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EXAMINATION OF FACTORS AFFECTING THE QUALITY
OF VACUUM INDUCTION-MELTED URANIUM

by

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EXAMINATION OF FACTORS AFFECTING THE QUALITY
OF VACUUM INDUCTION-MELTED URANIUMRoy W. Endebrock, Ellis L. Foster, Jr.,
and Ronald F. Dickerson

Uranium melting was investigated to determine what reactions, variable in nature, could be detrimental to ingot purity or soundness. Experiments were conducted with 10-lb uranium charges in a vacuum induction furnace 1200 liters in volume. A special manifold allowed sampling of the furnace atmosphere for mass spectrometer analyses at appropriate times after the furnace was isolated from the vacuum system. Melts were made with a selected production grade of pure uranium. The program included (1) exploratory melts in graphite with and without MgO crucible dressings, (2) melts in graphite and zirconia crucibles under dry and wet furnace conditions, (3) replicate experiments in which known quantities of hydrogen, nitrogen, CO, oxygen, CO₂, H₂O, and argon were each admitted to the furnace to determine pressure-time relationships and residual-gas compositions, and (4) a demonstration of the water-gas reaction within the furnace.

The MgO crucible dressing tended to peel during initial outgassing. During the melting cycle, MgO was reduced and formed a black magnesium deposit within the furnace. Gases and, especially, water vapor adsorbed by graphite components were difficult to remove. To lower the outgas rate at 2500 F from 3 to 0.45 μ per min, it was necessary to heat the crucible for 5-1/2 hr in the 2500 to 3100 F temperature range at 1×10^{-4} mm of mercury. Water and graphite at elevated temperatures produced hydrogen and CO, the products of the water-gas reaction. A secondary reaction between CO and uranium resulted in a furnace atmosphere that was mainly hydrogen. Temperature variations between surface and subsurface metal were large. Optical temperature determinations were affected by dross and varied considerably with dross thickness. The integrity of the surface dross was a controlling factor of the composition and amount of reactive gas remaining over the melt and of the ability to reproduce data.

From a thermodynamic viewpoint, small changes in CO partial pressure over the melt will result in large changes in the carbon-oxygen level of the melt, and the contribution of CO to contamination can be greater through this mechanism than by the direct CO-uranium reaction.

INTRODUCTION

Uranium fuel slugs for production-type reactors must meet rigid quality specifications for acceptance. Fuel-slug quality, however, is directly dependent upon the quality of the ingot from which slugs are fabricated. Metal quality is related to a variety of chemical and physical effects which manifest themselves in variable degrees of metal soundness and purity and which appear to originate in the melting and casting phases of processing. The over-all study of the cause-and-effect relationship of the processing parameters that contribute to metal rejection is complex as is attested by the amount of continuing research directed toward a better understanding of these process variables.

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Through continuing and increased controls of the uranium melting cycle significant improvements have, in the past, been made in both the quality and the yield of fuel slugs. Statistical analyses of charge-makeup and melting-cycle variables^(1,2) contributed to process changes that led to these improvements. Although the production of uranium ingots by the vacuum induction-melting process is now characterized by a relatively low metal-rejection level, it is believed that further major improvements necessary for consistently high uniformity of ingot production can only come from detailed studies of the basic melting variables that contribute to out-of-specification metal. National Lead of Ohio, as operator of the Fuel Materials Production Center, has a direct and continuing interest in such studies. Consequently, NLO initiated a research program at Battelle Memorial Institute to gain a greater insight of the chemical reactions that take place during the vacuum induction melting of uranium and especially those reactions that have a deleterious effect on metal quality.

In the production of ingot uranium, virgin uranium from the green salt-magnesium reduction is charged into the crucible along with uranium scrap. Virgin, or as-reduced, uranium is somewhat high in magnesium and hydrogen; on the other hand, scrap in the form of croppings, briquetted chips, and reject metal could contribute variable quantities of carbides, nitrides, and oxides to the melt, and a variety of impurities in minor quantities. Both the crucible and the split mold used in the operations are composed of graphite. Both are coated with MgO* (applied as a slurry and then dried) to impede the carbon pickup from the crucible by the uranium during melting. Although the operation is carried out under vacuum, air leakage into the system can be relatively high. Water enters the system principally through its association with air leakage and by way of undried scrap. During the vacuum-melting operation, the furnace pressure sometimes increases to 0.5 mm of mercury and remains at this relatively high pressure throughout the cycle. Finally, the metal is bottom poured into the mold and then the furnace is flushed with nitrogen to aid in cooling.

The original objective of the program was to determine the role of each impurity in the kinetics and thermodynamics of reactions taking place during the production melting of uranium. However, early in the program it became apparent that before a meaningful evaluation of the role of the various charge impurities on metal quality could be made, a better understanding of the part played by the furnace-atmosphere contaminants, water and air, during melting should be a prime consideration. As the study progressed, this choice of direction was justified by the implications and the complexity of the reactions that occur in the high-temperature metal-graphite system. Consequently, the aim of the program became less broad by embracing the more specific study of the role of air and water as well as the associated contaminants resulting from secondary reactions peculiar to the system.

In addition to the experimental portion of the program, a survey of the literature was concurrently made dealing with previous research in this general field of interest. A review of this portion of the program is presented in the Appendix.

(1) References at end of text.

*Process developed at Los Alamos.

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EXPERIMENTAL PROCEDUREApparatus

Uranium melting experiments were carried out in a vacuum furnace which was originally designed to permit melting and casting of high-temperature alloys (see Figure 1). The furnace was equipped with a tilt-type coil arrangement and, with the particular type of crucible assembly used for all experiments, was capable of melting uranium charges up to 10 lb. The water-jacketed furnace shell served a dual purpose: (1) its main function was to dissipate the heat radiated to the furnace shell during melting, and (2) by using a hot-water mixing line, to aid in drying and outgassing the furnace shell. The jacket was maintained at roughly 100 F for all tests. Furnace-lead junctions simplified the use of thermocouples for temperature control, while appropriate sight ports permitted observations of the progress of an experiment.

A vacuum system with a rated capacity of 2500 cfm at 1×10^{-4} mm of mercury absolute pressure is an integral part of the vacuum furnace. This system employs a 105-cfm mechanical pump, an oil-injector booster, and two oil-diffusion pumps. A high-integrity vacuum valve located in the vacuum line between the furnace and the diffusion pumps is especially useful for obtaining over-all leak and outgassing rates and for isolating furnace atmospheres at specific points of interest.

The induction power source is a 50-kw motor generator which delivers a 3000-cps current to an impedance-matching capacitor station. From this station power is conducted to the water-cooled coil through parallel lead-throughs in a Micarta flange.

The crucible assembly, shown in position in Figure 2, is made up as follows: Soldered to the bottom turn of the induction coil, clamps support a disk of porous graphite. Directly inside the coil a liner of degreased and dried glass cloth is placed, and this, together with the bottom disk, serves as a container for the rest of the assembly. The graphite crucible is located at the center of the coil surrounded by a porous graphite (Carbocel) cylinder which permits easy removal of the crucible without the need of complete reassembly for each new melt. Zirconium oxide sand packed between the porous graphite cylinder and the glass cloth serves both to insulate the coil from the hot crucible and to position the crucible in the assembly. A graphite disk placed over the top locks the assembly components in place, and permits top pouring into a copper chill mold (which is also shown in Figure 2).

Except for a few experiments in which commercially available zirconia crucibles were used, the crucibles generally used throughout the program were fabricated from Grade CS312 graphite, a product of the National Carbon Company. The dimensions of experimental crucibles were, for the outside, 2-1/2 in. in diameter by 7 in. long and, for the inside, 2 in. in diameter by 6-1/2 in. deep.

Temperatures, which were recorded by an L and N recorder, were obtained with a platinum-platinum 10 w/o rhodium thermocouple, contained in an alumina protection tube which was immersed in the melt. Optical-pyrometer measurements of surface temperatures were made from time to time; however, these readings were only approximate at best and altogether unreliable when the melt surface was crusted over. Surface

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FIGURE 1. MELTING FURNACE AND VACUUM SYSTEM

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FIGURE 2. CRUCIBLE ASSEMBLY AND MOLD

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temperatures were generally found to be considerably cooler than the main body of the melt. Furnace pressures were obtained through the use of a McLeod gage (F. J. Stokes Machine Co., Model No. 276AC). A thermocouple pressure gage (Model 501, National Research Corp.) was also used; however, its main value was in qualitatively indicating gas-composition changes by comparing readings with those of the McLeod gage. During initial pumpdown periods at the beginning of experiments, it indicated whether moisture was present.

Charge Metal

Throughout the program, the charge metal used in the various experiments was selected as reduced uranium. This metal which was received as oval-shaped rods was reduced to round rods of a size convenient for the experimental charges by forging in air after heating in a helium atmosphere at a temperature of 1050 F and then quenching in water. In order to adjust charge weights, a portion of the metal was reduced to 1/8-in. -thick plate that was then cut into 1/2-in. squares. Prior to loading the crucible, the metal was pickled in a 50 volume per cent aqueous solution of nitric acid. A typical analysis of these forged uranium billets was as follows: carbon, 10 to 40 ppm; nitrogen, 10 to 40 ppm; oxygen, 4 to 8 ppm; and hydrogen, about 2 ppm.

Gas Analysis

The instrument used for analyzing furnace gases in the various experiments was a Model 21-620 mass spectrometer manufactured by the Consolidated Electrodynamics Corporation. This spectrometer utilizes the "cycloidal focusing" principle in the analyzer. The application of an electric field to the usual magnetic field causes the ions to traverse a cycloid path. Characteristic 360-deg ion paths result in a resolving power of 1 mass unit in 150 mass units and in a range of 250 mass units. The cycloidal analyzer incorporates an additional 180-deg collector which registers ions in the mass 2 to 12 range. The peak heights which are registered by the cycloidal analyzer are true amplitudes relative to the molecular composition of the sample. The ionizing current of the analyzer is variable but the slits are fixed.

Sensitivities of the Model 21-620 under normal conditions for typical compounds are listed below.

	<u>Divisions per Mm</u>
N-butane	250
Argon	300
Hydrogen	85

These sensitivities are quite dependent on analyzer-filament and preamplifier-tube characteristics, and can vary by approximately 100 per cent for different filaments and different amplifier tubes.

