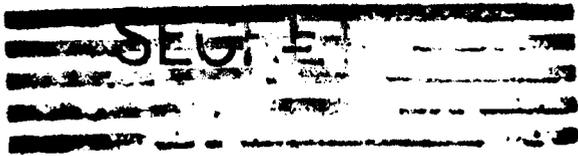


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# ORNL MASTER COPY

## METALLURGY DIVISION

### TERMINAL REPORT ON ORNL

### SLUG PROBLEM - CAUSES AND PREVENTION

By R. O. Williams

Period covered: September 1948 to July 1950

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For: H. T. Gray, Supervisor  
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~~SECRET~~TERMINAL REPORT ON ORNL SLUG PROBLEM - CAUSES AND PREVENTION

## Abstract

Efforts were made to obtain quantitative data of the various factors which seemed important in connection with the failures of the slugs in the ORNL pile. The investigation included both radiation and non-radiation studies on standard and modified Clinton slugs and diffusion work including rates with liquid phase present and the effect of a third element. This diffusion work was supplemented by some structure studies in uranium-aluminum alloys with and without a third element present. Some physical measurements were included on the compound  $UAl_4$ , the intermetallic compound about which the least was known.

The diffusion work has shown that the slugs do not, in general, fail in the minimum time necessary for the penetration of the can; but no quantitative data were obtained on the frequency distribution after this time. Temperature was the only factor studied extensively. It is very difficult to predict accurately the minimum time for failure at 250 C since there are several factors which are not known. It is, however, estimated that 70% of the 72 pile failures could have been caused by diffusion. The nature of the weakness of the weld is suggested. It is believed that about 40% of the slug failures could have been due to slugs which had holes when charged. Experience has shown that these holes were most likely at the welds.

Further work has been done with slugs which have the can metallurgically bonded to the uranium slug by an Al-Si eutectic as are the Hanford slugs. While tests have not been too extensive, no trouble has been experienced except that one slug failed at 550 C after 270 days as compared to a minimum

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life of one day for a regular slug. Evidence is presented to show the superiority of this type of slug with respect to the weld. All data indicate that the use of bonded slugs is a satisfactory solution to the problem and would permit raising the pile-operating temperature.

Results are presented to show that other elements besides silicon are effective in reducing the diffusion rate between the uranium and the aluminum. The most effective of these is bismuth. Semi-quantitative data are included to show that the main compound formed on diffusion is  $UAl_3$ .

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TERMINAL REPORT ON ORNL SLUG PROBLEM - CAUSES AND PREVENTION

INTRODUCTION TO THE PROBLEM

This study was initiated just under two years ago when it became apparent that the failure of fuel elements or slugs in the Oak Ridge National Laboratory pile (formerly known as the Clinton pile) was becoming a serious problem. Failures result in the oxidation of the uranium, contamination, and loss of operating time. As an initial and immediate solution, it was decided that filters in the outlet air stream should be installed to trap the entrained material. It was hoped that a study of the nature of the failures would provide means which would reduce or prevent them from occurring.

The reactor at Oak Ridge National Laboratory is a thermal pile containing natural uranium in a large graphite cube. Cooling air is sucked in by two large fans and discharged up a tall stack. The uranium is in the form of small slugs which lie in a channel 1-3/4" square turned on edge so that the slugs lie in a corner. The air has a velocity of 120 ft/second through this channel.

The air comes from the outside; and, hence, its temperature varies during the day and with the seasons. The mean hourly temperatures for the months vary from the low 30's in winter to the high 70's in midsummer. The average temperature variation during the day is estimated to be about 20 F. This air is passed through the pile and comes out at an average temperature of 90 C but has a maximum temperature of 110 C from the center holes. The pile, of course, has more heat generated near the center than at the edges; and the air enters at one end so that the maximum metal temperature is just past the center of the middle rows. The maximum metal temperature is about 245 to 250 C and is used to control the power of the pile. The slugs are 1.100"

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diameter x 4.1" long encased in an aluminum can which was probably drawn from 2S aluminum with a wall of about 0.030". The top (end with weld) is about 0.07" with the bottom approximately the same as the walls.

The fabrication of the slugs is as follows: The uranium stock, usually alpha rolled, is machined to size leaving in most cases a groove on the surface with a pitch of 1/16" and about 0.001" or less deep. On recent slugs the radius on the bottom has been decreased to 1/16". The slug is chemically cleaned and dried, placed in a chemically cleaned can, and the top put in position. Following a pass through a die which draws the can onto the slug and gives the wall a slight reduction, the excess of the can is machined off; and a weld is made on the rim by an argon shielded arc. See figure No. 1 for the finished unit and figure No. 7 for a weld cross section. The testing procedure is given in reference No. 1 and consists of two steps the first of which is designed to detect large holes by the weight gain and appearance of bumps on the surface, both due to the oxidation of the uranium that would occur in ten days at the test temperature of 300 C. The sound slugs are then given the modified bubble test which subjects the slugs to 300 psi He pressure for 16 to 18 hours after which they are placed individually under a collector submerged in acetone. Any slug releasing gas is discarded. The claim is made that this test is sensitive to holes as small as  $10^{-6}$  to  $10^{-7}$  inches in radius. After this test the slugs are either stored in a vault or charged into the pile.

It is necessary that the uranium be protected from the air at even slightly elevated temperatures for, otherwise, it will oxidize completely. The oxide is at most only slightly protecting to the uranium. Experience has shown that at 250 C the oxide is  $UO_2$  which as formed is rather hard and sticks together

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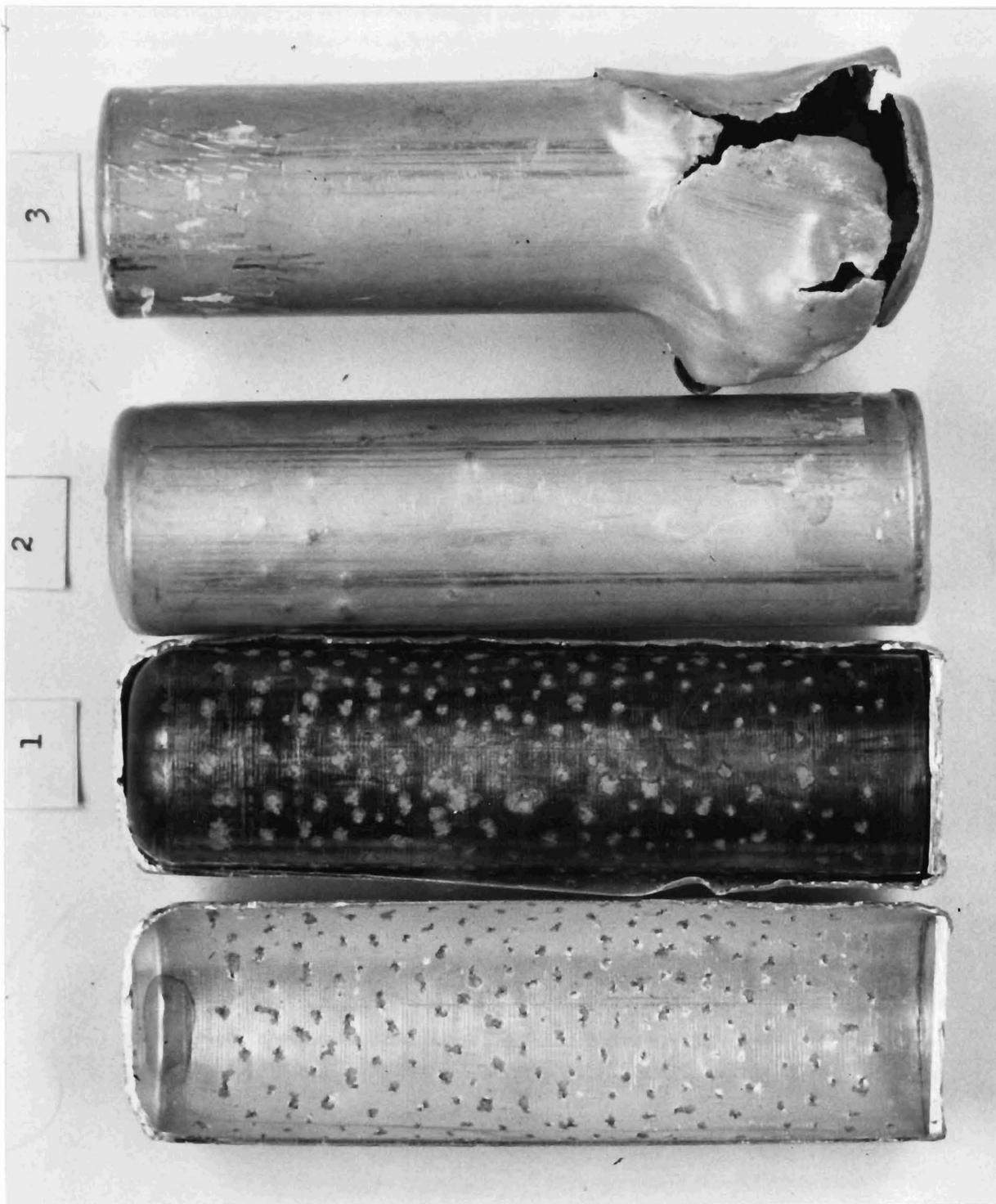


Figure 1

CLINTON SLUGS WHICH HAVE BEEN TESTED SHOWING BLISTERING AND RUPTURE

Class 1 Clinton slugs recanned and heated at 450 C for 72 hours

1. Extensive blistering
2. Unchanged except for a few small blisters
3. Al-Si coated. Rupture caused by a faulty weld.

Picture No. Y-91

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in layers parallel to the metal surface. It is known that uranium contact with air at 550 C yields  $U_3O_8$ , a heavy black powder which looks exactly like  $UO_2$  formed at 250 C except that it is formed as a loose powder and not as a layer. The temperature at which the higher oxide is formed in preference to the lower is not known, but it is recalled that the oxidation of slugs at temperatures as low as 350 C gave what appeared to be  $U_3O_8$ .

The high reactivity of the uranium for the gases left in a slug means that most of the gases will react to give solid products. For all practical purposes the oxygen and nitrogen will react completely leaving only hydrogen and argon since water will be dissociated by the metallic uranium. The hydrogen will react partly but is limited since the hydride has the rather high decomposition pressure of one atmosphere at 436 C. The British have shown that the equilibrium pressure of residual gases from air over uranium is about 27 mm Hg at 350 C<sup>2</sup> and dropping to about 13.5 mm at 250 C. It should be realized that argon would contribute about 8 mm at all temperatures. It seems safe, then, to expect a low residual pressure in the cans. This low pressure is considered a problem in heat transfer by some since the aluminum can will expand away from the slug of uranium if the uranium were cast because the coefficient of cast uranium is given as about  $12 \times 10^{-6}$  per degree C as compared to about  $25 \times 10^{-6}$  for aluminum. If, however, the uranium is alpha rolled, it may have a value as high as  $23 \times 10^{-6}$  perpendicular to the direction of rolling because of the preferred orientation established by rolling. This, combined with the initial tight fit, would probably keep the can tight on the slugs used in this pile. In the ORNL pile it is believed that the slug temperature is only a fraction of a degree higher than the can. The results of this investigation indicate rather good contact at all temperatures.

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During the operation of the pile it is found that some of the slugs will fail. To date there have been about 72 primary failures which have in some cases resulted in secondary failures. These represent 0.03% of all slugs used but does not include the failure of one or two special slugs. In the early stages of rupture or failure the can swells because of the formation of oxide whose specific volume is approximately four times that of uranium. Eventually the end is pushed off, or the can splits. Then in some cases the oxide is swept from the can break and results in contamination of the graphite and the air ducts from the pile. Figure No. 1 shows a typical failure with most of the oxide removed. The slug may expand and block the channel so that the entire row will get over-heated and rise to a temperature of about 350 C or higher. This increase in temperature endangers the other slugs which may give secondary failures. These swollen slugs can become so tight in the channel that it is very difficult to remove them and has resulted in such severe damage to the graphite that a few of these channels can no longer be used.

