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ATOMIC ENERGY COMMISSION CONTRACT AT(11-1)-190

INVESTIGATION OF MATERIALS
FOR USE IN A HEAT TRANSFER SYSTEM
CONTAINING LIQUID LEAD OR BISMUTH

FINAL REPORT

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FOR USE IN A HEAT TRANSFER SYSTEM
CONTAINING LIQUID LEAD OR BISMUTH

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INTRODUCTION

This is the concluding progress report on Atomic Energy Commission Contract AT (11-1)-190. It covers the work completed since our last report which was designated Report XV and dated December 31, 1953.

Report XV described the work with liquid bismuth. Reliable measurements were obtained on the iron and chromium which dissolved from Type 410 stainless steel capsules by liquid bismuth under various conditions. The most interesting finding was that the addition of from 100 to 150 parts of titanium metal to a million parts of bismuth greatly decreased the amount of iron and chromium dissolved. The inhibiting effect of titanium on the dissolving of iron and chromium from the steel capsules increased with repeated reuse of the capsules. The inhibiting effect gradually was lost when capsules were subsequently repeatedly reused with bismuth which did not contain titanium.

These tests indicate that the presence of titanium in the bismuth causes a barrier to form on the surface of Type 410 stainless steel. Such a barrier could be expected to greatly reduce the mass transport of Type 410 stainless steel in a dynamic bismuth system.

In January the work was changed to studies of the dissolving of iron and chromium in liquid lead. It was thought that the same techniques developed in the work with bismuth could be used with lead and that the work would be completed in a short time. Difficulties were encountered, however, and as a result it will be impossible to complete the work with liquid lead by the termination date of this contract.

The two major difficulties encountered were due to analytical troubles and to precipitation and segregation which occurred in the liquid lead. Analytical troubles were caused by the presence of a large amount of lead which interfered with the procedures worked out previously for bismuth (1). Standard spectrographic procedures were found inadequate for the extremely low concentrations of iron and chromium which were found in lead. This problem was solved by the development of a special spectrographic method by which sufficiently reliable measurements could be made. The troubles caused by precipitation and segregation of iron and chromium in the liquid lead have not been solved. The precipitation of solid iron-chromium alloy in liquid lead during capsule tests leads to erratic test results, and to date no means of overcoming this difficulty has been found. This precipitation is undoubtedly a part of the mass transport mechanism and while our work with lead did not produce reliable quantitative measurements, the qualitative observations may be useful.

(1) All references are at end of report.

CAPSULE TESTS WITH LIQUID LEAD

Details of capsule preparation and treatment procedures are given at length in a succeeding chapter of this report.

The degree of reproducibility previously achieved with bismuth was not achieved with lead. Extensive calibration procedures indicated quite conclusively that the wide spread of results was actual and not merely analytical errors, even though the concentrations dealt with were extremely minute.

Indications have become increasingly strong during the progress of our limited studies with lead that iron and chromium tend to precipitate from the lead during the test to a much greater degree than was the case with bismuth. Various sized droplets of residual lead almost always clung to the capsule during the pouring operation. In view of micrographic studies to be discussed later, it seems quite possible that significant concentrations of precipitated material may have been present in these droplets.

It was also suggested in the micro-examinations that different types of response to seemingly related circumstances were encountered. For example, sometimes a white layer appeared on the surface of the steel and other times the surface appeared to be corroded. This difference in mode of attack may have contributed to erratic results.

In view of the foregoing experimental difficulties, the quantitative interpretation of results must be regarded as tentative only.

Effect of Temperature

Several tests of twenty hours duration have been run at various temperatures. Results are shown in Table I and Figure 1.

The inability of the points to define a smooth curve is obvious. Spread seems to be particularly great in the 1500°F region. Both iron and chromium values seem significantly higher in the tests not thermo-vacuum cleaned prior to charging with lead. It may also be noticed that the two points for plain

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TABLE I EFFECT OF TEMPERATURE ON TESTS OF 20 HOURS
DURATION CAPSULES THERMO-VACUUM CLEANED AT TIME OF CHARGING

NO ADDITIVE

<u>Test No.</u>	<u>Fe (ppm)</u>	<u>Cr (ppm)</u>	<u>Test Temp. (°F)</u>	<u>Type of Steel</u>	<u>Remarks</u>
P-11	0.3	0.8	1352	410	
P-12	0.5	1.0	1425	"	
P-1	0.2	0.6	1498	"	
P-3	0.7	1.2	1499	"	
P-22	2.7	2.6	1499	"	
P-7	1.2	2.2	1500	"	
P-8	1.6	1.8	1500	"	
P-5	1.7	2.7	1502	"	
P-6	1.2	1.4	1502	"	
P-4	0.4	0.7	1503	"	
P-2	1.1	1.4	1504	"	
P-21	3.3	2.8	1504	"	
P-9	1.7	2.0	1572	"	
P-14	1.1	1.9	1643	"	
P-13	1.7	3.2	1645	"	
P-24	2.6	3.5	1700	"	After standing 70 Hrs at 1350°F.

