7.4	24	"
57	"	"	"	"	50	18.93	27	6.4	M 30	"
60	"	"	"	"	79	18.89	27	7.9	M 30	"
64	"	"	"	"	58	18.95	45	7.5	3.5	"
70	"	"	"	"	134	18.92	22	7.0	M 30	EG43
73	"	"	"	"	57	18.90	27	6.5	20	"
76	"	"	"	"	51	18.91	33	6.5	M 30	"

All results are listed in ppm

M = more than

L = less than

Lot composites are listed below.

<u>Lot Number</u>	<u>Carbon</u>	<u>Hydrogen</u>	<u>Chloride</u>	<u>Silica</u>
EC39	310	7.0	5	50
EC40	420	5.7	5	36
EE41	380	5.3	6	34
EG42	390	5.4	5	40
EG43	480	4.2	5	26

TABLE 4

Chemical And Physical Analyses Of The Fourth Egg

K Numbers of 4th egg	As	Cr	Ni	Boron	P	Co	Fe	Mn	Mg	Nitro- gen	Density	Carbon	Hydrogen	Chloride	Silica
9904-5-6	L2	L10	L10	L 0.2	15	L10	31	8.6	850	520	18.27	1260	19.6	--	10*
9907-8-9	"	"	"	"	7	"	19	4.2	370	440	18.50	1050	11.2	--	10*
9917-18-19	"	"	"	"	14	"	27	7.5	850	885	18.06	2760	10.9	--	10*
9922-23-24	"	"	"	"	8	10	27	7.7	950	885	18.00	1420	13.0	--	26*
9928-29-30	"	"	"	"	9	L10	26	7.2	420	510	18.38	860	6.7	--	26*
9931-32-33	"	"	"	"	-	"	21	6.1	800	640	18.14	1100	13.6	9	21
9943-44-45	"	"	"	"	8	"	24	8.9	800	1230	17.88	1280	20.2	--	26*
9946-47-48	"	"	"	"	11	10	27	7.8	800	1320	18.17	1310	16.5	--	26*
9949-50-51	"	"	"	"	8	10	11	6.0	605	1195	17.89	1380	30.4	--	16*
9952-53-54	"	"	"	"	8	10	17	5.8	1200	820	17.50	820	17.6	--	10*
9955-56-57	"	"	"	"	6	L10	33	5.8	950	825	17.69	870	15.3	--	16*
9958-59-60	"	"	"	"	-	"	10	3.3	740	900	18.36	1140	11.6	5	25
9962-63-64	"	"	"	"	-	10	16	4.6	700	550	18.45	1060	14.7	12	22
9968-69-70	"	"	"	"	-	10	10	3.7	545	640	18.57	960	14.9	--	16*
9971-72-73	"	"	"	"	9	10	15	4.7	950	1140	18.16	1480	18.9	--	16*
9974-75-76	"	"	"	"	5	L10	17	4.7	850	1500	17.95	1220	12.0	--	10*

All results in ppm

* 3 composite samples