These failures have resulted in otherwise unnecessary exposure of personnel, interruption and loss of experiments due to shutdowns, loss of material, and loss of operating time. While the ruptures have been taking place at about a constant rate for the past three or four years with 13, 14, and 14 occurring in 1947, 1948, and 1949, respectively,<sup>3</sup> they are such a serious problem that filters were installed 18 months ago in the outlet air duct. In addition the channels are scanned visually each week by placing a light at one end of the channel and looking down it from the other end. It is anticipated that the number of failures will increase since the average age of the slugs in the pile is over 5 years. The filters are expensive to maintain and operate

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because of the large pressure drop across them. The visual scanning requires some exposure of personnel and also a fair amount of time. For these reasons it was considered that a study of the causes of slug failure and possible methods of prevention would be well advised. Also, in view of the fact that there are several other planned reactors which may have the same problem, it would seem that the results might be helpful in predicting or anticipating trouble from these.

Since it is obvious that the slug can oxidize only if there is a hole in the can, the problem then is to determine the possible causes of holes. Insofar as it is known, the aluminum cans as received have never been porous or had holes in them. The holes then must be at the welds but not detected or else develop prior to or after being placed in the pile. There is good evidence, as has been previously presented,<sup>4</sup> that new holes can be found in slugs after storage. Some of these holes result from external corrosion promoted by dampness and other factors, but these holes are preventable and are not expected in the future since the storage vault has been heated and the boxes raised from the damp floor. Some of the other slugs previously passed as sound will have detectable holes in the welds after storage. This could possibly be due to increased sensitivity of the bubble test or the fact that a retest on the same slugs would be expected to pick up some defects not previously found. From the evidence it seems reasonable to think that some of these developed holes without corrosion, and a further discussion will be given with data and a photomicrograph in a later section to support this conclusion. It is known that some of the slugs which were charged in the pile must have had holes in them. It seems likely that some of the welds developed holes while in the pile just as they did during storage.

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The last method which seems likely to be partly responsible for failures is the interaction of, or more correctly the diffusion of, the aluminum and the uranium. That aluminum and uranium diffuse together was probably known rather early, but it apparently was never suspected that this could be a possible cause of trouble until after the pile had been in operation for several years, and then its importance was not immediately obvious. While it was known that this could be a problem under some cases prior to the initiation of this study, reliable data had never been obtained; therefore, one of the main objectives of the investigation was to determine the inter-diffusion rate of uranium and aluminum and the possible factors affecting it.

This investigation has revealed that, in the absence of radiation and at temperatures above that of the pile, the diffusion takes place usually at rather limited areas forming hard, brittle lumps of intermetallic compound between the can and uranium. While it is very true that this diffusion requires essentially a weld of the two metals over the diffusion area, it has been found that there is very low strength of the junction between the aluminum and the compound. It is not unreasonable then to expect a break along this interface after the aluminum has been consumed to allow the air to enter and form the oxide which would mechanically enlarge the hole. The compound will not oxidize so readily as uranium.

The problem then is to determine the relative importance of failures due to diffusion or due to weld failure or possibly other types of can failure independent of diffusion. A direct attack on the problem is complicated in that the slugs are so radioactive after discharge from the pile that some months must elapse before any useful examination is possible, and detailed examination is never possible. This means that the problem must, for the

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most part, be investigated independent of the pile and with non-radiated slugs. The two most important types of investigation were the study of standard and modified slugs held at elevated temperatures and the performance of diffusion studies. These diffusion studies were carried out between uranium and aluminum or aluminum alloys under more carefully controlled conditions which would allow measurement of the thickness of the compound layer with comparative ease and accuracy.

#### THE INVESTIGATION

The part of the investigation in which standard and modified slugs were tested in the absence of radiation was rather complete with one important exception about a year ago and is covered rather completely in a report issued at that time.<sup>4</sup> The work, however, will be reviewed here; and the new tests and results will be included for completeness and convenience.

A few terms should be defined first so that a minimum amount of confusion will result as some of the terms are used here and elsewhere rather loosely.

The terms "reaction" and "diffusion" are used more or less interchangeably in connection with this problem since it is by diffusion that the uranium and aluminum are mixed and form the compound or, more correctly, compounds. The product of the diffusion is mostly  $UAl_3$  which at room temperature is a rather hard, brittle substance with a gray color and similar to other intermetallic compounds.

Blistering as used in this report is different from the British usage since they call the interaction product blisters, even when solid. Also, it has no connection with the Hanford slug problem which is essentially that of distortion, and no voids are formed except possibly between the can

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and the slug. The term "blistering" refers to the phenomenon which results in a bump on the can and a void inside the can and under a thin compound layer. Figure 2 shows diffusion and diffusion resulting in blistering as found in sandwich studies.

The furnace tests in the absence of radiation consist mostly of taking the slugs as received and placing them in furnaces at temperatures of from 250 to 550 C. Observations were made on them to determine when they failed and, also, when and if blisters formed. In general, it would be impossible to detect failure before oxidation; and in many cases the entire slug would be oxidized before it was discovered. When a slug had started to oxidize, it was difficult--if not impossible--to tell where the can failed and whether or not there had been any diffusion. As a result the data available from such tests were rather limited. A modification of the test procedure which was adopted for other reasons helped to solve this problem also. It involved placing slugs in closed lengths of stainless steel pipe, connecting to a tank of helium, and then heating as before. The helium at 100 psi helped to maintain better contact of the can with the slug and resulted in diffusion over more of the area. Can failure would result in only a small amount of oxidation since little oxygen was present. Complete penetration was then observable, but the times would not be exactly known.

Since it was known from an early date<sup>5</sup> that a bonded slug as used at Hanford would not diffuse so rapidly as an unbonded slug, some of the slugs tested were coated by dipping into a molten bath of Al-Si eutectic and then canned. This did not give a metallurgical bond between the uranium slug and the can. The reduction of the rate of diffusion was attributed to the presence of the Si, and so bonding could do nothing but possibly increase the rate of diffusion.

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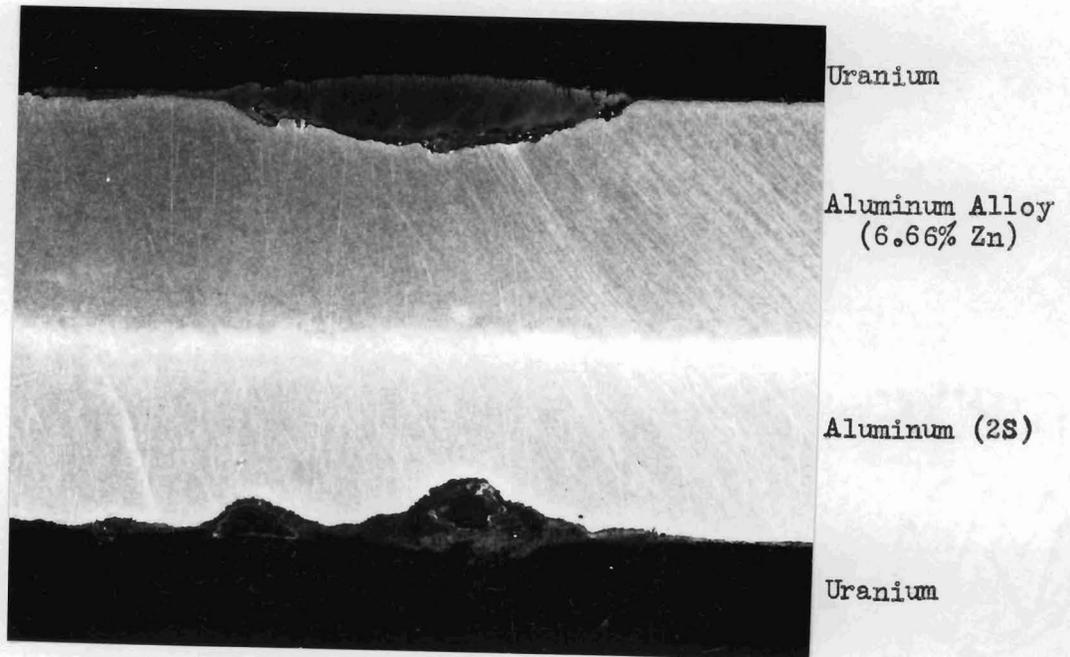


Figure 2

DIFFUSION OF ALUMINUM AND URANIUM FROM SANDWICH STUDIES

Magnification 100X 62 Hours at 550 C No etch  
Picture No. Y-67

Top: General diffusion without blistering  
to any marked extent  
Bottom: The formation of blisters

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The data for all new slugs not included in ORNL 269 are given in the Appendix I. Table I which follows is a summation of all the slugs tested to date.

#### DISCUSSION OF THE RESULTS OF SLUG TESTING

In the tabulation of the data it is difficult to get a very quantitative idea of the minimum time for failure in the absence of radiation; but it has been shown that the approximate times for failure are about one day at 550 C and about four at 450 C with very limited data at 350 C and then, as reported before, a time of about 540 days at 250 C.<sup>4</sup> The result at 250 C is based on very little data. It is believed that radiation would have a comparatively small effect. The table does beyond any doubt show the decided superiority of the slugs which are coated or bonded with Al-Si eutectic. Except for a few which failed in such a short time that there was no doubt that the welds were faulty, not a single slug coated with Al-Si failed. Their testing times were not so great as that for the bonded slugs. Only one of the several bonded slugs which failed was valid since in all other cases the furnaces overheated. Even this slug had been abused on two occasions by overheating but lasted several months after the last occasion.

The observed effect of testing the slugs under helium pressure was that the blisters formed sooner, in greater number, and were smaller. Also, the rate of penetration was greater, not because the pressure increased the maximum rate of diffusion but because it helped to maintain better contact between the uranium and the can. It is possible that some of the slugs failed under these conditions but went undetected since the first failure would result in the consumption of the small amount of air present, and

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TABLE I

SUMMARY - RESULTS OF TESTING CLINTON SLUGS AT ELEVATED TEMPERATURES

Conditions of Test		Class of Slugs	No. of Slugs	No. to Blister	Average Time to Blister	No. to Diffuse	No. to Fail	Average Time to Fail	Average Time at Temperature
Degrees C	Psi He								
		Hours			Hours				
250	0	Virgin	6	0		4	0		2,376
	0	Faulty	4	0			3	2,587	3,953
	0	Bonded	2	0			0		876
		Total, Ave.	12	0		4	3	2,587	2,652
350	100	Virgin	9	0		2	0		41
	0	Virgin	7	1	7,200	7	0		7,753
	0	Cycled	1	0		1	0		640
	0	Bonded	2	0			0		6,360
		Total, Ave.	19	1	7,200	10	0		3,986
450	100	Virgin	13	7	4.5	8	0		30
	0	Virgin	21	18	54.0	20	3	302	245
	0	Degassed	4	0		2	3	215	179
	0	Cycled	6	5		6	2	376	517
	-	Recanned	6	2		3	0		124
	-	Al-Si Coated	5	0			1	72	218
	-	Brookhaven	2	0		0	0		179
	0	Other	7			2	2	25	199
	0	Bonded	3	0			0		4,752
		Total, Ave.	67	32	41	41	11	220	377
550	100	Virgin	18	11	2.7	13	0		34
	0	Virgin	17	10	36	14	8	170	200
	0	Degassed	5	0		3	1	408	349
	0	Cycled	7	4		4	7	117	117
	-	Recanned	15	5	21	12	1	408	127
	-	Al-Si Coated	15	0		0	2	75	384
	-	Brookhaven	5	0		0	0		77
	0	Hanford	4	0			2	67.5	67.5
	0	Other	12	3	36	7	3	38	251
	0	Bonded	7	0			1	3,960	1,464
		Total, Ave.	105	33	21	53	25	254	272

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then the next failure could be identified only by finding the hole. This is not generally possible.