Following are equivalent tests except not thermo-vacuum cleaned.

P-29	2.9	1.7	1350	410
P-30	4.2	3.3	1575	"
PC-3	2.1	Tr	1350	1010
PC-4	8.6	Tr	1575	"

carbon steel, PC-3 and PC-4, suggest a much steeper rise with increasing temperature than is the case with Type 410 steel. Chromium values seem to have somewhat less spread than the iron values.

Effect of Time

Apparent solubilities at various time intervals up to 240 hours are indicated in Tables II and III and Figures 3, 4, 5 and 6 for 1500°F and 1700°F.

TABLE II EFFECT OF TIME AT 1700°F

CAPSULES THERMO-VACUUM CLEANED AT TIME OF CHARGING NO ADDITIVE

<u>Test No.</u>	<u>Fe (ppm)</u>	<u>Cr (ppm)</u>	<u>Test Time (Hrs)</u>	<u>Type of Steel</u>	<u>Remarks</u>
P-26	4.6	4.1	1	410	
P-33	17.5	6.2	2	"	
P-34	17.5	5.8	2	"	
P-25	3.4	3.6	5	"	
P-24	2.6	3.5	20	"	Much lead distilled out during test and contacted capsule from the outside.
P-23	3.1	4.0	70	"	"
PC-2	5.6	Tr.	1	1010	
PC-1	3.6	Tr.	5	"	
N-7	8.5	7.5	5	304	
N-8	7.0	6.6	5	"	

TABLE III EFFECT OF TIME AT 1500°F

CAPSULES THERMO-VACUUM CLEANED AT TIME OF CHARGING NO ADDITIVE

<u>Test No.</u>	<u>Fe (ppm)</u>	<u>Cr (ppm)</u>	<u>Test Time (Hrs)</u>	<u>Type of Steel</u>	<u>Remarks</u>
P-19	2.6	2.5	5	410	
P-20	2.0	2.5	5	"	
P-1	0.2	0.6	20	"	
P-2	1.1	1.4	"	"	
P-3	0.7	1.2	"	"	
P-4	0.4	0.7	"	"	
P-5	1.7	2.7	"	"	
P-6	1.2	1.4	"	"	
P-7	1.2	2.2	"	"	
P-8	1.6	1.8	"	"	
P-21	3.3	2.8	"	"	
P-22	2.7	2.6	"	"	
P-15	3.0	2.8	70	"	Much lead distilled out during test.
P-16	1.6	2.2	"	"	"
P-17	1.2	2.3	"	"	"
P-18	2.7	2.7	"	"	"
P-27	1.7	2.2	240	"	Nearly all lead in capsule distilled out during test and contacted capsule on the outside.
P-28	1.6	2.3	"	"	"

The wide scatter of the 20 hour 1500°F tests is again outstanding. Aside from this, there seems to be no significant change in either iron or chromium content of the lead with time between 5 and 240 hours. These data suggest 1.9 ppm iron and 2.3 chromium as the nominal concentrations for any time longer than five hours at 1500°F. The spread of chromium values is again less than that of iron.

The variation in iron and chromium content with time at 1700°F is quite startling in that it appears to go through a rather pronounced and sharp maximum between one and five hours. There appears, as with the 1500°F tests, to be little change in concentration after about five hours.

An explanation of the peak at two or three hours is not readily apparent. The suggestion seems very strong that there is in some way a relatively high initial solubility which later diminishes. This indication derives further support from the micrographic observation that a layer of columnar crystalline matter clearly different from the body of the steel is sometimes noted on capsule surfaces after test.

The possibility of a complex interaction between silicates, iron and lead oxides was considered in view of the extremely low concentrations involved. Small but significant amounts of silicate could have been introduced to the capsules via the thermo-vacuum cleaning and charging procedures. As will be discussed later in the section on capsule preparation and testing details, little slivers of Pyrex glass that stick very tenaciously to the surface of distilled lead ingots undoubtedly entered the capsule along with the lead charge. An absolutely total absence of oxygen from the system can certainly not be argued even though good diffusion pump vacuums prevailed. In view of these facts, a pair of tests were conducted to evaluate the effects of iron oxide with and without the presence of Pyrex glass. In one test 37.70 grams of lead, a single chunk of magnetite weighing 1.94 grams and a single piece of Pyrex weighing 0.31 grams were suitably contained in Vycor, and evacuated and heated

exactly as would have been the case for a capsule test to a temperature of 1700°F for 24 hours. The other test was equivalent (36.14 grams lead and 2.37 grams magnetite) except that all Pyrex was carefully excluded. The results were identical with a value of 1.0 ppm iron and no chromium. (Iron content of the lead initially charged was not detectible by a procedure sensitive to at least 0.1 to 0.2 ppm.) It was noticed that there seemed to be an eminent lack of wetting among all the constituents present except that the softened but not molten Pyrex had fused to the Vycor on one side and the magnetite on the other.