The sample inlet system to the instrument consists of a room-temperature glass-ware system. As used throughout the program, a flask containing a sample of the low-pressure gas is attached to the sample inlet system in preparation for analysis. Although a continuous-sampling feature is also available which permits continuous monitoring of a given component in a process, this feature is unattractive (especially in the melting program), mainly because a qualitative spectrum, which usually requires 30 to 40 min of scan time, is required if the qualitative composition of a system has not been previously established.

An electronic micromanometer (Consolidated Electrodynamics Corporation) is used to give accurate sample pressure measurements at the micron level. All of this equipment is housed in an air-conditioned room maintained at a constant temperature (± 0.5 C).

For sampling the furnace atmosphere during the program, a special sampling manifold was incorporated as an auxiliary part of the furnace. A sketch of this manifold and attendant equipment in relation to the furnace is shown in Figure 3. The manifold was connected by way of a metal ball joint to a tube extending into the furnace. All stopcocks were large enough to allow sampling times of no greater than 1 min. The manifold, which would be isolated from both the furnace and an auxiliary vacuum pump, could accommodate five sampling flasks at one time. A thermocouple pressure gage which was attached to the manifold was especially useful in assuring that this part of the system was leak-free. Since a sample of approximately 150 μ liters will insure a suitable mass spectrum, sampling was ordinarily performed by using 3-liter flasks which were filled to a 50- μ pressure or more. Early tests showed, however, that reliable samples could be taken in as short a period as a 1/2 min at sample pressures as low as 20 μ .

The accuracy of the equipment was approximately ± 4 to 5 per cent of the reported value. Interference of mass numbers occurs between nitrogen and carbon monoxide and between carbon dioxide and argon which can be a source of error. In like manner, organic gases and vapors can interfere with most of the inorganic gases of interest. Water vapor presents the greatest problem. Its ability to condense or be adsorbed on the furnace, manifold, and sampling flask walls often leads to unreliable quantitative results, and this was especially true at the higher vapor-pressure levels. Frequent baking cycles of sampling flasks, leak checks of flasks prior to sampling, and minimum delays in flask transfer to the instrument all helped to reduce errors.

Discussion of Experiments, Data, and Results

In the over-all evaluation of results one must bear in mind that large differences in surface characteristics existed between the physical characteristics of the experimental melts and those found in production melting. For example, estimations of exposure differences indicated that the ratio of surface exposure of carbon to the volume of molten uranium was 5-1/3 times greater in the experimental tests than in normal production melting, but that the ratio of metal surface exposed to the furnace atmosphere in the tests was only one-third of that exposed in production furnace atmospheres. Marked differences were noted between surface and subsurface temperatures of the uranium melts (as much as 300 F), and temperature measurements (by optical

FIGURE 3. SKETCH OF SAMPLING MANIFOLD

pyrometer) of surfaces covered with dross varied radically with the amount and nature of this dross. To avoid measurement errors, temperatures of the experimental melts were based exclusively on subsurface thermocouple readings.

Initial Experiments

The decision was made to explore furnace atmosphere and gaseous products of reaction under static conditions, that is, with the furnace isolated from the vacuum system after pumpdown. Before any of the experimental work was begun, the furnace was thoroughly checked for leaks. After sufficient time was allowed for outgassing the system, a very low order of leak was observed (about 0.1μ per min). Also of considerable importance to experimental operations was the integrity of the valve which isolates the furnace from the vacuum system. This valve was found to seal tightly in the closed position, and its leakage was too low to detect by leak-rate checks.

Once system tightness was established, a test was made to determine the furnace-system volume up to the shutoff valve. This was done by expanding a known volume of argon at atmospheric pressure into the evacuated system. Furnace volume was calculated to be 1200 liters from the resulting increase in furnace pressure.

Tests were also conducted to determine the effect of heated crucibles held at temperatures of 1800 F and 2600 F (the extremes of temperature anticipated) on the average gas temperature in the furnace. These tests were simply repetitions of the volume tests described above but at the two crucible temperatures of interest. These temperatures were held constant (± 15 F or less) during the test period. The maximum pressure variation between room-temperature expansions and 2600 F expansions was found to be so slight that the temperature of the furnace gas could be considered to be essentially that of the outlet water of the furnace jacket.

Test Series 1. Exploratory Melts

The first series of melting experiments was of an exploratory nature in that an attempt was made to estimate the amount and composition of the offgas produced in bringing pure uranium metal up to a temperature of 2500 F (the temperature range in the production melting cycle). Graphite crucibles coated with a production formulation of MgO slurry were used in four of the tests. A fifth test using an uncoated graphite crucible was made to observe any effects that could be attributed to the MgO coating.

In three of the melting tests, the pressure was allowed to build up in the furnace as it was brought from 2000 F (below the melting point of uranium) to 2200 F. This gas was sampled for analysis in the mass spectrometer. The vacuum shutoff valve was opened, gases were quickly pumped out, and then the valve was closed again. The temperature was then raised to 2300 F, where again the accumulated furnace gas was sampled for analysis. This procedure was repeated at 2400 F and again at 2500 F. In one of the tests the accumulated gas produced in heating from 2000 F to 2500 F was likewise sampled for analysis.

Pertinent observations made during the five tests are indicated below:

Test 1. This was an uncharged blank test made with an MgO-coated graphite crucible. Little or no furnace deposits were found after the test. The MgO coating scaled off the crucible wall, leaving completely exposed graphite.

Test 2. The graphite crucible used in this test was coated with MgO. Bubbling at the surface of the melt occurred and became vigorous as the temperature was increased. A black sootlike material was deposited on crucible support surfaces within a well-defined zone about the crucible. At 2400 F, the surface of the melt crusted over completely with an abrupt termination of bubbling. Some evidence of attack of the porcelain thermocouple protection tube led to the exclusive use of alumina protection tubes during the program.

Test 3. This test was conducted with an uncoated graphite crucible. Throughout the test little or no bubbling occurred, and at the 2500 F temperature level no bubbling was observed. No heavy deposit (as in Test 1) was found; however, a brown powder was very lightly deposited on furnace surfaces. Although surface dross was evident on the melt, it was not solidly crusted over as in Test 2. No apparent attack of the alumina protection tube occurred.

Test 4. In this test, an MgO-coated graphite crucible was used. Vigorous bubbling occurred at a temperature of 2400 F and above and continued to the end of the test. As before, there was evidence of surface dross on the melt. A black residue, as observed in Test 2, was also observed at the conclusion of this test. A spectrographic analysis of the deposit showed that it was composed mostly of magnesium with lesser amounts of aluminum, iron, nickel, silicon, sodium, and zinc. Loss on ignition was 15 per cent.

Test 5. This test was also conducted in an MgO-coated graphite crucible. Very rigorous bubbling occurred soon after melting had occurred and continued throughout the test. The outgas rate at 2500 F was essentially the same as that of Test 4 at the same temperature level. As in Tests 2 and 3, a black deposit (of about the same composition as before) was found on the crucible-assembly supports in the same well-defined zone.

A summary of the data obtained in this series of experiments is presented in Table 1. Note that in Test 1 (blank test) at 2500 F there were nearly equal amounts of hydrogen and CO present in the furnace gas. In tests with uranium the predominant gas was hydrogen. Analyses of the cast ingots obtained after the above tests (Table 2) indicated that surface dross was probably picked up during top pouring which was mixed and then frozen as inclusions in the copper chill mold.

TABLE 1. TEST SERIES I

Test	Temperature, F	Graphite Crucible Coating	Uranium Charge, kg	Gas- Sampling Time, min	Gas- Sampling(a) Pressure, μ	Outgassing Rate, μ per min	Mass-Spectrometer Gas Analysis, volume per cent								
							H ₂	CO	N ₂	O ₂	H ₂ O	A ^(c)	CO ₂ ^(c)	Organics Calculated ^(b)	
														As n-Pentane	As Toluene
1	2000	MgO	None	20	19	1.0	62.8	9.6	20.0	Nil	5	0.2	0.7	0.8	0.2
	2000	MgO	None	135	160	1.2	70.1	8.5	17.0	0.2	3	0.2	0.1	0.2	0.3
	2500	MgO	None	45	150	3.3	41.9	44.3	10.0	0.5	2	0.1	0.4	0.3	0.1
2	2000	MgO	4.405	20	33	1.7	Sample lost								
	2200	MgO	4.405	60	100	1.7	93.8	1.3	1.9	Nil	2	0.2	0.1	0.3	0.4
	2300	MgO	4.405	42	100	2.4	93.8	1.6	1.0	Nil	2	0.1	Nil	1.1	0.4
	2400	MgO	4.405	45	95	2.1	88.9	0.8	7.9	Nil	1.5	0.1	Nil	0.1	0.7
	2500	MgO	4.405	35	90	2.6	Sample lost								
3	2000	None	4.415	25	120	4.8	94.7	0.9	2.2	0.1	1.5	0.1	0.1	0.6	0.1
	2200	None	4.415	40	55	1.4	92.4	1.3	2.5	0.2	2	0.1	0.1	1.3	0.1
	2300	None	4.415	40	100	2.5	92.2	1.4	3.3	0.9	2	0.1	0.1	0.2	Nil
	2400	None	4.415	31	100	3.2	92.9	2.0	1.2	0.2	2	0.1	1.0	0.1	0.2
	2500	None	4.415	48	145	3.0	Sample lost								
4	2000	MgO	4.318	35	65	1.9	93.3	1.6	3.0	0.1	1.5	0.1	0.1	0.3	0.2
	2200	MgO	4.318	41	50	1.2	89.9	1.2	6.1	Nil	2	0.2	0.1	2.6	Nil
	2300	MgO	4.318	40	75	1.9	87.7	1.6	3.0	0.1	6.5	0.1	0.1	0.4	0.2
	2400	MgO	4.318	41	85	2.1	94.7	0.6	1.6	Nil	1.5	0.1	Nil	1.4	0.1
	2500	MgO	4.318	37	100	2.7	Sample lost								
5	2000	MgO	4.370	40	65	1.6	Sample lost								
	2500	MgO	4.370	52	140	2.7	96.6	0.5	0.5	Nil	1.5	0.1	Nil	0.2	0.6

(a) McLeod-gage readings in microns (10^{-3} mm of mercury).