The other classes which are listed are discussed in the previous report<sup>4</sup> and do not have a great deal of bearing on the usefulness of the results or conclusions reached. The degassed slugs were given vacuum treatment and then recanned. The fact that none of them blistered is believed important and is discussed later. The slugs which were given some cycling from elevated to room temperature before being held at constant temperature are listed as cycled. Conclusions on these are difficult because of the complexity of treatment. The recanned class consists of slugs which were stripped from the cans and then recanned. There is no obvious difference between these and the other virgin slugs when treated the same. The last minor class is that of "other" which contains those which do not fall clearly into other classes.

The last class of importance is that of the Brookhaven slugs which were miniature elements for the Brookhaven pile and consist of a single Clinton-sized slug canned by the Brookhaven method. This method is different mainly in that the aluminum is given an anodized coating which effectively prevents the interdiffusion. No case of diffusion was noticed; however, the slugs were not nearly so bright as are the usual Clinton slugs; and this would help to prevent diffusion. It has been shown by other investigators that anodizing is effective in preventing diffusion.<sup>6</sup> In this investigation it has been shown that oxide on the slug is also rather effective. No slug which had a deliberate oxide coat was found to have diffused or to have failed from diffusion.

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Figure 1 shows typical results at 450 C or above when blistering is present. The failures are about the same at all temperatures above and below 450 C. In Figure 3 very extensive diffusion is shown. Diffusion to this extent was found mostly when using an external pressure of He at 550 C. Usually the diffusion product is more like that shown in Figure 2, and in many cases the hills have even steeper slopes and especially so at lower temperatures. The next picture (Figure 4) shows slugs which apparently had too much oxide on the surface for diffusion and two cases of very extensive blistering. Slug No. 1 would look very much like 2 and 3 when opened. Figure 5 shows a slug which was coated with a eutectic melt of Al-Si before canning. The dark surface of the slug is due to some diffusion and is assumed to be a mixed compound. There was virtually no penetration of the can. Figure 6 shows some of the slugs which were canned by the Hanford method, two of which failed because of overheating of the furnace. The tear suggests incipient fusion, so the temperature must have been about 570 C as the presence of uranium does not lower the aluminum-silicon eutectic by more than a degree or so as shown by cooling curves. It is evident that slug CBS-8 has diffused so completely that the compound is protecting. The compound has oxidized slightly, however, and spalled badly.

Fifteen of these bonded slugs have been placed in a blocked channel in the pile and operate at a maximum temperature of 330 C. They have been in for almost ten months to date; and, as expected, no irregularities have developed yet.

As was mentioned before, the failure of the welds of regular Clinton slugs is shown to be a serious problem by the past experiences. It is known that a great number of pile failures occur at the welded end. Previously

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Figure 3

A CASE OF ALMOST COMPLETE DIFFUSION WITH NO BLISTERING  
Slug degassed and recanned. Heated at 550 C for 72 hours  
Note the one spot of spalling.

Picture No. Y-16

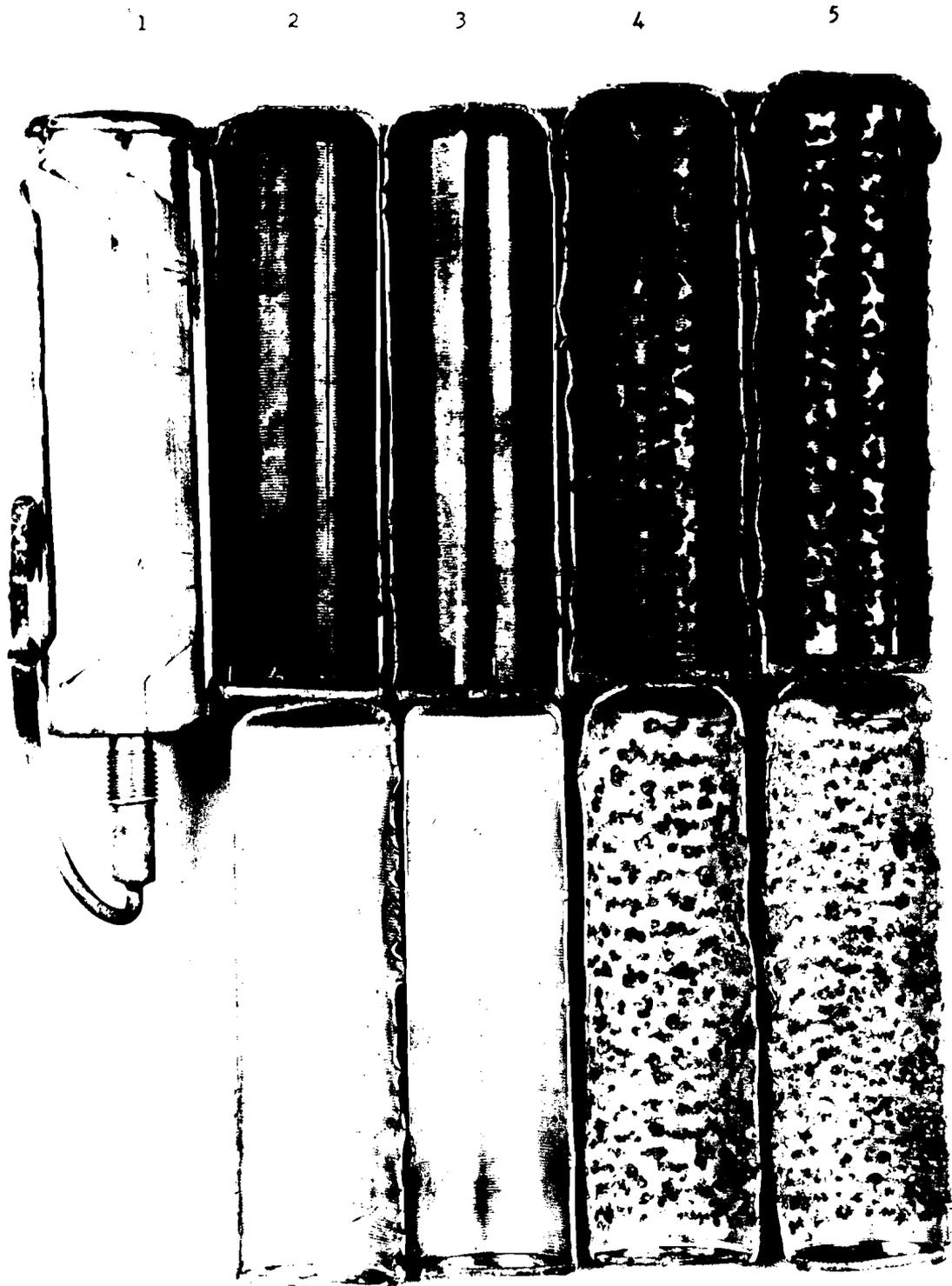


Figure 4

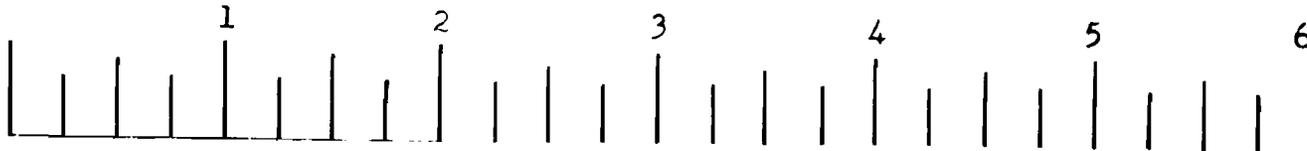
A COMPARISON OF DIFFUSION RESULTING IN  
BLISTERING AND SLUGS WHICH DID NOT DIFFUSE

Clinton slugs heated at 450 C for 262 hours

1. CS-216 Brookhaven Method
2. CS-203 Recanned
3. CS-210 Ground to 1.097 in., Class 1
4. CS-222 Class 1
5. CS-221 Class 1

Picture No. Y-90

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Figure 5

A TYPICAL COATED SLUG AFTER TESTING SHOWING THE DARK SURFACE

Clinton slug coated with Al-Si eutectic and re-canned. Heated at 550 C for 186 hours. The bright area on the slug at right is some of the coating which did not stick to the can.

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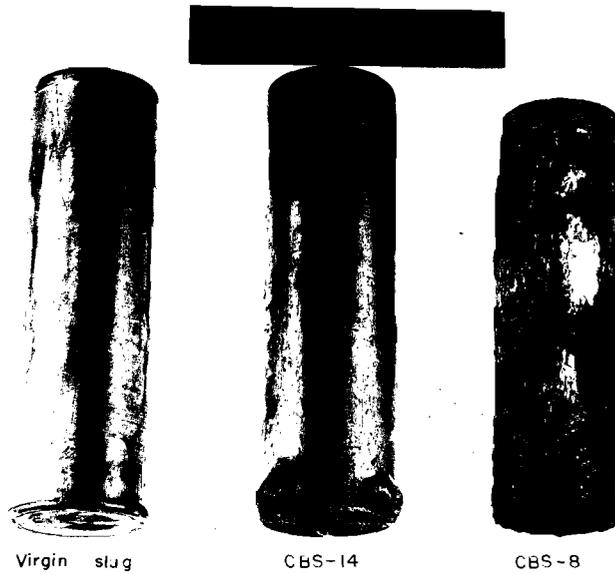


Figure 6

CLINTON SLUGS BONDED BY THE HANFORD METHOD

Virgin slug as received  
CBS-14 120 hours at 550 C before furnace  
overheated.  
CBS-8 4,248 hours at 550 C before fur-  
nace overheated. Can melted off.

Picture No. Y-1933

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the data have been presented<sup>4</sup> on the case of some 30,000 slugs which had been stored for about  $2\frac{1}{2}$  years in the regular vault. These slugs had been previously tested before storage, and those used in the pile were taken directly from the storage. It was found, however, that some of the slugs had holes in the side apparently from corrosion and failed shortly when in the pile. This initiated a retesting program with the following results. There were some 16,500 slugs remaining; and, of that number, 56 had failed by corrosion where the aluminum cans had come in contact with the corrugated board used for packing. This board had sodium silicate as a cementing agent, and the boxes were set on the damp floor of the vault. The relative humidity was always near 100%. It was not, however, these slugs which are of most interest since now the boxes are not on the floor and the vault is heated. The more important were the other 14 slugs which were found to have leaks in the welds but had no visible signs of corrosion. The leaks or holes were small and were detected by the bubble test. One of the slugs was selected and a microsection made in the vicinity of the leak in the weld. A picture of this area is given in Figure 7. Earlier preparation showed what appeared to be an oxide film preventing welding to the depth of penetration. This discontinuity was observed to extend to within 0.010" of the surface and presumably came all the way through at one point giving the leak. The possibility is suggested that slugs might be found sound by the test but which have this oxide layer close to the surface--or possibly all the way through--but no hole around it. Then because of handling, thermal cycling, or just standing, these welds open up; and the slugs are then subject to failure. It will be noticed that these detected weld failures after storage represent 0.085% while total failures in the pile are only 0.03%.

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Figure 7

SECTION THROUGH THE WELD OF A STANDARD  
CLINTON SLUG IN THE VICINITY OF A LEAK

Magnification 30X Etch 1% HF  
Specimen No. 675 Picture No. Y-1968

Note the rather thin weld and the oxide barrier.

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On the basis of diffusion studies, a re-examination of the data suggests that about 70% of the failures in the pile could have resulted from diffusion. An estimated 50% could have been due to holes in the slugs when placed in the pile. The minimum time to fail by diffusion at these low temperatures is not known accurately, nor is the frequency distribution after this time known. Very little data are available on the life of a faulty slug in the pile, and nothing quantitative is known about the probability of weld failures occurring in the pile. The conclusions, then, must be very approximate.

The cause of the blisters has been debated at some lengths, but the following data and analyses are the only direct evidence as to the postulated cause.