Effect of Thermo-vacuum Cleaning of Steel Capsules Immediately Before Charging

The operation of thermo-vacuum cleaning consisted essentially of heating the steel capsule to a temperature of about 1700°F while under high vacuum so that surface oxides were effectively removed through combination with carbon from the steel. When gas evolution had ceased and a good vacuum again achieved, temperature was lowered to about 1000°F whereupon the lead charge was lowered into the capsule by a magnetic device without disturbing the vacuum. Details of the operation along with data relative to gas evolution are given in a succeeding chapter on details of capsule preparation.

One reference to the effect of this operation has already been made in connection with the variation of temperature where it was indicated that thermo-vacuum cleaning prior to lead charging resulted in lower iron and chromium contents at any temperature. It was further suggested that this treatment decreased the rate at which iron and chromium concentration increased with increasing temperature.

These together with other direct comparisons of cleaning vs. not cleaning are given in Table IV. Indications are that the beneficial effect of thermo-vacuum cleaning is lost as the available oxygen during conduct of the tests increases. The static (sealed) tests P-43 and P-41 show only a slight margin in favor of cleaning while those of somewhat lower pressure but continuing

availability of oxygen (air) P-37 through P-40 exhibit an actual detriment due to cleaning.

Tests in which titanium additions were made show slight margins in favor of cleaning.

In general iron values seemed to be more sensitive to thermo-vacuum cleaning than those for chromium.

TABLE IV. EFFECT OF THERMO-VACUUM CLEANING OF STEEL CAPSULES
IMMEDIATELY PRECEDING CHARGING

Test No.	Fe (ppm)	Cr (ppm)	Thermo-vacuum Cleaned	Type of Steel	Ti metal Added (ppm)	Vacuum Condition		Test Time (Hrs)	Test Temp. (°F)
						Pressure Micron (Approx)	Type		
P-11	0.3	0.8	Yes	410	0	0.01	Dynamic	20	1352
P-29	2.9	1.7	No	"	0	0.01	"	20	1350
P-9	1.7	2.0	Yes	"	0	0.01	"	20	1572
P-30	4.2	3.3	No	"	0	0.01	"	20	1575
P-31	7.0	3.1	Yes	"	138	0.01	"	2	1698
P-32	10.0	6.2	Yes	"	128	0.01	"	2	1692
P-35	14.0	7.5	No	"	137	0.01	"	2	1694
P-36	8.0	4.5	No	"	146	0.01	"	2	1701
P-37	8.5	4.6	Yes	"	0	1	"	5	1700
P-39	6.0	3.0	No	"	0	1	"	5	1700
P-38	26.0	7.8	Yes	"	0	40	"	5	1700
P-40	21.0	5.3	No	"	0	40	"	5	1700
P-43	8.1	4.3	Yes	"	0	100	Static (sealed)	5	1700
P-41	9.9	4.3	No	"	0	100	Static (sealed)	5	1700

Effect of Ambient Atmosphere

The tests described in Table V were designed to show possible effects of ambient atmosphere. The tentative conclusion appears to be that continuing availability of oxygen rather than its maximum concentration is the vital consideration. There is little doubt that the increase of iron and chromium concentration in the lead with increasing dynamic pressure is real rather than chance variation. It may also be noticed, as in previous instances, that iron is more sensitive to changes in circumstances than chromium.

Tests with various atmospheres in sealed capsules were not conclusive. Variations were not sufficiently large in magnitude to rule out the possibility of chance deviations. Although cleaning and degasing prior to filling with the test atmosphere was relatively thorough, including a soak at 400°F, there may still have been significant release of gases upon heating to test temperature of 1700°F. Not only could there have been a further release of surface absorbed gases, but the elevated temperature would undoubtedly permit a relatively rapid diffusion of residual gases entrained or actually dissolved in the metals under test. It is thus not impossible that considerable partial pressures of a number of unwanted gases might be encountered in a sealed capsule test. In view of these uncertainties, the drawing of conclusions from such limited data seems rather unwarranted. These single tests suggest, however, that CO₂ leads to the greatest iron and chromium concentrations and hydrogen least with air and argon about equal to each other and intermediate between carbon dioxide and hydrogen.

As previously indicated, the beneficial effect of thermo-vacuum cleaning appears to be not only lost for more strongly oxidizing conditions, but actually detrimental.