(b) Organic components: There was a small organic contribution in most of the samples. This appeared to be a complex mixture of paraffin and aromatic hydrocarbons. It was not possible to definitely identify these organic components because of the complexity of the mixture and because they are present in low concentrations. They were therefore calculated in terms of n-pentane and toluene. This is not to imply that these two compounds were definitely present, but only that they were compound types similar to those in the samples and that they offered a means of obtaining approximate volume percentage values.

(c) Argon and CO₂: The presence of organic material interferes with the measurement of argon and CO₂. The values presented in the table are calculated from residual peaks which remained after the organic contribution (calculated as n-pentane) was subtracted from the original measured peak heights. These values for argon and CO₂ should be considered only as the maximum per cent possible. There is probably some residual organic other than that calculated as n-pentane which still contributes to the n/e 40 (argon) and the n/e 44 (CO₂) peaks.

TABLE 2. URANIUM ANALYSES^(a) FOR TEST SERIES 1

Test	Initial Analysis, ppm				Final Analysis, ppm			
	C	N ₂	O ₂	H ₂	C	N ₂	O ₂	H ₂
2	10	35	8	2.2	2000	15	74	0.3
3	15	20	7	1.7	2345	15	20	0.2
4	15	20	4	2.2	2025	27	72	<0.1
5	10	10	4	2.5	1445	10	40	<0.2

(a) Carbon and nitrogen by conventional chemical methods; oxygen and hydrogen by vacuum-fusion method.

It is of particular interest that in those tests in which castings were analyzed, the carbon content range was roughly 1400 to 2400 ppm. Oxygen, on the other hand, ranged from 20 to 74 ppm. These ranges appear high as suggested by known equilibrium relationships (at 2500 F the uranium + UC equilibrium indicates a carbon composition of about 1000 ppm). It is interpreted to mean that excess carbon and oxygen, as liquated UC and UO₂, are mechanically mixed during pouring and then retained as included carbide and oxide in the cast slug. Also, these high carbon analyses indicate that during the various tests, equilibrium is very probably attained between the graphite crucible and the charge. From the standpoint of obtaining data subject to thermodynamic evaluation, this is desirable. However, it must be recognized that this is not the situation in production melting since equilibrium carbon in the remelt ingot could not be tolerated.

In this first series of tests, it was noted that a deposit consisting mainly of magnesium was produced only when the MgO coating (used in production melting) had been previously applied to crucibles. The effectiveness of MgO as a coating was questionable since it was found to peel from surfaces in blank tests. However, the carbon content of the metal was lower in those tests where the coating was used. It is believed that MgO is slowly reduced by the uranium to magnesium and probably UO₂. As magnesium boils away, UO₂ remains at the carbon surface, at least at those places on the surface where the MgO remains in graphite pores. Urania is superior to graphite as a container for molten uranium. Moreover, the impregnation studies of Piper⁽³⁾ tend to substantiate such a mechanism for MgO. In addition, the MgO coating also contributed to dross formation over the melt early in the cycle. As shown in later tests, dross was found to affect reactions between uranium and furnace gases.

The initial exploratory tests (Table 1) showed that the predominant gas evolved during melting was hydrogen with small but significant quantities of CO. Ordinarily, the CO might be attributed to the reaction of air-leak oxygen with the graphite crucible. However, the control test run without a metal charge, Test 1, produced a furnace atmosphere with almost equal quantities of hydrogen and CO, suggesting that a water-gas reaction ($C + H_2O \rightleftharpoons CO + H_2$) had occurred between some source of moisture and the hot graphite. During these test melts, evolution of gas appeared to be produced at a fairly constant rate at any given temperature, and the quantity of gas appeared to be independent of the melt. It was reasoned that if a water-gas reaction had, indeed, occurred, CO would be expected to react with uranium. On the other hand, a thermodynamic treatment of both this reaction and the direct reaction between water and uranium ($2H_2O + U \rightarrow UO_2 + 2H_2$) indicated that they would be competitive, with the latter reaction having the greater reaction potential. In either case, the remaining furnace gas would be hydrogen, which complicates any experimental demonstrations of the role of a water-gas reaction in the uranium-graphite system.

Test Series 2. The Effect of Moisture

The various implications of the water-gas reaction led to a second series of experiments in which a dry system was to be compared with a system into which a known amount of water had been introduced. Four tests (Tests 6 through 9) were made which included dry and wet blank tests (no uranium) at 2500 F and dry and wet melting tests run under as nearly identical conditions as the equipment and the nature of the tests would permit. In order to eliminate any possibility of complicating side reactions with MgO, uncoated graphite crucibles were used exclusively in these tests.

Additional tests (Tests 10 through 12) for this series were conducted in a graphite-free system using zirconia crucibles in which an attempt was made to compare the CO-uranium reaction under dry and wet furnace conditions. The main purpose of these tests was to observe the relative reactivities of CO and H₂O with uranium as an aid to a better understanding of the mechanism of the competitive reactions of water with the uranium metal and with the graphite crucible and accessories. A summary of test conditions and of the corresponding analyses of gas samples taken during the tests is given in Table 3.

Analyses for carbon and nitrogen were made of the castings produced in each melting test to show pickup of carbon by uranium through the CO-uranium reaction, and are listed in Table 4. However, in the tests using graphite, the near carbon saturation of uranium under test conditions completely masked this effect. Nevertheless, the over-all data helped to clarify the role of water in the uranium-graphite system.

It is of interest to note that in preparing the crucible (and assembly) for gas sampling under dry furnace conditions a period of approximately 5-1/2 hr of continuous heating in the 2500 to 3100 F temperature range at a pressure of less than 1×10^{-4} mm mercury was required to reduce the outgassing rate at 2500 F from about 3 μ per min to 0.45 μ per min. In those tests of the series which were run under wet furnace conditions water was injected with a hypodermic syringe into a section of rubber tubing attached to an opening to the furnace. Carbon monoxide gas additions to the furnace were made at the sampling manifold.

In the dry blank experiment, Test 6, a relatively low outgassing rate at 2500 F was achieved only after outgassing the crucible and assembly components at high temperature for 5-1/2 hr. This rate was, for all practical purposes, the leak rate of the system as indicated by a gas composition (Table 3) that was essentially that of air except for a quantity of CO that was stoichiometrically equivalent to the percentage difference of oxygen. Significantly, this low-pressure furnace gas contained no detectable hydrogen. Although it was not immediately clear, this analysis, compared with that of earlier tests and especially that of Test 1 (Table 1), pointed to the fact that moisture in the crucible assembly was removed very slowly, even at high temperatures, and then not as water but as the products of a heterogeneous water-gas reaction. Two implications of this situation were indicated: (1) graphite (especially porous graphite assembly components) could become activated and hold large quantities of water that (2) would provide a constant supply of CO.

Although melting experiments of the second series were timed alike in an effort to show greater carbon pickup by the uranium under wet conditions, the large surface exposure of carbon to metal volume in the experimental crucible presumably resulted in a saturated carbon condition for both tests that masked the pickup effect.

TABLE 3. TEST SERIES 2

Test	Crucible	Uranium Charge, kg	Temperature, F	Water Added, cm ³	CO Added, liter (STP)	Time at Temperature, min	Gas- Sampling ^(a) Pressure, μ	Mass-Spectrometer Gas Analysis, volume per cent							
								H ₂	CO	N ₂	O ₂	H ₂ O	A	CO ₂	n-Pentane
6	Uncoated graphite	None	2500	None	None	70	33	Nil	12.7	68.5	14.9	2.2	0.9	0.2	0.6
7	Ditto	None	2500	1.1	None	30	90	68.3	24.9	2.1	0.03	3.7	0.05	0.3	0.7
8	Ditto	4.330	2500	None	None	30	26	94	2.9	1.5	Nil	2	0.15	0.16	0.94
9	Ditto	4.370	2500	0.2	None	30	20	0.8	5.0	71	20.7	2	0.9	0.09	0.2
10	Zirconia	4.335	2500	None	None	30	44	71	2.6	24.2	0.09	2	0.2	0.18	0.3
11	Ditto	4.405	2500	None	0.82	40	21	75	1.9	7.3	0.2	2	1.3	0.48	2.0
12	Ditto	4.370	2500	0.1	0.82	54	55	Sample lost							

(a) McLeod readings.

In the second part of this series of experiments, in which CO was added to a graphite-free system under dry and wet furnace conditions, it was found that in both cases CO reacted rapidly. However, under wet conditions the furnace pressure did not fall to the base-line level (Figures 4 and 5), giving the first indication of the formation of a protective metal cover by the interaction of an oxide-carbide crust. The plots shown in Figures 4 and 5 (furnace pressure versus time) are termed pressure profiles throughout this report. It is noteworthy that in the dry test stoichiometric carbon was found in a center section of the cast metal (no dross on the metal surface during melting) while in a center section of the wet-test cast metal the carbon content was 35 w/o less (dross formed early by water admission).

TABLE 4. URANIUM ANALYSES FOR TEST SERIES 2

Test	Initial Analysis, ppm		Final Analysis, ppm	
	Carbon	Nitrogen	Carbon	Nitrogen
8	40	30	1650	20
9	35	20	1600	20
10	20	20	60	30
11	30	25	130	35
12	95	20	85	40

Test Series 3. Replicate Pressure Profiles

A series of experimental melts was made by introducing to the furnace chamber in significant amounts each of the various background gases which apparently stem from the operational impurities - air and water. Gases used were also those found in the furnace atmosphere in previous experiments. The objectives of this experimental series were (1) to obtain data that could be studied from the standpoint of chemical thermodynamics, and (2) to demonstrate reproducibility of these data. The incorporation of pressure profiles during this investigation provided a means for indicating the proper point for gas sampling, and for giving qualitative information regarding the mechanism and relative reactivity of the reactions taking place within the furnace.