From observations of Clinton slugs, it is known that the blisters form in shorter times at the higher temperatures (shown by Table I) but are smaller at 550 C than at 450 C while too few have been observed at lower temperatures to compare the sizes. Figures 2, 4, and 8 show, respectively, macrophotographs and a radiograph of slugs which have blistered. It is evident or suggested that the uranium-aluminum compound layer is rather uniform and pushes up the aluminum can. Its thickness is estimated to be about 0.010" thick and forms more or less a cone with a 45° angle. There is nothing inside the void except possibly a gas. Insofar as is known, these blisters form rapidly as it has not been found possible to get a blister to grow on further heating or to become smaller by applying a pressure of 100 psi externally at 550 C overnight. The radiograph suggests that there are cracks in the compound so that it is not continuous at these conditions. This was also found when the aluminum can was chemically removed from CS-283 as shown in Figure 9. It would seem that a considerable force must be necessary for the formation of such blisters,

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Figure 8

RADIOGRAPH OF BLISTERED SLUG

CS-164, 120 hours at 450 C

Note the separation of the can from the slug adjacent to the blisters.

Picture No. Y-42

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Figure 9

BLISTER FORMED ON SLUG CS-283 DURING 336 HOURS AT 450 C

The can was removed with a solution of NaOH so that the blister was not disturbed. The material which has disappeared was probably cracked loose and fell off.

Magnification 15X Picture No. Y-1844

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and some conditions have been observed where blisters form with no less than an estimated 1000 psi. It is known that the blisters do not necessarily result from diffusion, but diffusion is always necessary for the formation of blisters. The holes or cracks observed at room conditions in the compound part of the blisters could be explained by the stresses which are set up by the cooling since there is a difference of thermal expansion. This does not seem unreasonable and is necessary in the posing of the two most plausible explanations. The compound must deform plastically at the elevated temperatures but is found to be brittle at room temperature. It is noticed that there is about 40% elongation in the formation of a blister.

The earliest explanation proposed that, due to the 15% increase in volume upon the formation of  $UAl_3$ , there is a stress built up which either causes the blister to rise suddenly or to grow up. Many of the reasons that this theory does not fit the known facts are obvious. In fact, there are no points which are in complete agreement with it. The cracks and spalling are believed to be due to the difference in thermal expansion rather than this volume increase. Figures 3 and 6 exhibit spalling, while Figures 8 and 9 show cracks.

The other possible explanation has always been in better agreement with the observations, but there were objections based on the lack of knowledge. The essential part of the theory is that there is some gas dissolved in the uranium or aluminum, or both, the solubility of which is decreased by the presence of the other element. Consequently, when this gas gets a chance to expand, it will start pushing up the layer and the can. The first objection is the lack of a suitable gas since all common gases except the inert ones would react with the uranium. The compound with the highest decomposition pressure is uranium hydride having a pressure of one atmosphere at 436 C.

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This is believed far too low to explain the blisters; but, if the separation is not between the uranium and compound but actually within the compound, then hydrogen could possibly explain it. To check this a slug which had blistered at 450 C in 264 hours (CS-279) was stripped, and three points were selected for point spectrographic analyses. One point was the bare uranium, the second a diffusion zone, and the third the dull gray area beneath a blister. Table II shows that the surface of the diffusion zone and that surface exposed by a blister have the same composition. Microscopic examinations have suggested, but not proven, that the blisters were in the compound. In many diffusion studies the blisters had considerable compound beneath the void and next to the uranium, but on slugs this layer always seemed to be thin.

The uranium may have one or two parts per million of hydrogen dissolved in it and may have some uranium hydride formed on the surface which reacts with the aluminum to generate the gas. Since the aluminum atom is believed to be more mobile, assume that it can diffuse into the uranium without driving out the hydrogen but decreasing the solubility until the gas can nucleate and cause a blister. Possibly the uranium contains uranium hydride which is at first unattacked by the aluminum but is later decomposed by higher aluminum concentrations to cause this phenomenon. It will be noted that the geometric figure expected from the growth of a blister would not be a hemisphere since the force is proportional to the projected area and the gas pressure while the resistance is proportional to the perimeter. This would mean that the pressure would drop as more of the material is pushed up and that the material would presumably not be a hemisphere, but something more like a cone or parabola. This theory, then, seems to fit the conditions rather well but leaves the exact source of the hydrogen unknown and some doubt as to why it does not

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TABLE II

SPECTROGRAPHIC ANALYSES OF CLINTON SLUG CS-279

<u>Element</u>	<u>Top of Diffusion Peak</u>	<u>Surface of Slug Which Had Blistered</u>	<u>Surface Without Diffusion</u>
Al	S	S	T
Ca	FT	FT	FT
Cu	T	T	-
Fe	T	T	-
Mg	FT	FT	FT
Mn	FT	FT	-
Si	T	FT	FT
U	VS	VS	VS

Elements sought but not found: Ag, Ba, Be, Bi, Cb, Cr, Eu, Mo, Ni, Pb, Sn, Ta, Ti, V, Zn

VS - Very strong  
S - Strong  
M - Moderate  
W - Weak  
VW - Very weak  
T - Trace  
FT - Faint trace

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diffuse into the uranium. If the theory is correct, it could possibly be checked by careful hydrogen control. The lower temperature at which blisters can form is not known, but one was observed at 350 C in the furnace tests while one was observed at 290 C on a slug which had been in the pile. It is assumed that they are not important at 250 C since the diffusing area is so limited normally, but this is really not known. In one or two cases where slugs had just started to fail, the break was noted to be directly above a blister, and possibly this could happen in the pile at 250 C, but proof would be difficult.

An attempt to analyze the gas which might be in the blisters and caused them was made by drilling the can in vacuum and collecting a small amount of gas which was inside the can. Upon drilling, any gas inside the can would diffuse out; and a sample could be sealed off in a glass sample tube with a quartz capillary to be run spectrographically. Because of the small amount of gas present, careful techniques were necessary and had to be refined further before successful analyses could be made. The least amount of gas which can be run by this method is not known, but difficulty was experienced in running a blank on an unblistered slug which would contain at most about 2 micron liters of argon ( $2.6 \times 10^{-3}$  cc under standard conditions). If the apparatus had been designed for less free volume, its sensitivity would be better.

The apparatus consisted essentially of a chamber connected to a high vacuum system by means of a packless valve. One end of the chamber contained a spindle with a drill in the end for penetrating the can. An electric hand drill was used for power while "O" rings were used for sealing around the shaft. Two small outlets were included for the glass sample tubes which were sealed off with a torch. The glass sample tubes were heated to about 450 C

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overnight to burn out any organic matter and then were connected, and the whole unit with the slug in place was pumped down by means of the vacuum unit. The apparatus was heated to promote outgassing. Once this had been accomplished and everything cooled, the valve was closed, the slug drilled, and several minutes allowed for the gas to distribute itself before the tubes were sealed off.

In order to get more gas into the tubes, some of them were cooled with liquid nitrogen which should increase the amount nearly four times. In some cases a number of bulbs were sealed into the stems, and all may have been cooled prior to sealing.

The bulb farthest from the glass sample tube was heated while the rest of the bulb was cooled and then a seal made between the two. This was repeated to get the last bulb off. It is difficult to determine actually how effective these methods were but did help to make analyses possible even though it was never possible to get a really strong tube.

It was found that it was never possible to outgas the system completely, and the lowest rate of outgassing found was about 0.005 micron liters per second. This was great enough to collect a sample of gas from the chamber alone in about 20 minutes using the modified technique. This gas was reported to be composed mainly of C, N, and H with O as a minor constituent. A blank run which had been made on an unblistered slug heated at 450 C for one day and slowly cooled gave results of almost pure argon, the remainder from the entrapped air. A few bands were present but disappeared before photographing. These were presumably the outgassed elements above in smaller concentrations.

A run was made on a slug (CS-279) which had been in the furnace for 11 days at 450 C and had developed some 20 blisters. The blisters were broken

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down with a hammer on the cold slug, and then it was run just as the other one. The results showed that the main gases present were A and H with the usual other impurities. This seems to be a good indication that the gas causing the blisters is hydrogen. One further observation which indicates that the gas might be hydrogen is that, as listed in the summary table, degassed slugs gave no blistering but about as much diffusion as the others. The slugs were degassed above 550 C for several hours under a vacuum of less than 10 microns. The equilibrium hydrogen would be very small; and the surface, at least, is well degassed.

It is not certain that the foregoing conclusions are correct, but they are the most satisfactory and are more or less in agreement with the known facts. There are no similar phenomena known by the author; so no conclusions can be reached by comparison. The evidence presented here is not conclusive and leaves much unknown but does explain all observed facts with some degree of satisfaction, and no other theory known is so nearly acceptable in view of the observations.

As has been shown by the furnace tests, the bonded slugs seem to last much longer than ordinary slugs. Exact data are not available since too few slugs have been run for long enough times, but a decidedly greater resistance to failure is shown at elevated temperatures. A factor as great as ten for times to fail is suggested but not proven by the data. Other work which is presented later in this report suggests that the bonded slugs should have had time to fail at the two higher temperatures; but, as is true of regular slugs, the maximum diffusion rates are not observed under such conditions. In the case of bonded slugs one reason is that the can breaks away from the uranium and reduces the degree of contact. A picture, Figure 10, is included

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Figure 10

SECTION THROUGH THE BOTTOM OF A CLINTON SLUG  
BONDED BY THE HANFORD METHOD

Magnification 60X Etch 10% NaOH  
Specimen No. 565 Picture No. Y-678

It is seen that the slug almost touches the can here and that the bonding is not uniform. A thin layer of compound can be seen on the uranium (0.001").

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to show that the bond may be very thin at some places (here, the corner) and that the uranium already has a compound layer which, as shown in Table V, is rather rich in silicon. This may account for the lower rates. It will be noticed that the bonded layer is not eutectic, and this may be due to the selective reaction of the silicon with the uranium. That the diffusion does proceed is shown by Figure 11. Here the silicon is seen to have diffused into the aluminum cans, and the reaction has proceeded irregularly. A third picture, Figure 12, illustrates what is believed the best argument for the use of bonded slugs. Here it is seen that the lid is essentially brazed into place by the eutectic, and then the closure is completed by a weld. In comparing this with the previous picture (Figure 7) it is certain that this unit is mechanically more rugged with much stronger welds. Another point which favors bonded slugs at higher temperatures is that they have never exhibited any blistering under any conditions. In some unbonded slugs blistering apparently resulted in failure before the uranium had interacted with more than one-half the can thickness. This has not, however, resulted in minimum observed times to failure but would certainly reduce the life of any given slug. Since the tentative plans call for operating the pile at a top temperature of 350 C, blistering would be important. It is postulated that blistering does not occur on bonded or coated slugs because the hydrogen is either driven off during canning or the diffusion rate is so low that the hydrogen concentration never builds up.

#### INTRODUCTION TO THE OTHER WORK DONE IN CONNECTION WITH THE SLUG PROBLEM

As the work progressed on the study of slugs in the absence of radiation, it was decided to study some uranium-aluminum alloys and the formation of the

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Figure 11

SECTION THROUGH A CLINTON SLUG BONDED BY THE  
HANFORD METHOD AFTER BEING HELD AT 550 C FOR 1,824 HOURS

CBS-10 Magnification about 100X Etch HF, HNO<sub>3</sub>, HCl, H<sub>2</sub>O  
Picture No. Y-1939

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Figure 12

SECTION THROUGH THE TOP CLOSURE OF A CLINTON SLUG  
CANNED BY THE HANFORD METHOD SHOWING THE BONDING LAYER AND WELD

Magnification 14X Etch 10% NaOH  
Specimen No. 658 Picture No. Y-676

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intermetallic compounds during the cooling since these were involved in the diffusion layers. Some other work which had been done with uranium-aluminum alloys containing up to 25 weight per cent uranium resulted in what appeared to be an equilibrium mixture of three phases in the binary system, and it was this observation which led to a study of the formation and the separation of the intermetallic compounds. The abnormalities were explained, and no unusual results were found which seem to have any direct connection with the conclusions reached on the slug problem. They do, however, permit a better understanding of the system involved.

Since the structure of what was known as  $UAl_5$  was unknown, one of the members of the division desired to determine its structure. Since samples were on hand which contained relative pure compound in aluminum, the task of separation was taken up to supply him with material. Direct measurements of the density and chemical composition were considered desirable and were made.