TABLE V SPECIAL TESTS USING TYPE 410 STEEL WITH VARIOUS ATMOSPHERES AT
REDUCED PRESSURE - NO ADDITIVE

<u>Test No.</u>	<u>Fe (ppm)</u>	<u>Cr (ppm)</u>	<u>Test Time (Hr)</u>	<u>Test Temp (°F)</u>	<u>Thermo- Vacuum Cleaned</u>	<u>Remarks</u>
P-25	3.4	3.6	5	1700	yes	Standard test for control dynamic vacuum at 0.01 μ
P-37	8.5	4.6	5	1700	yes	Dynamic vacuum about 1 μ
P-39	6.0	3.0	5	1700	no	Same (1 μ) but not thermo-vacuum cleaned
P-38	26.0	7.8	5	1700	yes	Dynamic vacuum about 40 μ
P-40	21	5.3	5	1700	no	Same (40 μ) but not thermo-vacuum cleaned
P-41	9.9	4.3	5	1698	no	Sealed in Vycor capsule with air pressure at about 100 μ
P-43	8.1	4.3	5	1699	yes	Same but thermo- vacuum cleaned prior to sealing
P-42	10.1	4.0	5	1699	yes	Sealed in Vycor capsule with CO ₂ pressure at about 100 μ
P-44	7.4	4.9	5	1701	yes	Sealed in Vycor capsule with hy- drogen pressure at about 100 μ
P-45	9.0	4.5	5	1701	yes	Sealed in Vycor capsule with Ar- gon pressure at about 100 μ

Special Tests Dealing With Titanium Additions, Type of Steel, and Various Capsule Treatments.

Table VI includes an assortment of data relating to several subjects.

Iron values encountered did not seem to vary greatly with increasing chromium content of the steel although it may have been slightly lower in higher alloy types. On the other hand chromium concentrations in the lead were clearly higher in the high chromium steels. The tentative conclusion is therefore that in the short tests involved, both iron and chromium concentrations in the lead were very roughly proportional to their respective concentrations in the steel. In these tests, a preferred solubility for chromium was indicated by the fact that chromium concentrations approximating those for iron were encountered even though chromium concentrations in the steel were not more than one fifth that of iron. Tests N-7 and N-8 with Type 304 steel of nominally 20% chromium and 10% nickel suggest that nickel promotes rather than inhibits solution.

Titanium metal additions in the order of 150 parts per million were definitely beneficial though not spectacularly so in single run tests. Our previously reported work with bismuth (2) indicated that tremendously greater inhibitions could be achieved with repeated use of capsules to which titanium additions had been made. Time limitations imposed by the termination of the project made it impossible to try multiple use tests with lead. Thus it can only be assumed by comparison with the preceding bismuth work that rather spectacular titanium inhibitions are possible. Thermo-vacuum cleaning appears to be of little consequence in first run titanium tests.

Tests in which thin walled capsules were deliberately decarburized were not particularly revealing (Tests TW410 and TWI). Capsules for these tests were very carefully machined to a wall thickness in the order of 0.01 inches after which they were repeatedly oxidized till a visible surface coating

TABLE VI SPECIAL TESTS COMPARING EFFECTS OF VARIOUS TYPES OF
STEEL, TITANIUM ADDITIONS AND CERTAIN CAPSULE PRE-TREATMENTS

Test No	Fe (ppm)	Cr (ppm)	Ti added as metal (ppm)	Type of Steel	Thermo-vacuum Cleaned	Test Time (H ₂)	Test Temp (°F)	Remarks
P-11	0.3	0.8	0	410	yes	20	1352	Standard test
PC-3	2.1	Tr	0	1010	no	"	1350	Same procedure but not thermo-vacuum cleaned
P-9	1.7	2.0	0	410	yes	20	1572	Standard test
PC-4	8.6	Tr	0	1010	no	"	1575	Same procedure but not thermo-vacuum cleaned
PC-1	3.6	Tr	0	1010	yes	5	1700	Standard procedure
PC-2	5.6	Tr	0	1010	yes	1	1700	" "
TW410	8.2	2.9	0	Decor-burized		5	1700	Capsules from 410 steel machined to wall thickness 0.01 inches and repeatedly oxidized and thermo-vacuum cleaned till no further evolution of CO observed
TWI	9.3	NF	0	Decor-burized		5	1702	Same but capsule of Ingot Iron
Mag	1.0	Nil	0	(Magnetite)		24	1700	
Mag-Py	1.0	Nil	0	(Magnetite + Glass)		24	1700	
P-33	17 1/2	6.2	0	410	yes	2	1707	Control test by standard procedure
P-34	17 1/2	5.8	0	"	"	"	"	Duplicate test
P-31	7.0	3.1	138	"	"	"	1698	Standard procedure with Ti metal added
P-32	10.0	6.2	128	"	"	"	1692	Duplicate
P-35	14.0	7.5	137	"	no	"	1694	Ti added without thermo-vacuum cleaning
P-36	8.0	4.5	146	"	no	"	1701	Duplicate

TABLE VI SPECIAL TESTS COMPARING EFFECTS OF VARIOUS TYPES OF
STEEL, TITANIUM ADDITIONS AND CERTAIN CAPSULE PRE-TREATMENTS