As mentioned previously, for the purpose of this report, pressure profiles are defined as plots of furnace pressure versus time after admitting a known amount of a given pure gas to the furnace. In this series of experimental melts each of the gases, nitrogen, hydrogen, CO, CO₂, oxygen, and H₂O, was admitted to the furnace in quantities sized to produce an initial furnace pressure in the 500 to 600- μ range. A single profile of the inert gas, argon, was also included as a control. A test gas contained in a 3-liter sample flask at a pressure of about 210 mm of mercury was conveniently expanded into the furnace by way of the gas-sampling manifold. High-purity gas samples were supplied in correct sample sizes by the Mass-Spectrometer Group at Battelle. Water samples were sized at 1.0 cm³, and were prepared by adding water to a 1-liter flask, freezing the water, and then evacuating and sealing the flask. These flasks were broken inside the furnace at the appropriate times.

FIGURE 4. PRESSURE PROFILE FOR A GRAPHITE-FREE SYSTEM WITH CO ADDITION UNDER DRY FURNACE CONDITIONS

CO added after 4 min.

FIGURE 5. PRESSURE PROFILE FOR A GRAPHITE-FREE SYSTEM WITH CO ADDITION UNDER WET FURNACE CONDITIONS

CO added after 4 min.

Gases were introduced in all cases according to the following test procedures:

- (1) Crucible (and assembly) was outgassed at 3000 F for 30 min and then cooled (furnace jacket maintained at 100 F throughout test).
- (2) Crucible was quickly loaded with about 4-1/4 kg of pure uranium.
- (3) Crucible and contents were brought to 2500 F and then outgassed for an additional 30 min.
- (4) An outgassing rate was taken (at 2500 F) at the end of the holding period.
- (5) Furnace and contents were isolated from the vacuum system and for the first 6 min the outgassing rate was again checked.
- (6) At the sixth minute after closing the vacuum valve to the furnace the test gas was expanded into the furnace and pressures were taken at regular intervals until the profile was established.
- (7) Temperature of the uranium was manually maintained at 2500 F throughout the test.

To reduce side reaction complexities with MgO, uncoated graphite crucibles were used exclusively.

Profiles for each gas (except hydrogen) were obtained in triplicate. The first profile served as an exploratory test to establish the initial pressure pattern. The second and third replicate tests were made as nearly like the first as possible, and gas samples for analysis in the mass spectrometer were taken at the apparent end point of the reaction. In some cases, samples for analysis were taken at other points along the profile to follow the progress of reaction. Pressure profiles obtained during the experimental series are shown in Figures 6 through 12. A summary of the analyses of the various gas samples is given in Table 5.

In the oxygen tests, a crust immediately formed over the metal. The reaction was very rapid, as manifested by the low initial furnace pressure (about 200 μ) and a rapid decrease in pressure (Figure 6). Analysis of furnace atmosphere (Table 5) 4 min after the oxygen addition showed that oxygen reacted competitively with both the metal and the graphite crucible. Since a large percentage of CO (from the oxygen-graphite reaction) was found, it was also available for reaction with the uranium. In like manner, nitrogen formed a crust over the melt. This gas continued to react during the test (Figure 7) and an analysis of furnace gas sampled 29 min after the nitrogen admission showed that the nitrogen content had fallen to roughly 3.5 volume per cent. The CO and CO₂ gases reacted similarly with the uranium to form a heavy crust of oxide and carbide over the melt, but these reactions appeared to be less rapid than those of oxygen and nitrogen with the metal-graphite system (Figures 8 and 9). A large percentage of CO was found in the furnace atmosphere 34 min after either CO or CO₂ had been admitted (40-min samples, Table 5). Amounts varied from 53 to 77 volume per cent CO. Pouring the metal with this furnace-atmosphere condition resulted in an abrupt drop (Figure 9) in furnace pressure. Water vapor in the water tests (Figure 10) reacted quite rapidly and

FIGURE 6. PRESSURE PROFILES FOR OXYGEN ADDITION

Temperature = 2500 F. Gas added after 6 min.

FIGURE 7. PRESSURE PROFILES FOR NITROGEN ADDITION

Temperature = 2500 F. Gas added after 6 min.

FIGURE 8. PRESSURE PROFILES FOR CARBON MONOXIDE ADDITION

Temperature = 2500 F. Gas added after 6 min.

FIGURE 9. PRESSURE PROFILES FOR CARBON DIOXIDE ADDITION

Temperature = 2500 F. Gas added after 6 min.

FIGURE 10. PRESSURE PROFILES FOR WATER ADDITION

Temperature = 2500 F. 1 cm³ water added
after 6 min.

FIGURE 11. PRESSURE PROFILES FOR HYDROGEN ADDITION

Temperature = 2500 F. Gas added after 6 min.

FIGURE 12. PRESSURE PROFILE FOR ARGON ADDITION CONTROL TEST

Temperature = 2500 F. Gas added after 6 min.

TABLE 5. TEST SERIES 3

Test	Gas	Uranium Charge, kg	Pressure Profile		Sampling Time, min	Calculated Expansion Pressure, μ	Sampling Pressure, μ	Outgassing Rate, μ per min	Mass-Spectrometer Gas Analysis, volume per cent									
			Figure	Curve					H ₂	CO	N ₂	O ₂	H ₂ O	A	CO ₂	As n-Butane	SO ₂	H ₂ S
14	N ₂	4.250	7	2	19	533	50	2.1	68.4	2.6	22.8	0.5	2.9	0.5	0.2	1.2	--	--
					24(a)	533	60	2.1	84.3	1.7	10.2	0.2	2.3	0.5	0.2	0.8	--	--
15	N ₂	4.250	7	3	24(a)	544	80	3.3	79.7	4.6	13.6	0.1	1.5	0.4	0.1	--	--	--
					35	544	130	3.3	91.4	3.3	3.5	0.1	1.5	0.2	0.1	--	--	--
17	O ₂	4.500	6	2	10(a)	533	75	5.1	64.9	24.1	3.3	0.1	1.4	2.3	2.0	1.9	--	--
18	O ₂	4.250	6	3	10(a)	548	90	2.9	28.5	54.1	0.7	2.9	1.1	2.0	10.3	0.1	0.4	--
20	H ₂	4.250	11	2	10	541	610	2.8	97.5	0.9	0.6	--	1.0	--	--	--	--	--
					35	541	610	2.8	98.1	0.5	0.8	--	0.5	--	--	--	--	--
22	CO	4.250	8	2	40(a)	538	220	2.1	34.3	61.6	2.2	0.1	1.2	0.1	0.1	0.5	--	--
23	CO	4.270	8	3	40(a)	536	110	1.5	43.0	52.7	2.4	0.2	1.5	0.1	0.1	--	--	--
25	CO ₂	4.250	9	2	26	533	120	1.8	32.1	62.9	2.9	0.1	1.0	0.1	0.2	0.7	--	--
					40(a)	533	135	1.8	17.3	77.2	0.4	0.1	0.2	0.1	3.9	0.8	--	--
26	CO ₂	4.250	9	3	40(a)	536	310	5.2	50.8	43.2	3.8	0.5	1.6	0.1	0.1	--	--	--
28	H ₂ O	4.250	10	2	12	790	600	4.0	89.5	3.8	1.1	Nil	5.0	Nil	0.2	--	--	0.3
					50(a)	790	910	4.0	92.7	3.1	1.7	0.3	1.4	0.1	0.7	--	--	0.2
					53	790	975	4.0	89.6	3.4	1.8	0.1	4.9	Nil	0.1	--	--	0.3
29	H ₂ O	4.250	10	3	50(a)	790	810	3.8	97.7	1.3	0.4	--	0.5	Nil	Nil	--	--	0.1
31	H ₂ O	4.255	Series 4		50	790	1050	4.9	71.7	25.0	1.6	0.1	1.2	--	0.1	--	--	0.3

(a) Time of apparent reaction end point.

completely, and the reaction gas was found to be predominantly hydrogen with small amounts of CO (about 3 volume per cent). In the hydrogen tests (Figure 11), except for a slight initial drop in furnace pressure (about 50 μ), hydrogen appeared to be nonre-active in the uranium-graphite system. In the argon control (Figure 12), the pressure dropped somewhat and then became constant. When the melt was poured there was an abrupt increase in pressure, similar in nature to the pressure increase in the H₂O profile (mostly hydrogen) at the time of pouring.

A theoretical treatment of the thermodynamics of reactions involving nitrogen, CO, CO₂, oxygen, and H₂O with uranium at 2500 F showed that at equilibrium each of these gases would be present over the melt in amounts much too low for detection by the mass spectrometer. Yet in the profile tests, varying amounts of these gases (or reactive gases stemming from reactions with graphite) were found in the furnace atmosphere after prolonged exposure to the melt held constant at 2500 F. In those cases where large residual pressures of reactive gas remained, the furnace pressure appeared to be dependent upon the carbon available for reaction at the surface of the melt. For example, the H₂O tests showed the smallest (but significant) residual CO partial pressure, the oxygen tests provided more residual CO, while in order of increasing residual CO partial pressure the tests with CO and CO₂ resulted in very large amounts of unreacted CO. Observations made during the series pointed to the fact that the integrity of the surface crusts was a controlling factor of the amount of reactive gas remaining over the melt and of the reproducibility of data in the replicate tests. Proof that the crust was truly protective was given when, at the end of a given test, the melt was poured in a furnace atmosphere containing residual reactive gas; the over-all furnace pressure was observed to drop abruptly, showing immediate continuation of a rapid reaction with the metal. This effect is compared with the abrupt rise in furnace pressure when the melt was poured in an argon-furnace atmosphere. The heat effect on the expansion of the inert argon by pouring hot metal (and perhaps by some mold outgassing) undoubtedly caused the pressure rise in this latter case. A similar pressure rise was observed in tests with water (hydrogen).

Despite the variability of surface conditions that could occur during the replicate tests, reproducibility of data was fairly good. Probably at no time during any of the tests were equilibrium conditions achieved since even at the apparent reaction end point the rate of reaction would be related to gas diffusional processes and rates. Test results in general indicated that an investigation of the rate-controlling mechanism of furnace reactions would help to clarify many of the problems associated with the production remelt process.