This material has been shown to be  $UAl_4$  structurally.<sup>7</sup> The structure is body-centered orthorombic with  $a = 4.41 \text{ \AA}$ ,  $b = 6.25 \text{ \AA}$ , and  $c = 13.60 \text{ \AA}$  with four molecules per unit cell. The theoretical density is  $6.12 \text{ gm/cc}$ , and the composition would be 68.8% uranium as compared with 63.8 for  $UAl_5$ . The physical measurements which were made have been tabulated in Table III.

Sample Y-15 was prepared by slowly cooling a melt of 25% uranium from 770 to 650 C in four hours. The lower part of the ingot which contained the primary crystals of  $UAl_4$  was removed and leached with NaOH in aqueous solution. This method was tried in many cases for the separation of aluminum from the compound and proved to work well except that, if the solution were too hot and concentrated, the compound would also be decomposed into a dark, amorphous

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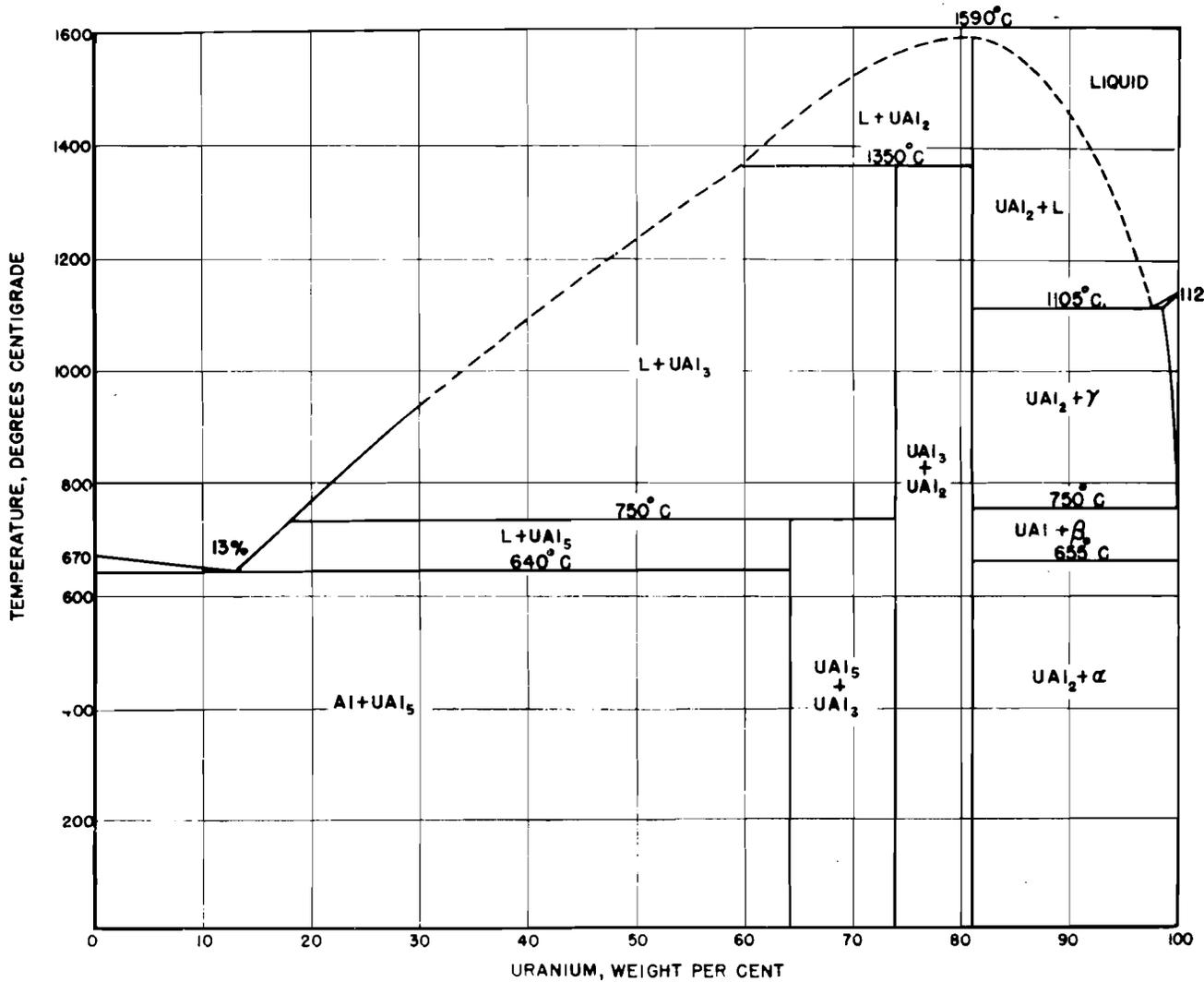


Figure 13

## THE ALUMINUM-URANIUM ALLOY SYSTEM

From "Preparation and Properties of Aluminum-Uranium Alloys" by H. A. Saller TID-65

TABLE III

CHEMICAL ANALYSES AND DENSITY OF UAl<sub>4</sub>

Sample	Weight % U	Atomic % U	Density, gm/cc				Formula
			Measured	Calculated <sup>1</sup>	Holes <sup>2</sup>	Substitution <sup>3</sup>	
Y-15	65.85 65.39	17.8	5.35 5.38	5.66	5.57	5.72	UAl <sub>4.62</sub>
68-1	65.27	17.6	5.57	5.62	5.72	5.90	UAl <sub>4.69</sub>
68-2	66.27	18.2	5.56	5.73	5.67	5.80	UAl <sub>4.48</sub>
75-1	64.23	16.9	5.34	5.52	5.35	5.55	UAl <sub>4.90</sub>
75-2	65.85	17.9	5.35	5.68	5.70	5.85	UAl <sub>4.50</sub>
Average	65.47	17.7	5.44	5.64	5.60	5.76	UAl <sub>4.65</sub>

<sup>1</sup>Calculated by  $2.70 \div 0.165 \times \text{Atomic \% U}$  where 0.165 was determined experimentally with 5, 10, 15, 20, and 25% U alloys

<sup>2</sup>Calculated by assuming uranium sites vacant

<sup>3</sup>Calculated by assuming substitution of Al for U

Theoretical density of UAl<sub>4</sub> - 6.12 gm/cc

68-1 and 75-1 from smooth part of ingot; 68-2 and 75-2, rough part

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substance. It is not known that the compound is not attacked under milder conditions, but the rate must be much slower. The most drastic conditions which are considered satisfactory for this work was about 20% NaOH at 40 C. The material which was separated from the fines was examined under the microscope and found to be long, uniform grains all looking alike with a fairly bright surface. X-ray studies gave no indications of impurities. These grains could be broken easily.

The remaining compound was prepared in a somewhat different manner. Pieces of uranium were placed in melts of aluminum calculated to give  $UAl_3$ ,  $UAl_4$ , and  $UAl_5$  in composition. The melt was held at 740 C for 6 hours and then furnace cooled overnight. There was enough aluminum present so that most of each ingot was  $UAl_4$  with possibly traces of free aluminum and  $UAl_3$ . The  $UAl_3$  as formed was massive, but the  $UAl_4$  was porous at some places. No difficulty was experienced in drilling out samples free of  $UAl_3$  except that the compound was hard and pyrophoric. A NaOH leach was used to remove the aluminum, and a weak  $HNO_3$  wash was used to remove any material not compound. It is known that this acid will attack the compound readily, but the large specific area was relied upon to reduce the undesirable portions. No impurities were detected by means of X-rays. Amounts of  $UAl_3$  which would seriously affect the results should be easily detectable since there are small differences in chemical composition and density between  $UAl_3$  and  $UAl_4$ . Samples were taken from rough areas which seemed to have an excess of aluminum and smooth areas adjacent to the  $UAl_3$ . These were analyzed separately but only a single analysis on each. It is seen that there is no significant trend. On the basis of this work, the composition of  $UAl_4$  would seem to be 65.5% uranium with an average deviation of 0.5%.

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Because of the nature of the material, special care was used in measuring the density by loss of weight in liquid. A small, glass bucket which would hold about 0.5 gm of compound and weighed less than 0.2 gm was used. After exercising special care to insure that no air bubbles were entrapped in the material, its weight in  $\text{CCl}_4$  was compared to its dry weight with appropriate corrections for the weight of the bucket. It has been found that the results are rather reproducible.

In some other work it was found that the change of density in grams per cc for a unit change in atomic per cent uranium in aluminum is 0.165 as determined in a series of uranium alloys up to 25 weight per cent uranium. The accuracy of this figure is not known, but the data when plotted gave a straight line. This value was used to calculate the density of the compound using the compositions as listed. It is noticed that the measured densities are always lower and by approximately the same amount. This is not unexpected since there are more reasons to expect a low answer. One reason for this is shown by a subsequent microstructure where it is seen that the compound is in the form of hollow needles containing aluminum. Sample Y-15 is the only one in which this could be expected. Another reason for low values is the possibility of entrapped air during the density measurements.

It is concluded that the compound can have a composition considerably richer in aluminum than  $\text{UAl}_4$ , but it was not shown beyond doubt that it could not have the composition of  $\text{UAl}_4$  under some conditions. When aluminum is in excess, as is the usual case, the best formula seems to be about  $\text{UAl}_{4.65}$ . As has been shown before, the best correlation of analyses, density, and structure is obtained by assuming that some of the uranium sites are vacant.<sup>7</sup>

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It is difficult to determine the range of composition which  $UAl_4$  can exhibit since it was never established that the compound as prepared was saturated with aluminum except in the case of Y-15. For the other samples the degree of saturation or depletion is not known. The chemical analyses are not believed to be too reliable. The temperature which this composition range represents is not known since the samples were slow-cooled.

### ALLOY STUDIES

Several alloys of uranium and aluminum--and in some cases, a third element --were made up in order to study the formation and nature of the compounds formed in the uranium-aluminum system. This work was done to determine the reason for the three phases present in some alloys and, also, to investigate the nature of the effect of a third element on the diffusion rates in the system. The work is discussed by considering the formation of the alloys in the binary system and then the effect of the third elements. The phase diagram is given in Figure 13 in order to assist the interpretation of the results.

The results are best shown by pictures with descriptions. In Figure 14 a section of an ingot of alloy is shown in which a uranium slug  $3/4$ " long and  $1.1$ " diameter was placed in molten aluminum at  $950$  C and held for  $2\frac{1}{2}$  hours followed by a quench. Here the uranium is seen to have been partially consumed by the formation of intermetallic compounds. Almost all the compound shown has been identified as  $UAl_3$  with possibly a small amount of  $UAl_2$  next to the uranium. There is a small amount of  $UAl_4$  as primary crystals. Although much of the  $UAl_3$  is in the form of small grains, it was never in solution but appears as a result of the breaking away of surface layers of  $UAl_3$  formed

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Figure 14

URANIUM SLUG ( $4/3''$  x 1.1 dia.) PLACED IN ALUMINUM  
AT 950 FOR 2-1/2 HOURS AND QUENCHED

Magnification 2X Etch none  
Specimen No. 514 Picture No. Y-544

The center part is uranium with possibly a thin coating of  $UAl_2$  and then a heavy coating of  $UAl_3$  containing cracks. The other gray parts are fine grains of  $UAl_3$  which broke off. A few primary grains can be seen at the top and are probably  $UAl_4$ .

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by the uranium-liquid aluminum diffusion. The bottom of the ingot is composed of all small particles of  $UAl_3$  from this source with a small amount of aluminum surrounding them. An analysis here would give more than 60% uranium. The next photomicrograph, Figure 15, shows how the massive  $UAl_3$  compound is broken up by the action of the melt into the small grains. The light region is the solid  $UAl_3$  shown in the last picture, while the dark field is the aluminum. It appears that the molten aluminum attacks and penetrates the grain boundaries allowing the small particles to form. These particles usually have regular geometric shapes.