(CONT'D)

<u>Test No</u>	<u>Fe (ppm)</u>	<u>Cr (ppm)</u>	<u>Ti added as metal (ppm)</u>	<u>Type of Steel</u>	<u>Thermo- vacuum Cleaned</u>	<u>Test Time (H₂)</u>	<u>Test Temp (°F)</u>	<u>Remarks</u>
N-1	6.0	7.8	137	446	yes	2	1700	Standard procedure Ti in higher Cr steel
N-2	6.0	8.2	143	"	yes	"	1700	Duplicate
N-7	8.5	7.5	0	304	yes	5	1701	Control test by standard procedure for Ni steel
N-8	7.0	6.6	"	"	yes	"	1700	Duplicate
N-9	7.7	4.9	147	"	yes	"	1702	Standard procedure with Ti
N-10	6.2	3.5	160	"	yes	"	1706	Duplicate

appeared and then thermo-vacuum treated to remove the surface oxide layer. This cycle was repeated a number of times before a condition was achieved in which neither a gas evolution nor surface cleaning could be observed in the thermo-vacuum cleaning treatment. Both capsules, similar in all respects except that one was Type 410 steel and the other ingot iron, were finally cleaned of surface oxide as well as possible by mechanical means (polishing) and tested with lead in the usual manner. Resulting iron and chromium values approximated those obtained in the standard tests conducted in a dynamic vacuum of one micron pressure. Micro-examination of the sectioned capsules after test revealed nothing but very large ferrite grains in the ingot iron and a depletion though not a complete absence of carbon in the outside thousandth inch or so of the Type 410 capsule.

The tests with magnetite additions have already been discussed in the paragraph dealing with the effect of time.

Micrographic Studies

Of the several capsules sectioned and examined micrographically, one tested 240 hours at 1500°F was among the most interesting. It was characterized by a comparatively thick layer of material inside and outside that etched to a brilliant, featureless appearance. This white layer was significantly thicker on the inside of the capsule than on the outside. Etching characteristics, general appearance, and hardness lower than that of the interior of the steel all seemed to point to ferrite as the identity of the constituent. The fact that virtually all crystal boundary lines were normal to the capsule surface pointed to deposition as the most probable mode of formation.

Appearance of the white layer on the outside as well as the inside surface of the capsule seemed to be of appreciable significance. Even though considerable lead was present outside of the capsule toward the end of the 240-hour run

(31.1% of the initial 32-gram lead charge distilled out of the steel capsule but was retained inside the Vycor test tube), it seemed impossible to think of all the white layer being deposited from solution by the lead. It was known that the lead which escaped the steel capsule into the Vycor containing tube was extensively volatilized in the lower part of the assembly and condensed on the header above the hot part of the furnace and refluxed back to the bottom. Thus the lead which was draining down the test tube wall and thereby contacting the outside of the capsule on the descent could only be impoverished in dissolved constituents from the steel. It therefore seemed inconceivable that such refluxing droplets could deposit a layer of matter on the capsule surface.

The reduced rather than increased hardness of the white layer relative to the parent steel seemed to rule out the possibility of its being sigma phase. It therefore seemed to follow that its mechanism of formation had to be negative i. e., a selective extraction process rather than one of deposition as the columnar grain structure indicated. It further seemed to follow that formation of the white constituent hinged on the concurrent loss of both carbon and chromium, leaving a simple ferrite which was able to homogenize itself into the peculiarly regular and large sized grain pattern.

In addition to the white layer phenomenon which seemed to be present in all samples observed, but to widely varying degrees; another commonly observed feature consisted of microscopically small islands of material dispersed in the droplets of lead which stuck to the capsule walls at the time of pouring the melt for analysis. Various observations seemed to link these particles of "precipitated" matter with the already described white layer. First, they etched and, in general, had the same appearance as the white layer material. Furthermore, numerous instances were observed in which individual crystals of white layer material had literally sprouted extensions into the lead bath.

Indications were that these incipient growths continued to increase in size until their connection with the surface could no longer be traced. Most of these islands of "precipitate" were in the immediate proximity of the steel surface. It was observed in almost all cases in which the islands were adjacent to the capsule wall that a region of selective attack on the body of the capsule had occurred. More often than not the region of selective attack beneath the island exhibited a thicker than average layer of white constituent. All this suggests a mechanism in which growths are in some way initiated on the steel surface, presumably through selective solution of chromium and depletion of carbon, and later reach sizes sufficient to effect significant transfer of matter from the steel surface. These growths seemed in time to reach sizes large enough to be easily detached from the parent surface, whereupon they became suspended particles in the lead bath. It should be emphasized that this theory has been advanced from a very limited number of observations and constitutes only a suggestion, not a positive declaration, of conclusions.