Test Series 4. Demonstration of the Water-Gas Reaction Over a Surface-Protected Melt

Observations made during Test Series 3 indicated that a protective surface cover formed over the melt when the hot uranium surface was exposed to an atmosphere of CO or CO₂. This effect suggested a method whereby a water-gas reaction could be demonstrated in a system containing uranium and graphite. Consequently, a final experiment was conducted in which a cover (or dross) was formed over the melt by treating the uranium surface with CO₂. After this treatment water was introduced in a manner identical to that used to obtain the H₂O profiles.

The experimental sequence of operations was as follows:

- (1) Pretreatment of the uncoated graphite crucible and the uranium charge was the same as in Test Series 3.
- (2) Three liters of CO₂ at 206 mm of mercury pressure (0.037 mole) was admitted to the isolated furnace, and a pressure profile was obtained over a 25-min period.
- (3) The furnace was evacuated, then again isolated from the vacuum system, and a like quantity of CO₂ was added. A pressure profile was taken after the second CO₂ addition for a 25-min period. This second treatment was made to demonstrate the effectiveness of the metal cover before the water addition.
- (4) The furnace was evacuated, then again isolated, and a bulb containing 1.0 cm³ of water was broken in the furnace. A pressure profile was taken after the water addition, and mass-spectrometer samples were taken at the same time elapse after the addition as in the case of the Series 3 tests with water.

The pressure profiles obtained are shown in Figures 13 and 14. The dotted-line curve in Figure 14 is the pressure profile obtained for water in Test 29, and is re-plotted for convenience of comparison. Table 5 gives the comparative furnace gas analyses of Tests 31 (Series 4) and 29.

Because the crust over the melt could not be broken, pouring was abandoned, and the melt was permitted to solidify in the crucible. Of considerable interest was the posttest observation made of the crucible and the uranium casting (Figure 15). Nearly half of the crucible side wall was transferred to the melt during the course of the experiment. Although the over-all time at temperature (2500 F) was quite long (3-1/2 hr), this exposure was of the same order as the exposures in Test Series 1. In no other case during the program was there visible evidence of a change in crucible dimensions at the conclusion of an experimental melt.

The final experiment of the program was conducted for the explicit purpose of demonstrating the water-gas reaction in the uranium-graphite system. In this experiment, advantage was taken of the protective nature of a dross over the melt. Carbon dioxide was chosen arbitrarily in the treatment of the molten uranium surface. After the water addition to the furnace, a 25 per cent increase in furnace pressure, compared at identical gas-sampling times, was observed over that of the profile tests with water. The water-gas reaction was demonstrated, since the increased pressure was directly proportional to the increase in residual CO over the melt.

Under such conditions it is possible that a fairly protective cover could be formed and then be intermittently broken or disturbed in such a way as to allow the intermittent buildup of high partial pressures of CO which would be free to affect the melt. Stirring effects, crust variations due to variations in charge and furnace conditions (especially those affecting water concentration in the furnace atmosphere), the kind and amount of gas adsorption of the crucible and assembly components, and even the condition of the furnace atmosphere at the time of pouring could result in large variations in carbon,

FIGURE 13. PRESSURE PROFILES FOR CARBON DIOXIDE ADDITIONS TO MELT FOR WATER-GAS REACTION DEMONSTRATION

Temperature = 2500 F. Gas added after 6 min.

FIGURE 14. PRESSURE PROFILE FOR WATER ADDITION TO MELT FOR WATER-GAS REACTOR DEMONSTRATION

Temperature = 2500 F. 1.0 cm³ water added after 6 min.

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FIGURE 15. GRAPHITE MOLD AND CASTING FROM TEST 31

hydrogen, nitrogen, and oxygen impurities in the finished uranium ingot. It becomes apparent through this line of reasoning that metal purity could vary considerably from melt to melt, depending upon the nature, the amount, and the integrity of the surface dross over the melt and upon the time after the metal becomes molten that the cover forms.

The existence of a furnace atmosphere rich in CO has another important implication. In a theoretical thermodynamic treatment of reactions in molten uranium, E. H. Roland of Westinghouse⁽⁴⁾ states that the role played by the presence of CO on the impurity level of carbon and oxygen in uranium and its alloys is very important. A small change in pressure will cause an appreciable change in the carbon-oxygen level. Roland illustrates this effect by plotting weight per cent carbon against weight per cent oxygen at 1500 C (2732 F) for various partial pressures of CO. Changing the pressure from 1 μ to 10 μ at constant carbon content will cause a marked increase in oxygen content. Similarly, a slight pressure change at constant oxygen will increase the carbon content appreciably. Roland points out that the variability of furnace pressures over the working range in vacuum-melting techniques can account for the differences in oxygen and carbon contents from melt to melt.

One final observation should at least be mentioned. The high dissolution of crucible graphite observed in the final experiment of the program is unresolved, but it suggests a mechanism of transferring carbon from the crucible to the melt that may be related to the kind and pressure of the gas over the melt and the variation in surface and subsurface crucible temperature.

Discussion of the Chemical Thermodynamics of Reactions

During the course of the program, a number of chemical reactions were considered in light of the uranium-melting operation. However, because of the time limitations imposed on such a program, only cursory treatments, for the most part, of the thermodynamics involved in these various reactions could be made. Nevertheless, calculations of this kind were often helpful in guiding the program and in evaluating experimental data. A partial list of the various reactions that were considered at a temperature of 2500 F is given in Table 6 in order of descending equilibrium constants. Throughout the program Battelle's thermodynamicist, J. J. Ward, contributed to the various thermodynamic evaluations.

Of considerable concern, at the time, was the gas analysis obtained in Test 6 (Table 3). The relatively high quantity of oxygen found in this blank test in which the hot graphite crucible had been very carefully outgassed presented a problem. For the reaction,

the equilibrium constant,

$$K = \frac{f_{\text{CO}}^2}{a_c \cdot f_{\text{CO}_2}} = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} ,$$

TABLE 6. REACTIONS CONSIDERED DURING PROGRAM

Equilibrium Constants Were Calculated for a Temperature of 2500 F

Reaction	Equilibrium Constant, K
$3U + 2CO \rightarrow 2UO_2 + UC_2$	1.24×10^{40}
$U + 2CO_2 \rightarrow UO_2 + 2CO$	1.93×10^{26}
$U + O_2 \rightarrow UO_2$	3.17×10^{25}
$2U + CO_2 \rightarrow UO_2 + UC$	3.14×10^{23}
$U + 2H_2O \rightarrow UO_2 + 2H_2$	3.59×10^{15}
$2C + O_2 \rightarrow 2CO$	9.41×10^{14}
$U + 2CO \rightarrow UO_2 + UC_2$	8.68×10^{13}
$2U + O_2 \rightarrow 2UO$	2.84×10^{11}
$3U + 2CO \rightarrow UO_2 + 2UC$	2.25×10^{10}
$2U + N_2 \rightarrow 2UN$	9.1×10^6
$2CO + O_2 \rightarrow 2CO_2$	2.76×10^4
$CO_2 + C \rightarrow 2CO$	4.87×10^3
$C + H_2O \rightarrow CO + H_2$ (heterogeneous)	1.51×10^3
$UO + 3C \rightarrow UC_2 + CO$	2.75×10
$2MgO + U \rightarrow 2Mg_{(g)} + UO_2$	8.60×10^{-1}
$UO_2 + 3C \rightarrow UC + 2CO$	3.6×10^{-4}
$UO_2 + 4C \rightarrow UC_2 + 2CO$	3.48×10^{-5}
$MgO + C \rightarrow Mg_{(g)} + CO$	5.29×10^{-5}
$C + N_2 \rightarrow (CN)_2$	6.1×10^{-9}
$UO_2 + 2H_2 \rightarrow U + 2H_2O$	2.79×10^{-16}
$UO_2 + 2CO \rightarrow U + 2CO_2$	5.18×10^{-27}

was calculated using data obtained in the test and was found to be $K = 3.49 \times 10^{-4}$. A calculation of K at 2500 F based on known free-energy data gave $K = 4.865 \times 10^3$. Assuming the gas-analysis values for CO and CO₂ constant and at equilibrium, the equilibrium volume per cent of oxygen was calculated. This value was so small (7.5×10^{-8} volume per cent) that its detection by the mass-spectrometer analysis would have been impossible. The discrepancy in results of these calculations pointed to one of two possible conclusions: (1) that the analysis or its associated sampling technique was in gross error, or (2) that no equilibrium condition could be considered. In sampling, flasks had been prebaked, carefully checked for leakage, and cross checked for pressure variation between pressure at the time of sampling and the sample pressure at the time of analysis. Since the instrument was functioning properly and gas sampling was not faulty, it was concluded that the furnace system was not at equilibrium but was dynamic, with the rate of conversion of oxygen (from the air leak) to CO evidently dependent upon gas-diffusion characteristics at the low furnace pressure.

Under wet furnace conditions the various analyses of gases taken during test showed considerably higher quantities of water vapor than would be expected from calculations similar to those made for oxygen. In this case, it was suspected that both diffusion and adsorption processes played a major role in preventing equilibrium within the time of the test.

In like manner, a comparison of the equilibrium conditions predicted by available standard free-energy information for the gases, CO, CO₂, and nitrogen, showed that none of these gases would be present in detectable amounts (by the mass spectrometer) if they were in equilibrium with pure uranium. Since analyses obtained during the pressure-profile work showed relatively high partial pressures of most of the above gases at fairly substantial pressures (greater than 100 μ), another reaction mechanism was sought that would permit highly reactive gases such as CO, CO₂, and even oxygen to exist as furnace gas over a uranium melt. As was discussed in an earlier section, such a mechanism was found in the formation of protective covers of oxide and carbide over the surface of the melt which effectively isolated the melt from further reaction with furnace gas.

From the beginning of the program there has been considerable concern regarding the effect of a water-gas reaction on metal purity during melting. As can be seen in Table 6, the reaction potential for a heterogeneous water-gas reaction between water and the graphite crucible is much less ($K = 1.51 \times 10^3$) than that of a direct reaction between water and uranium ($K = 3.59 \times 10^{15}$). Such a wide variation in equilibrium constants might lead to a dismissal of the occurrence of any harmful effects from a water-gas reaction in the furnace if it were not for the formation of protective dross covers. As demonstrated in Test 31 (Table 5) and in Figures 13 and 14, a true water-gas reaction between furnace moisture and the graphite crucible can occur which will result in substantial amounts of CO in the furnace atmosphere. Any disturbance (such as stirring) capable of breaking up this cover and exposing the melt to the CO gas over it would have a real effect on the amount of carbon pickup by the melt. The opportunity for the production of wide variability of process conditions from melt to melt and even within a given melting cycle seems clear based on such a reaction mechanism.