The next series of pictures--Figures 16, 17, and 18--were made from a similar ingot, but only half as much uranium was used so that there was no free uranium left. About 90% of the uranium lay in the bottom in the form of the small grains of  $UAl_3$  as shown in the lower part of the first picture. The analysis of this area near the bottom was 62% uranium. The amount of  $UAl_4$  was too small to detect by means of X-ray studies. It is assumed that the primary grains directly above the equiaxed grains are only  $UAl_3$  because there is not much  $UAl_4$  in this area, and that present was assumed formed from the eutectic. The top of photomicrograph, Figure 17, shows the first primary grains of  $UAl_4$ . The bottom will be noticed to be the same as in the previous photomicrograph since the two actually overlap. These small grains of  $UAl_4$  extend only a distance comparable to that of primary  $UAl_3$  which is shown. It then formed in larger grains which extended to the eutectic composition immediately above the next photomicrograph, Figure 18. This last photomicrograph shows fine eutectic and primary  $UAl_4$ . No  $UAl_3$  was detected by X-ray above the region shown in the bottom of Figure 17. Figure 18 shows the usual form of the primary  $UAl_4$  and the hollow needles mentioned before. As found by other investigators, a divorced eutectic is shown.

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Figure 15

PHOTOMICROGRAPH THROUGH A URANIUM-ALUMINUM  
INGOT SHOWING THE ATTACK OF THE  $UAl_3$  BY THE MELT

Magnification about 100X Etch NaOH  
Specimen No. 514 Picture No. Y-658

Uranium in aluminum at 950 C for  $2\frac{1}{2}$  hours and quenched

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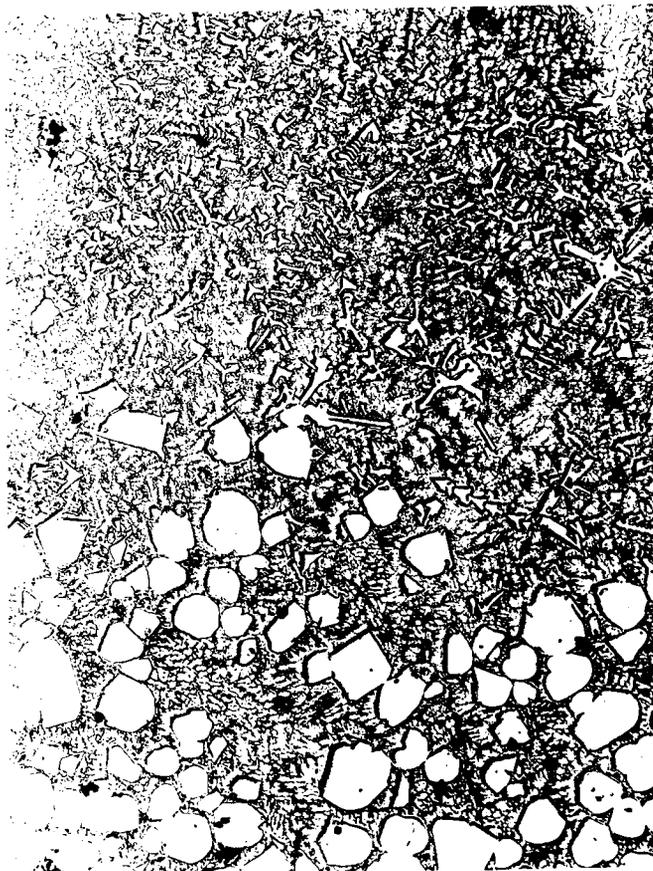


Figure 16

PHOTOMICROGRAPH THROUGH A URANIUM-ALUMINUM INGOT

Magnification 100 X Etch NaOH  
Specimen No. 487 Picture No. Y-598

The large grains are  $UAl_3$  which were formed by diffusion and were never in solution. The broken dendrites are primary  $UAl_3$  with some  $UAl_4$  present.

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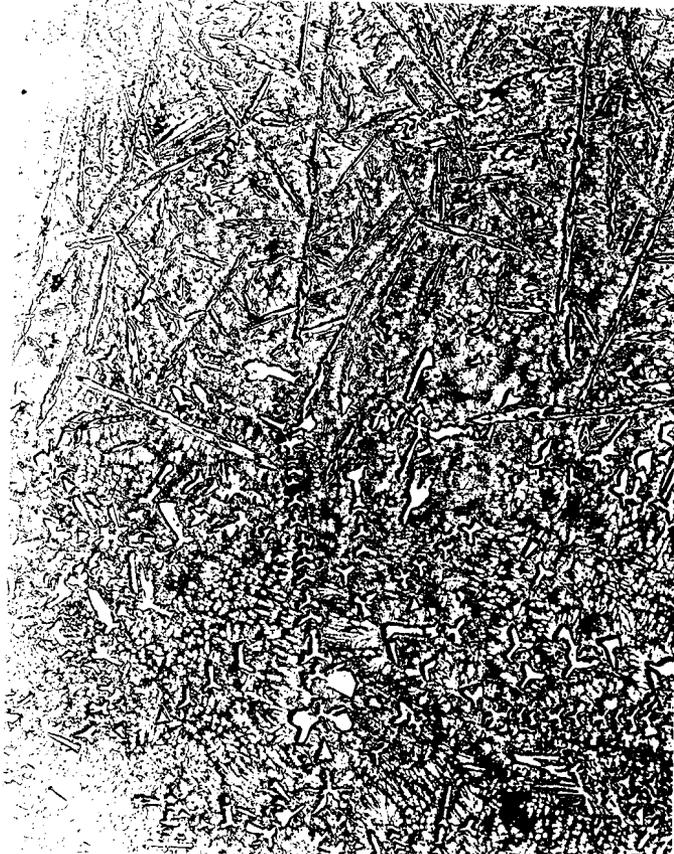


Figure 17

PHOTOMICROGRAPH THROUGH A URANIUM-ALUMINUM INGOT

Magnification 100X Etch NaOH  
Specimen No. 487 Picture No. Y-597  
Location 0.035" above Figure 15

The broken dendrites are  $UAl_3$  while the others are primary  $UAl_4$ . The fine  $UAl_4$  structure extends only about 0.050" and then larger grains of  $UAl_4$  are formed.

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Figure 18

PHOTOMICROGRAPH THROUGH A URANIUM-ALUMINUM INGOT

Magnification 100X Etch NaOH  
Specimen No. 487 Picture No. Y-549  
Location 0.40" above Figure 15

The primary grains are  $UAl_4$  surrounded by eutectic. Note the divorced eutectic around the primary grains.

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The foregoing results suggest nothing irregular; but some work done earlier on a series of alloys containing up to 25% uranium always resulted in a mixture of  $UAl_3$ ,  $UAl_4$ , and aluminum. The summation of the data is given in Table IV. The fractions listed in the table refer to the ratio of  $UAl_4$  to the sum of  $UAl_3$  and  $UAl_4$  as determined by X-ray diffraction work. These fractions were determined by dividing the sum of  $UAl_4$  line intensities by the sum of  $UAl_3$  plus  $UAl_4$ . The sums were taken between  $2\theta$  of 20 to 50 degrees. How close this method gives the actual ratio is not known; but, because of the erratic line intensities given by an X-ray spectrometer, no refinement was considered warranted. The results are reproducible as are shown by duplicate runs. As is now known, the presence of silicon is the cause of the  $UAl_3$  in these alloys. Holding at the elevated temperatures reduced the amount of  $UAl_3$  in contrast to rapid cooling which increased it. It is shown by slow-cooled samples that the primary  $UAl_3$  removes the silicon and gives a two-phase eutectic.

Before the cause of the discrepancy as described above was known to be caused by small amounts of silicon, it was decided to make up four uranium alloys containing a small amount of the more common impurities in aluminum --silicon, magnesium, copper, and iron. X-ray studies on them showed that the uranium was in the form of  $UAl_4$  in the copper, magnesium, and iron alloys. In the alloy of iron, however, there was a third phase which was not  $FeAl_3$ ; so it must have been a compound of iron and uranium with or without some aluminum. No third phases were detected by X-ray diffraction in the copper and magnesium alloys. The alloy containing silicon did not have any  $UAl_4$ ; instead, it was all  $UAl_3$  with a shifted lattice parameter. This alloy is listed in Table V which gives a calculated per cent of substitution of silicon

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TABLE IV

ANALYSES OF SERIES OF ALUMINUM ALLOYS  
WHICH CONTAINED FROM 5% TO 25% U AND SMALL AMOUNTS OF SILICON

Nominal Composition	Actual Composition			Ratio of $UA_{14}$ to $UA_{14} / UA_{13}$ <sup>2</sup>			
	% U	U	Si	Mg	As Received	Heat Treated	950 C Quench
5	4.95	2.28	0.075	.29	.62	.45	.56
				.36	.34	.85	
10	9.90	2.93	0.12	.73	.94	.87	.55
				.60	.94		
					.93		
15	15.16	2.04	0.070	.72	.92	.84	1.0
				.72	.94	.87	
20	19.70	0.23	0.20	.87	.96	.41	.68 bottom
				.92	.89		1.0 eutectic
25	25.09	0.48	0.12	.88	.92	.25 bottom	.54
				.75	.98	.42 top	1.0 eutectic
						.55 top	

<sup>1</sup>Analyses are of questionable validity.

<sup>2</sup>Ratio determined by x-ray line intensities

The alloys quenched from 950 C showed segregation in the 20 and 25% ones, while those which were slow cooled showed segregation in the 15% also. The amount of segregation was about twice as great in the slow cooled ones. The cooling rate was about 175 C per hour to 600 and then room cooled.

The heat-treated ones were held at 450 for 12 days or 350 for 36 days.

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TABLE V

LATTICE PARAMETER OF  $UAl_3$  IN SILICON-URANIUM-ALUMINUM ALLOYS

<u>Material Number</u>	<u>Material</u>	<u><math>a_0</math></u>	<u>% Replacement<sup>1</sup></u>	<u>% of Total Si in <math>UAl_3</math></u>
Y-2	14.4 U, 1.58 Si	4.22	17	65
Y-16	34.69 U, 6.02 Si	4.18	35	71
BS-1	Bonded Slug <sup>2</sup> - Uranium Side	4.17	39	
BS-2	Bonded Slug - Aluminum Side	4.21	22	
$UAl_3$	$UAl_3$	4.26	0	

<sup>1</sup>Calculated by using for  $UAl_3$   $a_0 = 4.26$ , and for  $USi_3$   $a_0 = 4.03$  and a linear change of  $a_0$  with aluminum replacement.

<sup>2</sup>Slug bonded by Hanford method untreated. Can be peeled off and runs made on the two surfaces.

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for aluminum in the compound. The photomicrograph in Figure 19 shows the microstructure of the magnesium alloy. This structure is not modified by the presence of the magnesium. It was found, however, that the alloy was much harder than a corresponding uranium-aluminum alloy. The microstructure for the silicon alloy, Figure 20, is much different than a binary alloy of the same uranium composition. The hardness is about the same as that found for the same concentration of uranium in a binary alloy. The aluminum still has about 0.6% silicon in solution or precipitated. The amount of silicon which is necessary for all the uranium to be in the form of  $UAl_3$  is not known, but it must be rather small since no shift of parameter has been noticed in compiling data listed in Table IV. A shift of as much as 0.3 degree would have been noticed if present; so the amount of silicon in the  $UAl_3$  must have been less than about 8% of the aluminum present in this compound. The silicon analyses for the three alloys containing the least amount of uranium must be in error.

The other data in Table V show that the compound which forms on the bonded uranium slug has a higher silicon-to-aluminum ratio than does the aluminum-silicon eutectic. A melt was made containing about 15% uranium with a sodium addition in an effort to modify the alloy as is done with aluminum-silicon alloys. The addition was larger than desired, approximately one per cent, but did not give any changes observable by X-ray diffraction or metallography. On the basis of this, it is believed that a sodium addition will not affect the grain size or structure of uranium-aluminum alloys.

#### DIFFUSION WORK

Since it was observed that the presence of silicon between the can and the uranium slug reduced the diffusion rate, it was thought possible that

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Figure 19

PHOTOMICROGRAPH OF 13.13% URANIUM-ALUMINUM ALLOY CONTAINING 1.97% MAGNESIUM

Magnification 100X Etch 10% NaOH Alloy Y-1  
Specimen No. 621 Picture No. Y-752

Second phase is all  $UAl_4$ .