PRODUCTION OF HIGH PURITY DISTILLED LEAD FOR CAPSULE TESTING

Distilled lead of exceptionally high purity was produced in approximately kilogram lots in a Vycor still such as illustrated in Figure 7. Iron and chromium assays on the distilled product are shown in comparison to undistilled lead in the following table.

TABLE VII. IRON AND CHROMIUM IN LEAD BEFORE AND AFTER DISTILLATION

	<u>Tadanak Lead Before Distillation</u>	<u>Distilled Lead As Used In Capsules</u>
Iron	1.6 ppm.	not found at sensitivity 0.2 ppm.
Chromium	0.5 ppm.	not found at sensitivity 0.1 ppm.

Distillation was carried out under the best vacuum we could produce, which amounted to approximately 10^{-5} mm Hg inside the still. The system was allowed to pump down thoroughly--overnight or longer--at a temperature of 1000°F before raising the temperature to 1700°F for distillation. Even though the cleanest available lead was used for charging the still, there was always a copious gas evolution for a considerable time after melting as well as much smaller evolution upon increasing the temperature from 1000°F to 1700°F. The evolved gas was undoubtedly the same as that previously analysed and reported (3) as consisting mostly of CO₂. There was a gradual disappearance of the dross-like scum on the lead surface during this degasing period. It was also apparent by the rapid formation of bubbles that much gas originated from within the melt.

Distillate metal was collected in a half inch diameter Pyrex tube about 36 inches long, sealed at one end and supported inside the vacuum system. Temperature was maintained at about 800°F at the bottom and graded continuously upward to about 1000°F at the top.

Solidification of the three feet tall column of distilled metal without breaking the glass mold was the most difficult part of the whole operation. Lead bonded so tenaciously to the Pyrex container that it very frequently set up compressive

Figure 7. VYCOR LEAD STILL
(Scale: Approx. 3/16
natural size)

stresses in the containing glass sufficient to rupture it as the solidifying and cooling metal contracted. It seemed best to solidify the metal as nearly as possible from one side to the other simultaneously with solidification from the bottom up. This procedure apparently tended to relieve stresses on the glass somewhat by maintaining a "pipe" of still molten metal adjacent to the glass while most of the volume was solidifying. If the Pyrex mold did not break, spectacular looking "worm holes" could always be observed to form very slowly as room temperature was approached and the already solid metal receded from the glass container wall. Development of these shrinkage cavities was noticable for periods up to ten or twenty hours even though they were perhaps seventy-five percent complete by the time the lead was cool enough to be comfortable to the touch.

DETAILS OF CAPSULE PREPARATION AND TREATMENT PROCEDURES

A typical capsule testing assembly is illustrated in Figure 8, Capsules were machined from solid bars and had an inside diameter of half an inch and a depth of one and a quarter inches below the Vycor cover. An average charge of lead contained about 33 grams. Thus the interfacial contact area between the molten lead and steel capsule was about $1/3$ square centimeters per gram of lead. Several initial tests were run to evaluate the influence of varying the amount of lead in the capsule along with heat-up rates. Results are shown in Table VIII from which it may be concluded that these are not significant variables within the limits of our tests.

TABLE VIII. REPRODUCIBILITY TESTS FOR 20 HOURS AT 1500°F IN TYPE 410 STEEL

HEATING RATE AND AMOUNT OF LEAD CHARGED AS VARIABLES

Test No.	Fe (ppm)	Cr (ppm)	Test Time (Hrs)	Test Temp. (°F)	Amount of Pb. (Gm)	Heating Procedure
P-3	0.7	1.2	20	1500	33.0	Cold test in preheated furnace
P-4	0.4	0.7	"	"	30.5	Soak 3/4 hour at 1000°F then heat directly to 1500°F
P-1	0.2	0.6	"	"	24.3	Start with cold furnace and heat directly to 1500°F
P-2	1.1	1.4	"	"	32.8	"
P-5	1.7	2.7	"	"	31.6	"
P-6	1.2	1.4	"	"	22.5	"
P-7	1.2	2.2	"	"	31.0	"
P-8	1.6	1.8	"	"	19.0	"

Our preceeding work with bismuth has shown conclusively that the condition of capsule surfaces is of great importance to solution (2). Other work has also shown that considerable gas is evolved from the surface of steel heated strongly under high vacuum (4). It was therefore felt that possibly significant effects

Fig. 8. Vycor Capsule Test Unit
(Scale: Approx. one-half actual size.)

Fig. 9. Vycor Capsule Filling Unit
(Scale: Approx. one-half actual size.)

might be achieved by pre-cleaning the capsule surface and introducing the molten lead without disturbing the vacuum. A special capsule-filling apparatus (illustrated in Figure 9) was therefore constructed. It was possible with this apparatus to support magnetically the lead above the furnace zone until any desired heat treatment had been imparted to the steel capsule.