There are other considerations of an even more drastic nature that appear to be imposed on a melt when the CO partial pressure over it becomes great. As mentioned in the previous section of this report, a thermodynamic treatment by Roland⁽⁴⁾ of the

role played by the CO pressure is important in that a small change in pressure will result in a large change in the carbon-oxygen level. In his treatment Roland assumes that Raoult's law is applicable and that the chemical activity of the CO gas is equal to its partial pressure over the melt. In a system in which uranium is melted in a graphite crucible, it is believed that such a treatment should take into account the massive carbon present and the compound formation. In such a case, Raoult's law does not apply. Moreover, if saturation of any element exists, particularly of carbon, the thermodynamic driving force or chemical potential is equivalent to the driving force of that element considered as 100 per cent. This is the same as saying that on a mole fraction or activity basis the chemical activity is equal to unity for the saturated element.

A treatment of the thermodynamics of the reaction assuming an activity of unity for carbon and assuming also that, instead of Raoult's law, Henry's law applies in this case was worked out by J. J. Ward of Battelle and is shown below. A comparison of the two treatments indicated that in both cases a small CO pressure change over the melt will produce a large change in carbon content in the uranium, but in the treatment by Ward, this effect is at a much greater order of magnitude than Roland's calculations would imply.

Ward's thermodynamic treatment of the reaction $U_{(liquid)} + C_{(graphite)} \rightarrow \underline{C}$ where $\underline{C}$ is carbon in solution is as follows:

$$\Delta F_{298} = -41,000$$

$$\Delta H_{298} = -40,000$$

$$\Delta S_{298} = +2$$

From the Brewer rule and data given by Quill⁽⁵⁾,

$$\Delta F_T = \Delta H_{298} - T\Delta S_{298}$$

$$\Delta F_T = -40,000 - 2T$$

If ΔH of fusion for UC is assumed as zero (melting point = 2550 K) then,

where the subscripts s and l are solid and liquid, respectively. This equation is reversed and then added to the $UC_{(s)} \rightleftharpoons \underline{C}$ equation. In the case of the latter equation it is assumed that Raoult's law applies and that UC has no heat of fusion.

Then

For $p_{\text{CO}} = 1 \text{ atm}$: $\log \underline{\text{C}} + \log \underline{\text{O}} = \frac{28,089}{T} - 8.252$,

also,

and for p_{CO} in mm: $\log \underline{\text{C}} + \log \underline{\text{O}} = \frac{28,089}{T} - 11.13 + \log p_{\text{COmm}}$.

SUMMARY AND CONCLUSIONS

The most important findings of the experimental program are summarized as follows with no particular order of importance intended:

- (1) MgO Coating. MgO is slowly reduced to magnesium during the melting cycle, and the magnesium is boiled out of the melt. Since melting in MgO-coated graphite crucibles results in lower carbon in the metal than melting in uncoated crucibles, a protective UO_2 coat probably replaces the MgO coat provided the original coating is bonded in the surface pores of the crucible. There is evidence that when subjected to high temperatures the MgO coating may peel off the graphite surface.
- (2) Outgas. Adsorption of gases and vapors by the graphite crucible can be responsible for very high and prolonged outgassing rates in the melting- and pouring-temperature range. Water is definitely adsorbed, and there is some experimental evidence that CO and other gases may

be held tenaciously by the graphite. In the 1800 to 2600 F temperature range, adsorbed water in the graphite reacts with carbon to yield hydrogen and CO as products of a water-gas reaction.

- (3) Temperature. In experimental melts there were wide variations (as much as 300 F) between the internal temperature and the surface temperature. In all cases, metal surface temperatures were lower than the internal temperatures. Also, there was a noticeable variation in surface temperature, depending upon the nature and thickness of the dross on the surface.
- (4) Protective Covers. In a graphite-free and dry system (without surface dross), CO reacted to produce stoichiometric carbon in the uranium. In a graphite-free system with water vapor present (and dross over the melt), CO reacted mainly at the surface, and substantially less than stoichiometric carbon was added to the metal. In similar experimental melts in uncoated graphite crucibles, CO (or CO produced from the reaction of gases with the graphite) reacted at the dross-covered surface and effectively sealed the uranium from further reaction with the reactive gases. With the molten metal so sealed, water in the system reacted with graphite to produce hydrogen and CO as major constituents of the furnace gas. (Contrariwise, without a protective cover the furnace gas was almost exclusively hydrogen.) Since the formation of a protective dross affects the furnace gas composition in such a way as to significantly increase the CO partial pressure, any disturbances causing breaks in cover continuity would expose the metal to the high CO partial pressure.
- (5) The Thermodynamics of Carbon Monoxide. The partial pressure of CO over molten uranium contained in a graphite crucible probably affects the solution of carbon and oxygen in the melt. A thermodynamic treatment of the reaction,

shows that a small change in the pressure of CO over the melt will result in a large change in the carbon-oxygen level in solution with the melt. Considered in the light of dross covers and the variable CO partial pressures that can occur in the furnace atmosphere, variations in carbon contamination of the melt can be much greater than is implied by the simple reaction between CO and uranium.

- (6) Equilibrium Considerations. It is believed that in no case during the execution of the various tests was an equilibrium condition reached. Variations in temperature within the melt at operating temperature, in leakage and outgassing rates, and in surface conditions over the melt all contributed to nonequilibrium conditions. Despite this situation, fairly good agreement of data was obtained in the various replicate experiments.

An evaluation of the findings of the experimental work as related to production practices leads to the following basic conclusions:

(1) Operating Pressure. Improvements in operating furnace pressure during the production melting cycle would be expected to result in generally lower metal contamination. Outgassing of crucible, mold, and other furnace components along with large air leaks and initially wet charge material can account for the bulk of furnace gas. Water and the components of air (nitrogen, oxygen, and H_2O) are very reactive with molten uranium, and oxygen and H_2O react with system graphite (which includes both the crucible and the hot, empty mold below it) to form CO in one case and CO and hydrogen in the other. Although a H_2O + uranium reaction has a higher chemical potential than the water-gas reaction, the kinetics of the system (large carbon surface to relatively small uranium surface at low pressure) would probably favor the water-gas reaction. Moreover, moisture driven off during heatup probably would be absorbed by the empty mold casting which could then serve as a continuous source of hydrogen and CO throughout the entire melting cycle.

(2) Protective Cover. Under certain conditions a cover or dross can form over the surface of the melt that will protect the uranium from further reaction with furnace gas (air, water, and CO), but by so doing it also allows a substantial increase in the partial pressure of CO in the furnace gas. As long as this cover remains intact, furnace gases should not affect the metal, but if the cover, for one reason or another, is broken up, then the effect of the high CO partial pressure above the exposed metal could be especially detrimental to the metal. Thermodynamics indicated that high CO partial pressures will affect the reaction potential between the crucible and the metal.

It appears likely that a protective dross might be incorporated to advantage in the melting procedure. In the experimental work a mixture of oxide and carbide was most effective; however, oxide by itself might serve just as well provided there is minimum stirring.

(3) Inert-Gas Flush. In production practice, helium is introduced as a low-pressure cover gas after pouring. Flushing the furnace with dry helium before pouring would serve to sweep out of the system any reactive (especially CO) furnace gases.

(4) MgO Coating. Experimental work points to three possible sources of trouble in the use of MgO wash on production crucibles: the bond of the MgO-graphite interface, the potential source of bound and free water, and the ability to react with uranium to produce volatile magnesium. Any improvements in the MgO-graphite bond would reduce the carbon exposure to the melt; however, the evolution of vaporized magnesium during melting infers that a better, more inert, crucible dressing should be sought.

- (5) Temperature Variations. Laboratory investigations indicated that major variations could occur between surface and subsurface temperatures. Also, major variations in temperature readings (optical pyrometer) were observed at the surface of melts, depending upon the kind and amount of dross. Such variations could cause large variations in reaction rates. In production, melt temperatures are read exclusively by optical pyrometer (surface temperatures). The use of a protected thermocouple, either submerged in the melt or attached to the outside crucible wall and appropriately calibrated, would give more realistic temperature measurements that should be more accurately reproduced from melt to melt.

FUTURE WORK

As the investigation of melting variables progressed, it became apparent that detailed studies of certain facets outside the scope of the program would be especially fruitful in understanding and correcting the causes of nonuniformities in vacuum induction-melted uranium. Of special interest would be a detailed investigation of both natural and synthetic slags that could be used as protective covers over the melt. Such a program should lean toward rate studies to permit evaluations directly applicable to production innovations and controls.

As an integrated part of the above study on slags, an expanded exploration into the effect of the partial pressure of CO as a controlling solution mechanism by which carbon and oxygen are dissolved in the metal would be warranted. This phase of research should also deal with the reaction kinetics of a low-pressure system.

Experimental observations indicate that more effort should be placed on graphite-crucible dressings. There is reason to believe that during the melting cycle the MgO coating is converted to UO_2 which, in turn, is an effective barrier at the metal-crucible interface. Since impregnation studies of Piper⁽³⁾ indicate the effectiveness of graphite-impregnated UO_2 as an agent in reducing carbon contamination, a study of the value of a crucible wash using a slurry of UO_2 instead of MgO seems to follow as a natural consequence of these considerations.