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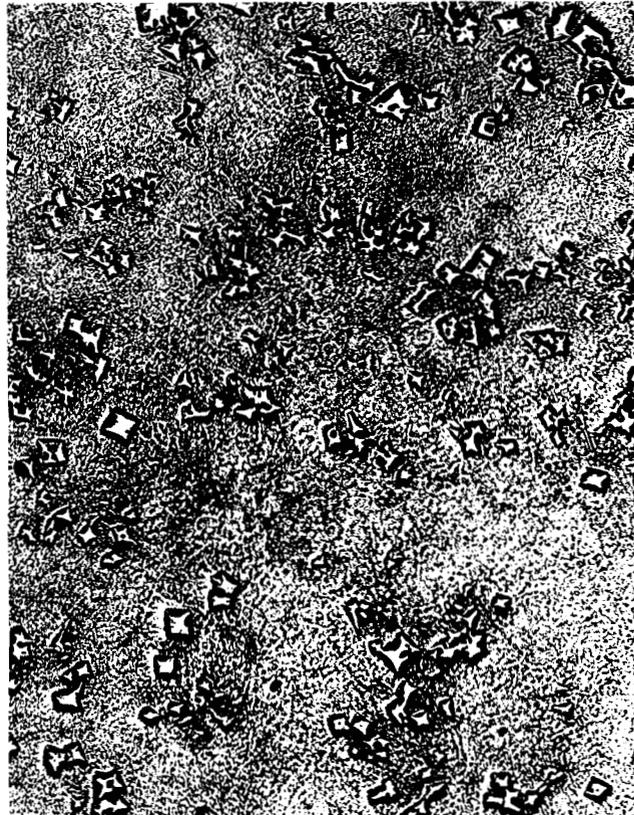


Figure 20

PHOTOMICROGRAPH OF 14.4% URANIUM-ALUMINUM ALLOY CONTAINING 1.58% SILICON

Magnification 100X Etch 10% NaOH

Alloy Y-2 Specimen No. 617 Picture No. Y-748

Contains only  $UAl_3$  with  $a_0 = 4.82$  ( $UAl_{2.4}Si_{0.6}$ )

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other elements alloyed with the aluminum might be more effective in reducing the diffusion rate. Then, too (as has previously been shown) it is difficult --if not impossible--to get quantitative results from furnace tests since the reason for failure and the time are often not known; and, even if they were, experience has shown that there is no reason to expect uniform maximum rates from such tests. It then seemed desirable to be able to perform more quantitative tests with more types of diffusion couples without the involved process of canning the slugs in the various aluminum-base alloy jackets. In order to fulfill these requirements, a series of diffusion studies referred to as "sandwich" studies was initiated.

For the diffusion of two metal phases, the process can be represented by the equation

$$L = Dt^{\frac{1}{2}} \quad (1)$$

where L is the thickness of any new phase formed or the distance between points of fixed composition. Time is represented by t, and D is a diffusion coefficient. A few systems are known for which this equation does not hold, but this is believed a result of cracks or extremely thin layers. Limited experimental data on the uranium-aluminum system support equation 1.

A modified form of the Dushman and Langmuir's equation

$$D^2 = Be^{-\frac{Q}{RT}} \quad (2)$$

is valid as long as there are no phase transformations within the temperature range considered. B is a constant, R the gas law constant, and T the absolute temperature. The term Q is known as the heat of diffusion analogous to the heat of activation in chemical reactions. It can be shown that for the binary system where there are more than one new phase this Q is actually a

composite of the Q's for each layer when the thickness used in equation 1 is the total of all the phases. Combining equations 1 and 2, the thickness of the products of diffusion is given by

$$L = B \frac{1}{2} e^{-\frac{Q}{2RT}} t^{\frac{1}{2}} \quad (3)$$

Even when a third element is present, these equations seem to hold as long as the temperature under consideration does not involve the appearance or disappearance of any new phases.

In this investigation the total thicknesses of the compounds formed by the diffusion of uranium and aluminum were used. The value of Q, then, does not have an exact meaning. If it had been possible, however, to measure the thickness of each layer, independent values of Q could have been obtained. The terminal solid solutions in the binary system under study are very limited, and, so, can be ignored.

When two metals diffuse together, all the intermediate phases stable at that temperature should be formed. The relative amount is a function of several factors. Two of these factors are the diffusion rate and composition range of the phases. In a ternary system it is believed that the kind and order of the phases are given by a straight line connecting the two initial compositions on the isothermal section of the ternary phase diagram at the temperature of diffusion.<sup>8</sup>

A third element might do several things when it is present. It could change the relative stability of the different phases, form binary or ternary compounds, or possibly be so insoluble in any phase that its influence would be mechanical. Since a system with a third element is so complex, only a few of the possible effects are mentioned here. This study was concerned with additions to the aluminum, so the discussion will be limited to these

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cases; but similar reasoning would apply for the other cases. If the addition formed a compound with the aluminum which was stable in the presence of the uranium and which did not change the stability of any phases, then its effect would be mechanical; i.e., the diffusing atoms would have to take somewhat longer paths to travel the same distance. This type of interference is inefficient since the effect would be approximately proportional to the volume of this phase. Since a reduction by a factor of at least two is desirable, this method is not very useful.

The next way in which the third element could change the diffusion rate would be to change the relative stability of the different compounds and thereby increase or decrease the diffusion rate. The possible magnitudes of such an effect are not obvious. A third way in which a change could take place would be by the formation of new compounds or phases not present in the binary system. If these phases were discontinuous layers, then the effect would be partly mechanical.

It has not been shown that the new phases will be continuous, the form in which they would have the greatest effect if they were more stable than the other original phases. Observations have been made which suggest that in some cases the layers are continuous, and in others they are not. As mentioned before, it is thought that the new phases will form in continuous layers. Examination is difficult, however, since all the compounds have similar appearances and, in general, cannot be identified or distinguished.

The scope of this work included diffusion studies on binary and commercial alloys of aluminum with project grade uranium and did not consider the use of other combinations. In the beginning it was not realized that it would be so difficult to get consistent results, and much work was necessary

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for the development of suitable techniques. A detailed account is attempted only of the best procedure found, and most of the results are based on runs made in this manner.

Those alloys bearing an "A" number were prepared in this division by melting aluminum in a graphite crucible and adding the alloy element. After being stirred at a high temperature for a time thought to be long enough for solution, the melt was cast into an ingot about  $1\frac{1}{2}$ " x  $\frac{1}{2}$ " x 4" for rolling. These ingots were then hot-rolled to 1/16" plate from which samples were cut with a metal band saw. The numbers below A-28 were made with commercial 2S aluminum, while those above were made from 99.9% aluminum.

The uranium was rolled from standard slugs using essentially the following procedure. Best results were obtained by giving the uranium about 20 to 40% reduction in some five passes between anneals. In order to keep the grain size small and to give a good surface, it was necessary to anneal the uranium in the alpha range. All the annealing was done under vacuum, while a silicone oil bath was used to keep the uranium at 300 C for rolling. The material works much better when kept as near to 300 C as possible since only a few degrees' drop in temperature makes the uranium much harder. The slug was kept round down to about 3/8", and then the round rod was put through square passes until it reached about 0.20". It was then passed through flat rolls and would spread to about 3/8" in being reduced to about 1/16" thick. Since it had to be reasonably straight, the uranium was held on edge across an anvil while hot and struck on the edge with a hammer. Persistent straightening resulted in good material. The lengths were then cut off with an abrasive cutoff wheel with a soluble oil and water coolant.

Cleaning proved to be one of the hardest problems connected with this study. It is observed that uranium will form an oxide coating at room tempera-

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ture requiring only a day to yield a dark blue coat. Aluminum also oxidizes at room conditions; but, since its oxide is clear or white, the appearance of the surface is not changed. Chemicals used for cleaning would not be completely removed from the surface by simply drying as is amply demonstrated by vacuum work. Such things as touching the samples with the bare fingers and cleaning a day or more prior to assembling was obviously never considered good technique, but in the start of the work it was not realized how much effort would be required to give satisfactory results. To begin with, the uranium was cleaned in nitric acid, washed in distilled water, and then dried with absolute ethyanol immediately before assembling, while the aluminum samples received similar treatment except that sodium hydroxide and/or phosphoric acid were substituted for the nitric. This did not work too well, presumably because some of the chemicals were adsorbed on the surface and reacted on heating without an opportunity to escape. This gave junctions which in many cases did not diffuse at all; and, when they did, only local areas diffused resulting in peaks of compound.

Next it was decided to remove the surface containing adsorbed materials by the use of abrasive papers. This was tried on several samples, but still the results were not so good as desired. Chemical cleaning was then retried, but it was followed by a vacuum degassing operation so that as much of the material would be removed as possible before reacting with the surface.

The most refined technique used consisted of cleaning the aluminum in 20% NaOH solution at 40 C for 3 minutes followed by a 5-minute etch in 20%  $H_3PO_4$  at 35 C and then a distilled-water wash. The uranium was cleaned with 35%  $HNO_3$  at 40 C for 15 minutes and then a 1%  $HNO_3$  wash for 30 minutes followed by distilled water. The materials were dried by a light, blotting action and

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then placed immediately in a vacuum furnace. After being pumped down, the furnace was turned on and the temperature advanced to 320 C in 70 minutes with the pressure never exceeding 0.01 micron. After cooling back to room temperature, the furnace was opened; and the aluminum alloys and the uranium were assembled in alternate layers by using rubber gloves. The picture in Figure 21 illustrates the various stages. In less than one hour the samples had been loaded in a tensile machine to 12,000 pounds with a deformation of about 0.1 inch per inch. Most of the specimens were then sealed in glass under vacuum while heating to 300 C for outgassing. They were then placed in a furnace for the required times. A few runs were made in a vacuum furnace.

After cooling, the specimens were removed and mounted in cold-setting plastic before cutting with an abrasive wheel. The samples were then polished before being examined and measured under the microscope. Figure 22 shows a representative layer from a run which gave good results.

It was very difficult to get reproducible results since the rates are so sensitive to preparation. This difficulty caused a wide spread of points as is shown graphically by Figures 23, 24, and 25. Here log D is plotted against the reciprocal of absolute temperature. The thicknesses used were measured by means of a microscope and represent the maximum values for the layer, and the D's were calculated by the use of equation 1. The higher values are from later runs where the techniques were better.

#### RESULTS OF DIFFUSION STUDIES

It will be noticed that D at 550 C varies by a factor of 100 for 2S aluminum. This means that in one instance it was possible to get the compound layer 100 times as thick as another at the same time. This is a factor