Automatic records were made of both vacuum and temperature during these thermo-vacuum pre-cleaning operations. (Vacuum record was made by adapting a VG-1A vacuum gauge to activate a high speed Brown recorder.) It was noticed immediately that the gas evolution was not a steady and continuous process. The extreme and sharp fluctuations in pressure suggested that evolution was by discrete puffs or bursts as if bubbles were bursting. Bubbles could not have been present, however, because there was no liquid in the system. It was also apparent from these charts that the temperatures at which evolution maxima occurred varied considerably. Temperatures higher than about 1700°F could not be tried because of the structural limitation of Vycor.

A standard practice was finally evolved in which the steel capsule was heated to 1700°F and held under diffusion pump vacuum until a steady state indicating cessation of gas evolution was achieved. Temperature was then reduced to about 1000°F at which point the lead was lowered into the furnace zone where it melted and poured through a glass funnel into the capsule. It should be stressed that even though the funnel held back all the large Pyrex fragments from the mold there undoubtedly were varying quantities of "fines" admitted to the test capsule along with the lead. The possible significance of such "tramp" Pyrex has been discussed elsewhere in this report. The filled capsule was allowed to cool under diffusion pump vacuum to room temperature. This cooling operation consumed several hours due to the slowness of heat transfer through the vacuum. The cool, filled capsules were then transferred through air, untouched by hands or other moist or greasy object, to the test units illustrated in Figure 8.

Pumping was resumed as quickly as practical after sealing into the final test apparatus. Leak testing with a DPI freon type leak tester was performed as routine on each test to check the O-ring seals as well as all other elements of the vacuum system. Pumping was then continued till a steady state in the range of three to ten millimicrons ($\text{mm Hg} \times 10^{-6}$) was achieved.

A period of about 30 minutes was required for bringing tests up to control temperature after a good vacuum had been achieved. Temperature was measured by three calibrated thermocouples secured to the outside of the Vycor test tube at 120 degree intervals. One couple was fitted with a double connection so it could be read on a precision potentiometer while still operating a standard potentiometer type controller (Celectray). This arrangement made it possible to adjust the controller to give a precisely predetermined temperature with accuracy. Loose insulation was piled copiously over the whole of the test unit to give as nearly as possible black body conditions in the furnace.

The entire Vycor test tube unit was rotated 180° about the O-ring seal, at the conclusion of the test cycle, so that the liquid metal poured from the steel capsule into the Vycor cup where it solidified and cooled to room temperature under diffusion pump vacuum. There was no provision for dealing with precipitated material that might be in suspension in the lead or attached to the capsule surface.

The test tube assembly was finally sawed open near its top end. Lead which distilled out of the capsule during conduct of the test, which ranged in amount from nil to 20 or more percent depending on time and temperature, was scraped from the Vycor test tube with a molybdenum probe and analysed along with the rest of the lead. It is of interest to note that this "mirror" of escaped lead bonded much more tenaciously to the glass when the vacuum was poor as in the 40 micron pressure tests as compared to those conducted under vacuums of 10 millimicrons even though visible oxidation was not present in either case.

Sample Preparation

The poured lead slugs together with scrapings of distilled lead from the test tube were dissolved in hot nitric acid. 33 grams of lead was a typical quantity with which 200 ml. water (free of Fe and Cr) was put followed by 50 ml. concentrated nitric acid (1 gm HNO_3 per 1 ml.). This was allowed to set on a hot plate adjusted for a temperature just below active boiling till all evidence of action had ceased, a period usually requiring several hours.

Varying amounts of nitric acid insoluble residue remained at this point. Visual inspection showed most of the residue to be glass dust from the operation of sawing open the test tube. Much smaller amounts of black material could also be seen. Some of the black matter was influenced by a powerful magnet while some of it was not. The non-magnetic black particles may be assumed to be abrasive dust from the saw used in opening the test tube while the magnetic portion would appear to be tiny grains of Fe-Cr alloy.

The approximately saturated lead nitrate solution through which the insoluble residue was dispursed was allowed to settle overnight after which most of the clear liquor was very carefully decanted. The remaining liquid, usually about 40 ml., was centrifuged; the liquor being combined with that just decanted and the residue washed back into the original flask. The total residue, amounting only to a few milligrams, was treated with about 30 - 40 ml. water and 10 - 15 ml. concentrated hydrochloric acid. This was allowed to stand on a hot plate just below active boiling till the liquid was nearly all gone. A little concentrated nitric acid was then added after which the whole was evaporated to absolute dryness over a bunsen flame. If there was the slightest evidence of magnetic residue remaining after resolution in nitric acid, the whole hydrochloric-nitric acid treatment followed by evaporation was repeated. In some samples a single hydrochloric treatment was sufficient to dissolve all

visible magnetic material. Two and sometimes three treatments were frequently required. In a few instances, especially for tests with high chromium content, all the magnetic material could not be dissolved. The entire residue from such instances was saved by centrifuging, dried, weighed and later introduced in aliquot proportion to the solid lead sulfate to be spectrographed. The combined liquors containing all the nitric acid solubles were adjusted to a final volume such that each ml. contained exactly 0.1 gm. Pb as nitrate. This was nearly a saturated solution.