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APPENDIX

LITERATURE SURVEY OF RESEARCH DEALING WITH
FACTORS THAT AFFECT THE QUALITY OF
VACUUM INDUCTION-MELTED URANIUM

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APPENDIX

LITERATURE SURVEY OF RESEARCH DEALING WITH FACTORS THAT AFFECT THE QUALITY OF VACUUM INDUCTION-MELTED URANIUM

Introduction

Perhaps the most important of the uranium-processing steps are the melting and casting operations since ultimate fuel-slug quality appears to be related directly to the process variables associated with these operations. In the process sequence, melting and casting follow the thermite reduction of green salt^(1,2). Massive derbies are formed by the reduction of green salt (UF_4) with magnesium, forming magnesium fluoride slag as a reaction by-product. This reaction takes place in steel reduction bombs whose liners are made up of reprocessed slag (MgF_2). The derbies are separated from the slag and are either chipped or leached and pickled before being remelted. One, two, or three derbies are then charged into an MgO -coated graphite crucible to which sufficient scrap of various types is added to provide composite charges of equal weight. The scrap portion of the charge can consist of reject slugs, rolling-mill scrap, reject ingots, and briquetted turnings. The charge is remelted in a vacuum-induction furnace for approximately 2 hr and is bottom poured at a temperature of 2550 F into an MgO -coated graphite mold. After cooling, the ingot is removed from the mold, cropped, and then sent to the rolling mill for reduction in size preparatory to the final fabrication of metal into slugs.

Many processing variables at the remelt stage may affect ultimate metal quality. Included in these variables are melting temperatures, furnace pressure and system tightness, variations in furnace-gas composition, adsorption and subsequent outgassing of furnace components, variations in charge material, and exposure of the melt to the reactive effects of the crucible and crucible dressing. To supplement the experimental phase of the program, which dealt with the examination of some of the factors affecting the quality of vacuum induction-melted uranium, a library survey of a somewhat cursory nature was made emphasizing research of the remelt variables.

Process Temperature

Although pure uranium has a melting point of 1132 ± 1 C (2070 F), it is of interest that in the determination of the melting point by Dahl and Cleaves^(3,4) at the National Bureau of Standards it was shown that uranium containing 300 to 500 ppm of carbon first melted at 1125 C. When the metal was kept just above the melting point for a period up to 15 hr, its solidification point rose gradually to 1130 to 1132 C. During this period of time the carbon content decreased from 500 to 5 ppm, and the remaining carbon was largely segregated as carbide in the crust formed on the metal. These determinations were made in thoria and beryllia crucibles in an atmosphere of helium and with an induction furnace.

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In production melting, uranium is poured at a temperature of about 2500 F (1370 C). Within certain limits, heating the melt above the melting point (termed "superheat" in the industry) is required for subsequent casting of a sound ingot. Since melting is done in MgO-coated graphite crucibles, the effectiveness of the MgO coating, the degree of metal stirring, and the temperature before and at the time of pouring are prime considerations in maintaining reasonably low-level carbon transfer from crucible to the melt. The work of Dahl and Cleaves shows that a "self-purity" effect (known as liquation) was obtained over a long hold time. Although this liquation of carbide which has been recognized for some time is not clearly understood⁽⁵⁾, it is, nevertheless, taken into consideration in the production melting cycle.

In casting tests conducted by Buntz and Weber⁽⁶⁾ of Mallinckrodt, results indicated that the metal fluidity, as expressed by the metal temperature at the time of pouring, does not greatly affect the number of cavities in the casting. The reaction between carbon and uranium becomes more rapid at high temperatures and the improvement in internal soundness is not marked (this appears to be related to ingot size). In general, however, billet surface improves with an increase in pouring temperature.

Melting cycles have been established empirically in various attempts to balance the desirable effects of liquation and high pour temperatures against the undesirable effects of increased reaction rates (that raise impurity levels in the ingot) and greater induction stirring of the melt (which reduces the effectiveness of the beneficial liquation process. In plant melting practices, the cycle is based on timed furnace-power settings. Considerable effort has been directed in both pilot-plant and full-scale plant studies for obtaining optimum melting conditions and pour temperatures. At National Lead Company of Ohio, H. M. Eikenberry⁽⁷⁾ found that for a given power cycle increasing the pour temperature from 2500 to 2550 F reduced the slug rejection substantially (from 13.0 to 6.7 per cent based on a pilot-plant test). By modifying the power cycle of melting and retaining the 2550 F pour temperature, he was able to demonstrate an even lower slug-rejection level (3.0 per cent). This work was followed by full plant tests⁽⁸⁾ in which 200 ingots were cast to confirm the results of the initial tests. In these tests, two heating cycles were compared.

Cycle A: 100 kw (5 min), 165 kw (43 min), 80 kw to a temperature of 2550 F (60 min), 45 kw (4 min); total power time = 112 min

Cycle E: 100 kw (5 min), 175 kw (39 min), 120 kw to a temperature of 2475 F (29 min), 60 kw to pour at 2550 F (30 min); total power time = 103 min.

Results of these tests showed a significant decrease in slug rejection of Cycle E over Cycle A. In addition, ingot density and carbon content of Cycle E metal were noticeably improved.

Process Pressure and Furnace Gases

It is difficult to separate the effect of degree of vacuum (in the 10 to 1000- μ range) from the effect of the residual gases in the furnace chamber. However, general considerations of vacuum melting indicate that the lower pressures are desired to prevent

deleterious reactions from taking place. Although little information was found for the pressure effects on uranium, there is some experimental support in the manufacture of certain super alloys. For example, in his general considerations of vacuum-induction melting, Jones⁽⁹⁾ cites data on rupture life and elongation at fracture of two super alloys which help to illustrate orders of magnitude and trends. Heats of G.E. Alloy J-1570 (cobalt base) made in a 400 to 800- μ pressure range were compared with production melts in the 20 to 70- μ range. For the higher pressure melts the rupture life (at 30,000 psi) was 125 hr and elongation was 10 per cent; the low pressure melts resulted in a rupture life of 245 hr and an elongation of 17 per cent. Experimental heats of Udimet-500 made at 1000 μ and 10 μ showed a similar trend.

According to Jones and others⁽¹⁰⁾, of possibly greater importance than the vacuum of the furnace system is the manner in which the pressure in the melting chamber behaves when the valves to the pumps are closed and the total pressure rise in a given period of time is recorded. This increase in pressure may be due to air leaking into the furnace chamber, to adsorbed gases from the various furnace parts, to water leaks, or to gases coming out of the liquid metal. The pumping system can be of sufficient size that it can maintain low pressures even though large quantities of gases may be passing over the liquid metal. For instance, a pressure of 1 μ can be measured in the furnace chamber, yet on isolating the vacuum system the rate of pressure increase will be 100 μ per min. It is, therefore, of considerable importance to identify the gases entering or being formed in the system and to pinpoint their sources if vacuum-melting operations are to be controlled.

Identification of gases at low pressures has presented a challenge. Two methods have been used successfully to identify and measure amounts of system gases. One is the "low-pressure fractional freezing method" which is, as the name implies, a method by which gases are frozen and then measured as pure fractions. The method is used in vacuum-fusion analysis⁽¹¹⁾, but is generally adaptable to the analysis of low pressure gases from other sources. The other method makes use of the mass spectrometer^(12,13,14) and is rapidly finding its way into production control as an industrial tool⁽⁷⁾. In this regard, it has been used to advantage in monitoring outgas compositions during heatup and in checking reaction gases throughout a melting cycle. Of considerable interest is the monitored gas analysis taken during the melting cycle of Udimet-500 as given by Jones⁽⁹⁾. He found hydrogen at various periods of the cycle which he feels came from the dissociation of water vapor or from the raw materials. There was a considerable amount of this each time a charge was melted and a short burst during pouring as a result of outgassing of the pouring basins or the ingot mold.

Of the several gases and vapors that have been identified during the vacuum-induction melting of uranium, probably the one that is capable of causing the greatest harm to the metal, either directly or indirectly, is water. It may enter the furnace chamber by way of three main routes: (1) by its association with air leakage, (2) by free moisture present on furnace components or on the charge material itself, and (3) by adsorption on the surfaces of furnace components or, most importantly, in the refractory materials used in the melting process. It is this latter source of furnace-system water and other gases, for that matter, that often receives too little attention.

In certain foundry practices charcoal is used as a cover in the melting procedures⁽¹⁵⁾. Yet, charcoal, either lump or powdered, is an excellent gas-adsorbing agent. It will not only adsorb large amounts of water vapor while merely standing in air, but

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will cause it to condense within the pores to remain as adsorbed water. Consequently, the amount of water it can retain is almost as large as if the charcoal were actually dipped in water, yet it will appear perfectly dry. This water can be expelled only by comparatively long heating at a red heat. Under conditions of high humidity, even perfectly dry charcoal present on the surface of molten metal in a fuel-fired or electric furnace will react with water vapor to form carbon monoxide and nascent hydrogen⁽¹⁵⁾

$$(C + H_2O \rightleftharpoons CO + 2H).$$

This adsorption effect of carbon carries over to graphitic products (e.g., crucibles and molds). It has been shown⁽¹⁶⁾ that large quantities of such gases as CO, CO₂, oxygen, and nitrogen, to name a few, can be adsorbed by activated carbon. It is of interest that these gases are adsorbed at different rates. For example⁽¹⁶⁾, it is more difficult to adsorb hydrogen than carbon dioxide (or, significantly, carbon monoxide). Melting experiments⁽⁶⁾ have indicated that the nitrogen content of uranium could be affected by adsorbed nitrogen in the crucible. An estimate based on the amount of outgassing occurring during the heatup period indicated that enough gas is given off to account for as much as 60 ppm of nitrogen in the metal in either laboratory or plant operations.

An interesting account regarding the degassing of graphite is given by Dushman⁽¹⁷⁾. Samples of graphite were degassed at 2150 C (3900 F) so that subsequent heating at a higher temperature gave no further gas. The gas evolved in the 1700 to 2200 C (3090 F to 3990 F) range was predominantly nitrogen. A piece of graphite, which had been degassed completely, on subsequent exposure to air adsorbed oxygen, and some of this so firmly bound that it only desorbed as CO upon heating to 2150 C (3900 F). The gases evolved consisted mainly of hydrogen, CO, and nitrogen with a much smaller percentage of CO₂.

At NLO, Blasch, Jennings, and Wuller⁽⁵⁾ reported that although the ingot molds are subjected to an outgassing operation (800 to 1100 F) prior to use in uranium remelt furnaces, it was believed that adsorbed gases are present in the pores of the graphite and in the mold coating at the time of pour due to (1) insufficient outgassing, and (2) exposure to atmospheric conditions prior to assembly in the vacuum furnace. The release of these gases when hot metal comes in contact with the mold at the time of pouring can have deleterious effects on surface and subsurface quality. Impurities in the uranium ingot, such as nitrogen and hydrogen, may also be increased. Observed furnace-pressure increases of 50 to 400 μ during the pour is indicative of this outgassing phenomenon, and is similar in action to that of the Udimet-500 melts observed by Jones and mentioned earlier.