Colorimetric Methods for Iron and Chromium

Our previous work with bismuth produced a very satisfactory colorimetric scheme for Fe and Cr determination in bismuth-rich solutions (1). This scheme was based on selective extraction of bismuth by solution in a mixture of ethyl acetate and amyl alcohol followed by detection of Fe and Cr by standard methods. Attempts to selectively extract lead were not entirely satisfactory. Precipitation as lead sulfate showed the greatest promise, it being quantitative with regard to iron, but giving significant coprecipitation of chromium.

Trials at determining Fe and Cr in the presence of a huge excess of lead were then tried. Lead in a pipetted sample for iron analysis was precipitated with hydrochloric acid and left in suspension. Hydroxylamine hydrochloride was then added to reduce all iron to the ferrous state after which ortho-phenanthroline was used to develop its characteristic color. The lead chloride was filtered out as a final step after making to standard volume preparatory to reading the density with a Beckman spectrophotometer.

It was found that quantitative results could be expected from this procedure only if pH values were controlled within exceedingly narrow limits. pH had to be held at 4.1 within plus or minus 0.1. This could be achieved only by using an electronic pH meter and continuously agitating the solution rather violently with an air jet. The large amount of solid phase present made it

exceedingly difficult to achieve pH equilibrium.

Chromium determination was less troublesome from the lead precipitation standpoint because the lead remained in solution at the required acid normality of 0.2. There were other interferences however that left the chromium procedure no more reliable than that for iron. The interference seemed to be in the oxidation and reduction operations. Quantitative results could be achieved only if time, temperature and reagent concentrations were controlled to a degree comparable to the pH control required for iron determination.

Spectrographic Procedures

10 ml. portions of acid soluble liquor containing one gram lead as nitrate were heated to boiling and just sufficient sulfuric acid added to insure precipitation as sulfate. The whole was then evaporated to complete dryness which left a fine white powder. This powder was "ground" and thoroughly mixed by extensive rubbing with a rubber policeman in a beaker. After that, it was violently mixed in a mechanical shaker for five minutes.

Cup type electrodes were cut from special purity graphite. 20 mg. portions of the lead sulfate powder were burned to completion in an Applied Research Laboratory (ARL) 2-meter spectroscope. A D.C. arc at about 12 amperes and 240 volts was used (short circuit at 14 amp. and 240 volts). Film was Eastman's Spectrum Analysis No. 2. A lead line at 3118.9 $\text{\AA}$ was used as internal standard to which iron lines 3020.6 and 3021.1 or chromium lines 3021.6, 4274.8 and others were compared.

Each sample was spectrographed in triplicate and satisfactory reproducibility was achieved. Although the working curve for Cr 3021.6 was not quite straight, just as good results were achieved with it as with others for which the curves were quite straight. The combination of three lines at about 3021 was especially convenient because one setting of the densitometer scanner read all three. Use of these three lines alone gave satisfactory precision over a range of iron

compositions from $7\frac{1}{2}$ ppm to 100 ppm and chromium from 4 ppm to 20 ppm. Use of chromium line 4274.8 extended the useful chromium range down to $1\frac{1}{2}$ ppm.

Still lower iron and chromium concentrations had to be dealt with in many samples. Use of 75 mg. samples together with filters on the Pb 3118.9 (25% transmission) and Cr 4200's lines (50% transmission) extended the lower limiting concentrations to about 0.2 ppm for Fe and 0.1 ppm for Cr. The only observed difficulty peculiar to the use of 75 mg. samples was an increased tendency for significant amounts of the sample to be blown out of the cup during the very first seconds of arcing. Perhaps as many as one electrode in twenty were lost in this manner. Even this, however, was not catastrophic since each sample was arced in triplicate. The line to background intensity ratio was markedly improved with the larger samples.

Spectrographic procedure was not altered for samples involving acid insoluble material. Since the amount of insoluble matter added was almost negligible in comparison to the amount of lead sulfate normally present, it was felt that arc conditions were essentially unaltered so the already established calibrations were used directly. Preparation of suitable aliquots was mechanically a very difficult matter because of the smallness of the amounts that had to be weighed to predetermined values. If the amount of residue to be introduced to the lead sulfate powder was smaller than 1 mg., an intermediate mixture was prepared in which a portion of the residue was diluted with lead sulfate of known iron and chromium values. All samples, including intermediate mixtures, involving the addition of insoluble residues were subjected to a double period of mechanical mixing, i.e. ten minutes instead of five as per normal practice.

Since the spectrographic procedure just described gave superior results it was used in the determinations presented in this report.

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