The action of the gases that are associated with uranium melting is, of course, a major consideration in terms of ultimate uranium metal purity and metal soundness. Although this survey is only of a cursory nature, highlights of some of the more important furnace gases in relation to metal purity are presented as follows.

Hydrogen and Water Vapor

Hydrogen in uranium is blamed for difficulties in further processing and in the end use as fuel slugs. It has been suggested⁽¹⁸⁾ that during the canning procedure the rejection rate of uranium slugs is greatly influenced by the hydrogen content of the uranium. The solubility of hydrogen⁽¹⁹⁾ at 1200 F and 1300 C (2190 F and 2370 F) was measured at

pressures of 5 to 760 mm of mercury. It was found that at both these temperatures, the hydrogen solubility varied directly as the square root of the hydrogen pressure over the bath and at 760 mm of mercury is 27 ppm at 1200 C and 32 ppm at 1300 C. The proportionality of solution to the square root of pressure indicates that hydrogen is dissolved in the form of free atoms⁽³⁾. During pouring, considerable quantities of hydrogen that were dissolved in the melt may remain occluded in the cast metal.

Solubility rates of hydrogen in molten uranium exposed to water vapor have been compared⁽²⁰⁾ with rates using dry hydrogen under identical pressure-temperature conditions. The equilibrium hydrogen solubilities obtained with either water or hydrogen were in good agreement with the values reported above. However, hydrogen was adsorbed more slowly from water vapor. In comparing adsorption rates for the two methods, the difference in rates became greater as pressure was increased. It was suspected that the oxide film or crust produced in the water-vapor reaction inhibited the passage of water vapor to the metal.

Nitrogen

In the preparation of uranium nitride by the reaction of nitrogen with uranium (at temperatures up to 2375 F) it has been shown⁽¹³⁾ that the reaction does not slow down at the composition, UN, but proceeds to the composition of the U_2N_2 -UN₂ phase.

Oxygen

The solubility of oxygen in uranium is very small, even at temperatures above 2000 C⁽³⁾. There appears, however, to be a direct relationship^(21,22,23) between oxygen solubility and the partial pressure of carbon monoxide over the melt when uranium melting is carried out in graphite crucibles.

Carbon Monoxide

Carbon monoxide at first reacts rapidly with uranium at high temperatures and then slows down. A black flaky crust is formed on the surface which has been identified as UO_2 and UC⁽²⁴⁾. Solubility of carbon (or UC) in liquid uranium at 1350 to 1400 C (about 2500 F) is about 1000 ppm. This temperature is roughly the pour temperature of the remelt cycle of processing (2550 F) and, of course, carbon content near saturation cannot be tolerated. Nevertheless, a thermodynamic treatment of the effect of carbon monoxide partial pressure over uranium melts presented by E. H. Roland⁽²¹⁾ indicates the importance of this gas. His calculations imply that a small change in the pressure of carbon monoxide over the melt will cause a large change in the carbon-oxygen impurity level in the metal. Roland concludes that the variability of furnace pressures over the working range in vacuum-melting techniques can account for the differences in oxygen and carbon contents from melt to melt.

Charge Material

Perhaps the most difficult variable to evaluate in the melting procedure is the metal charge. As mentioned earlier, the charge can consist of variable portions of virgin as-reduced uranium and scrap. Reject slugs, rolling-mill scrap, reject ingots, briquetted turnings, and cropped metal in variable proportions go to make up scrap. This materials variation, coupled with furnace-atmosphere variations, makes any charge evaluation only qualitative in nature. Nevertheless, one of the most informative uranium-charge evaluations was made by Eikenberry and co-workers at National Lead Company of Ohio⁽²⁾. Charge types included the following: four chipped derbies, four pickled derbies, three chipped derbies plus briquettes, all unpickled rolling-mill scrap, all pickled slugs, and all briquetted machine chips. Melts with as-chipped derbies resulted in metal with somewhat lower carbon levels but higher nitrogen levels. The all-scrap melts produced ingots containing low nitrogen levels as compared with melts with all or part derbies. The lowest level nitrogen was found in ingots made from charges containing only briquettes. Of considerable interest is that the all-scrap heats improved in quality as a result of a 10-min hold time at 2550 F without increasing carbon levels. It is also possible that heavy protective carbide and oxide dross forming at the time of melting was instrumental in this effect.

During the survey, there were many references that suggested possible beneficial value of dross floating on the melt and of certain impurities acting as fluxes in metal purification. One such reference⁽²⁵⁾ that serves as an example reported that uranium-2 w/o zirconium was cast into ingots in a plant test. Analysis of the cast metal showed that the carbon content was only 20 to 30 ppm. It was postulated that zirconium aided in the removal of the uranium carbides by forming zirconium carbide which liquated easily and was then cropped off the ingot. Plant and pilot-plant tests^(2,26,27,28) have successfully demonstrated that uranium can be melted and poured in atmosphere provided certain melting conditions are observed which include the use of protective slag covers.

Crucible and Mold Dressings

The only common refractory materials that do not react with uranium at elevated temperatures (up to 1700 C) are CaF_2 and UO_2 ⁽²⁹⁾. Since CaF_2 softens somewhat at the melting point of uranium it does not lend itself readily as a crucible material. For very-high-purity-uranium melting, Blumenthal⁽¹⁰⁾ used pure urania crucibles. In this type work, he found experimentally that lime formed a slag and contaminated the metal with oxygen; Alundum contaminated it with aluminum and oxygen; zirconia with zirconium and oxygen; magnesia with oxygen and silicon (an impurity of the magnesia); and titanium carbide with titanium and carbon. Although urania reacts with uranium to form uranium monoxide, the reaction is slow at moderate temperatures (less than 1700 F). The brittleness of this material and its low thermal conductivity, however, make it unsuitable for production use. The most satisfactory material for melting uranium in production is graphite. In a like manner, this is also true for the mold. Although graphite reacts slowly at temperatures below 2900 F, the carbon level can become troublesome despite some evidence⁽³⁾ that when uranium is melted in a graphite crucible, the crucible is protected by a film of uranium carbide formed at the interface. As a means for controlling the rate of solution of carbon in the uranium, MgO is used as a dressing for both

crucibles and molds. However, it has been shown^(30,31) that MgO reacts slowly with uranium to produce UO_2 and vaporized magnesium at temperatures slightly above the melting point of uranium. Tests have been made⁽⁶⁾, which have been mostly inconclusive, to study the magnesium vapor evolution as a possible contributor to billet cavitation.

Although MgO has been fairly successful as a dressing for graphite, improved graphite dressings and methods of applying them have been the objective of continual research. The ideal graphite-crucible dressing should be (1) easy to apply, (2) chemically inert to uranium, (3) capable of preventing the transfer of carbon to the metal, and (4) adherent so as not to cause inclusions in the metal.

At Mallinckrodt, Piper^(6,25,32) has successfully impregnated graphite crucibles with UO_2 , MgO, and CaO. In the case of UO_2 impregnated crucibles, he has been able to demonstrate a marked reduction in the carbon content of uranium melted in these crucibles. In addition, the resulting metal met specifications.

At Harwell (Berkshire, England), N. R. Williams and F. Leach⁽³³⁾ have successfully flame sprayed graphite with a wide variety of refractory materials. The equipment used was a modified oxyacetylene torch of conventional design into which were fed powders of the refractory materials. Although all coatings applied by this technique are porous to a degree, good thermal-shock properties have been obtained with coatings up to 0.005 in. thick. Thicker coatings (about 0.010 in. and greater) do not stand up to thermal shock. A partial list of materials that have been successfully sprayed includes:

Al_2O_3	MgF_2
$\text{UO}_2 \cdot 20 \text{ w/o } \text{Al}_2\text{O}_3$	CaF_2
$\text{UO}_2 \cdot \text{CaF}_2$	$\text{CaO} \cdot \text{UO}_2$
$\text{MgO} \cdot \text{UO}_2$	$\text{ZrO}_2 \cdot \text{UO}_2$
$\text{MgO} \cdot \text{ZrO}_2$	$\text{ThO}_2 \cdot 10 \text{ w/o } \text{Al}_2\text{O}_3$

In thermodynamically evaluating the ability of various elements to act as deoxidizers for the uranium alloys, E. H. Roland⁽²¹⁾ considers the action of aluminum, beryllium, calcium, magnesium, and zirconium. His calculations serve a twofold purpose in that they also predict the best crucible material (corresponding oxides of these elements). The calculations indicate that CaO and BeO should be superior to MgO or ZrO_2 as crucible material. As a crucible material Al_2O_3 would appear to be a very poor choice.

Because of the implications of his calculation, Roland's work was examined very carefully and then independent calculations were made as a check. A brief résumé of the examination is as follows:

- (1) Good agreement was obtained in the expressions for beryllium, calcium, and zirconium.

- (2) In the expression for aluminum there was disagreement in the last term of Roland's equation.

$$\begin{aligned} \text{Roland's equation: } \log (w/o Al)^2 + \log (w/o O)^3 = \\ - \frac{151,144}{T} - 0.819 \log T + 11.117 \end{aligned}$$

$$\begin{aligned} \text{Ward's* equation: } \log (w/o Al)^2 + \log (w/o O)^3 = \\ - \frac{151,140}{T} - 0.82 \log T + 9.117 \end{aligned}$$

- (3) A check derivation of an expression for magnesium varied considerably from that of Roland's, however, absolute values from either expression checked fairly well.

$$\begin{aligned} \text{Roland's equation: } \log w/o Mg + \log w/o O = \\ - \frac{8517}{T} - 1.611 \log T + 8.348 \end{aligned}$$

$$\begin{aligned} \text{Ward's equation: } \log w/o Mg + \log w/o O = \\ - \frac{7255}{T} - 0.052 \log T + 2.534 \end{aligned}$$

Dr. Roland should be commended for his work. He is currently engaged in research aimed at experimental verification of the thermodynamics.

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