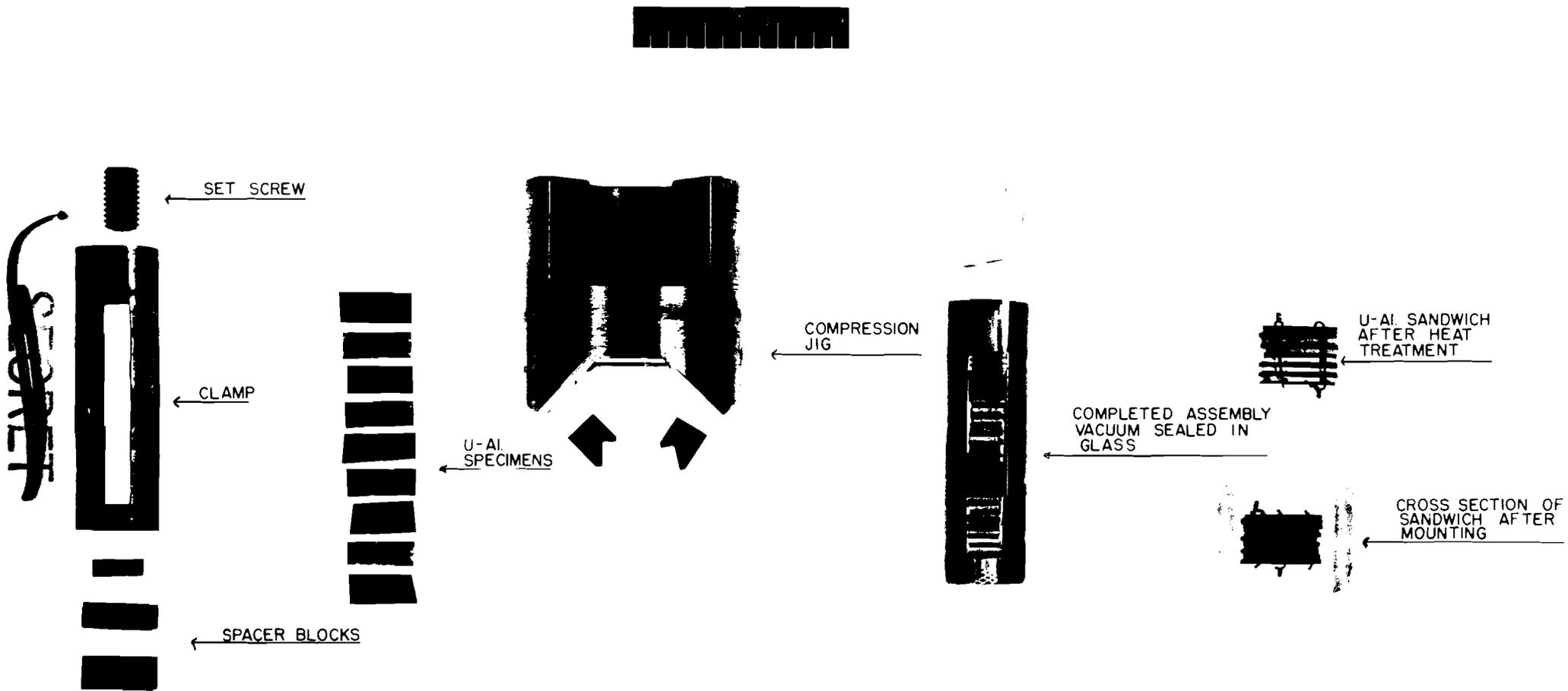


Figure 21

ILLUSTRATION OF MECHANICAL DETAILS USED IN THE DIFFUSION STUDIES

Picture No. Y-1807

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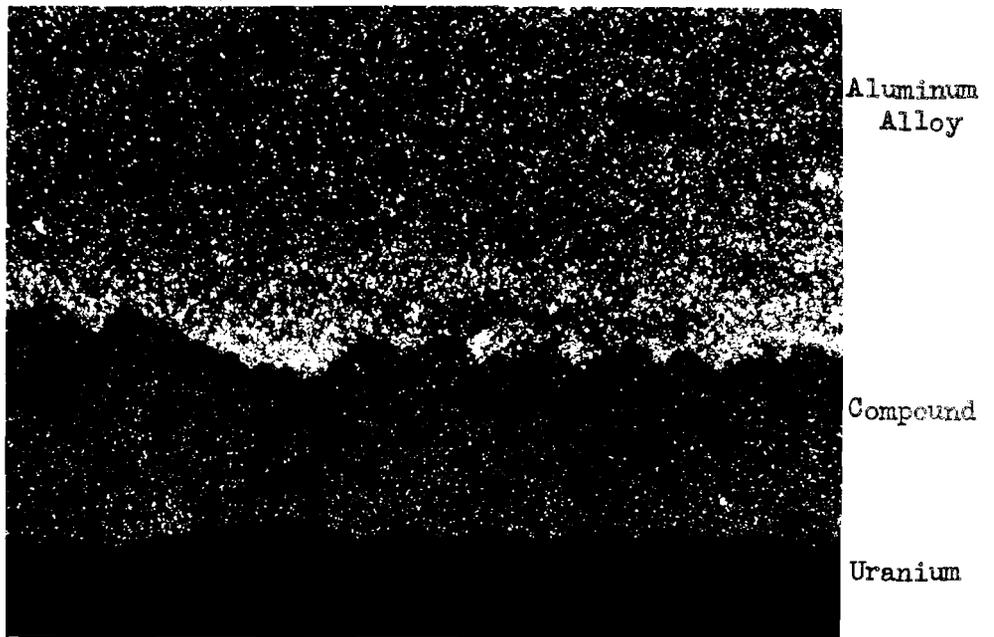


Figure 22

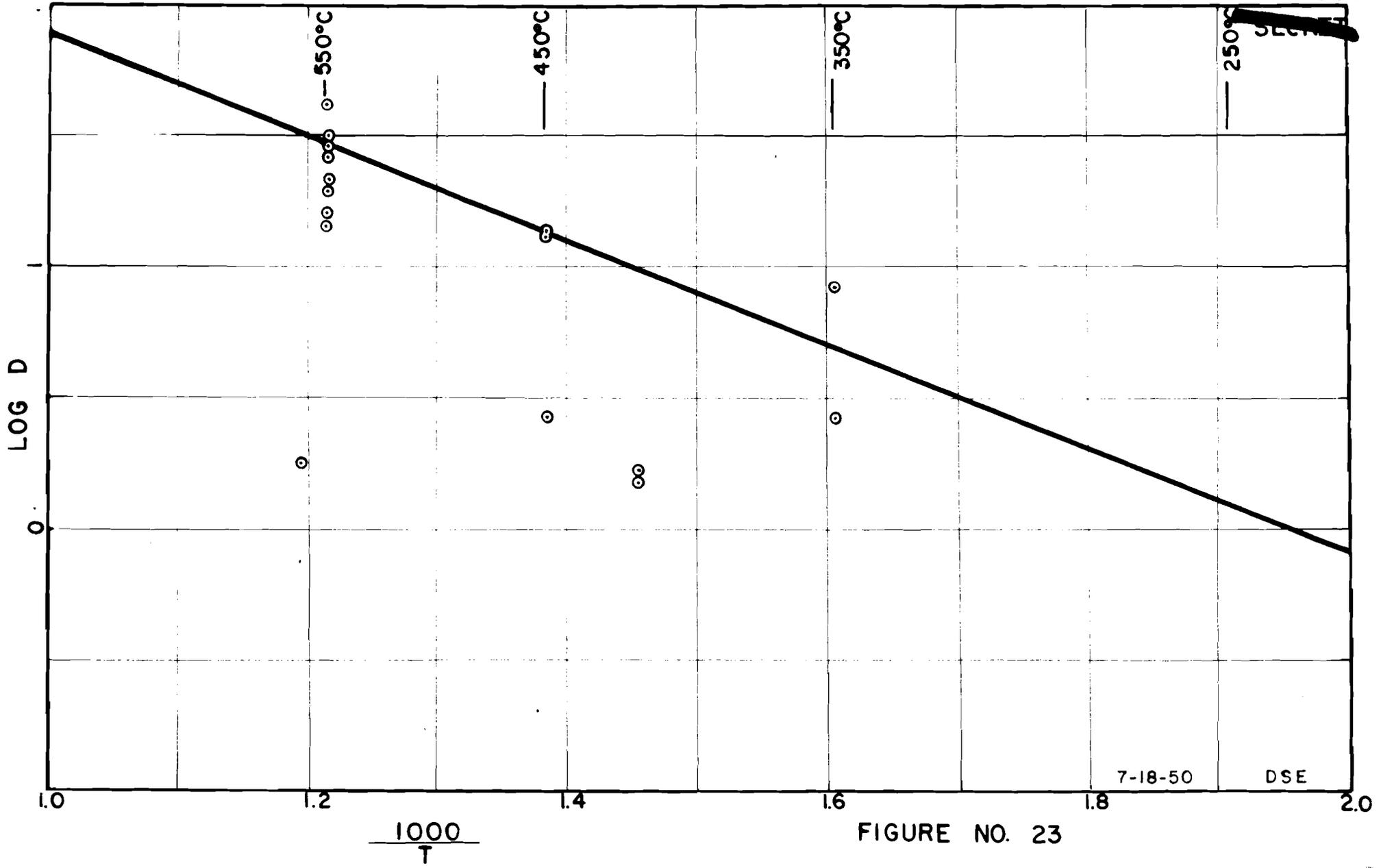
PICTURE OF DIFFUSION ZONE FORMED AT 350 C IN 52.5 HOURS

Magnification 100X Etch none Alloy A-7 Run D-35 14.7% Zn  
Specimen No. 1151 Picture No. Y-1952

Polarized light

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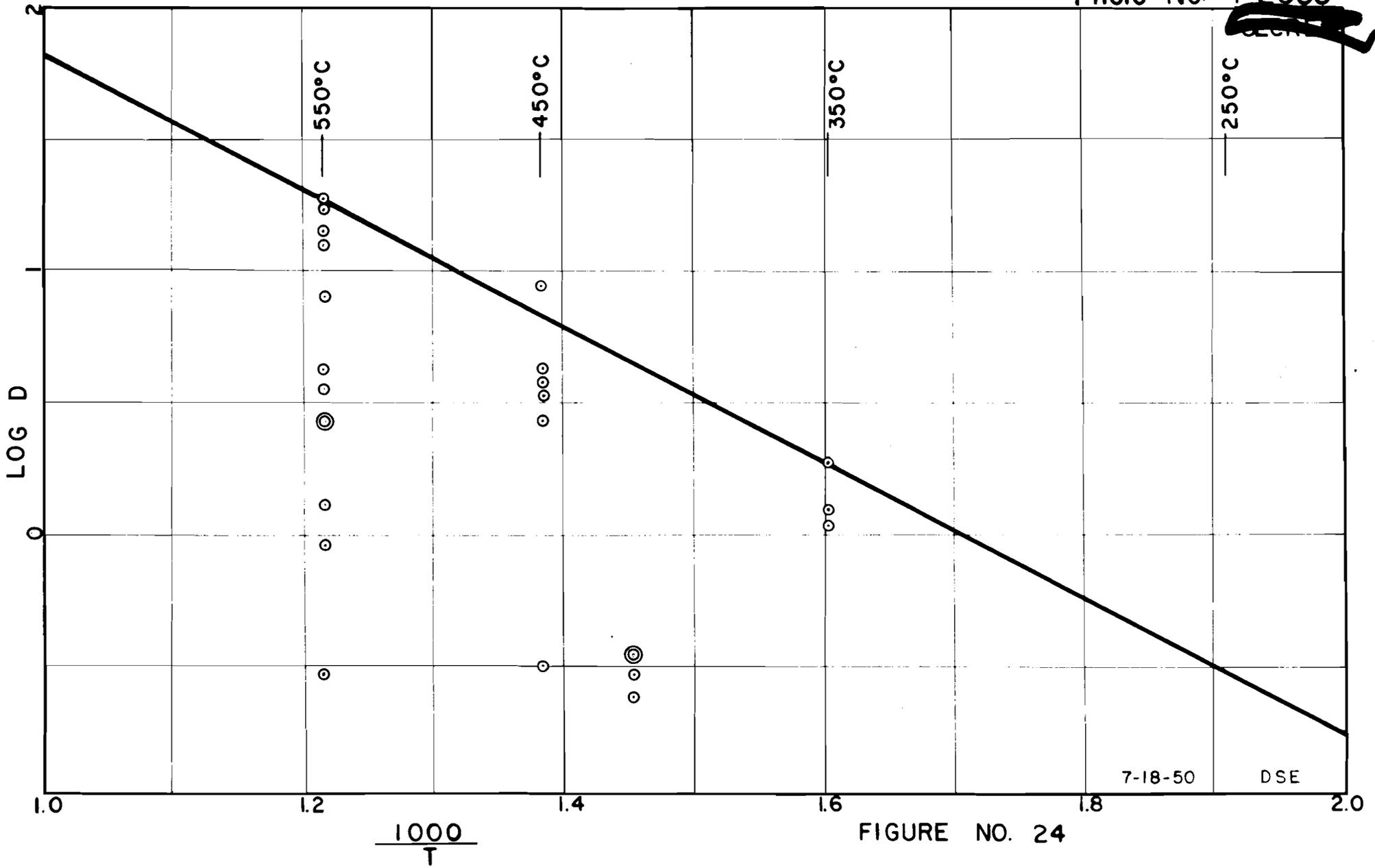
DIFFUSION OF 99.9% ALUMINUM & URANIUM

FIGURE NO. 23

7-18-50

DSE

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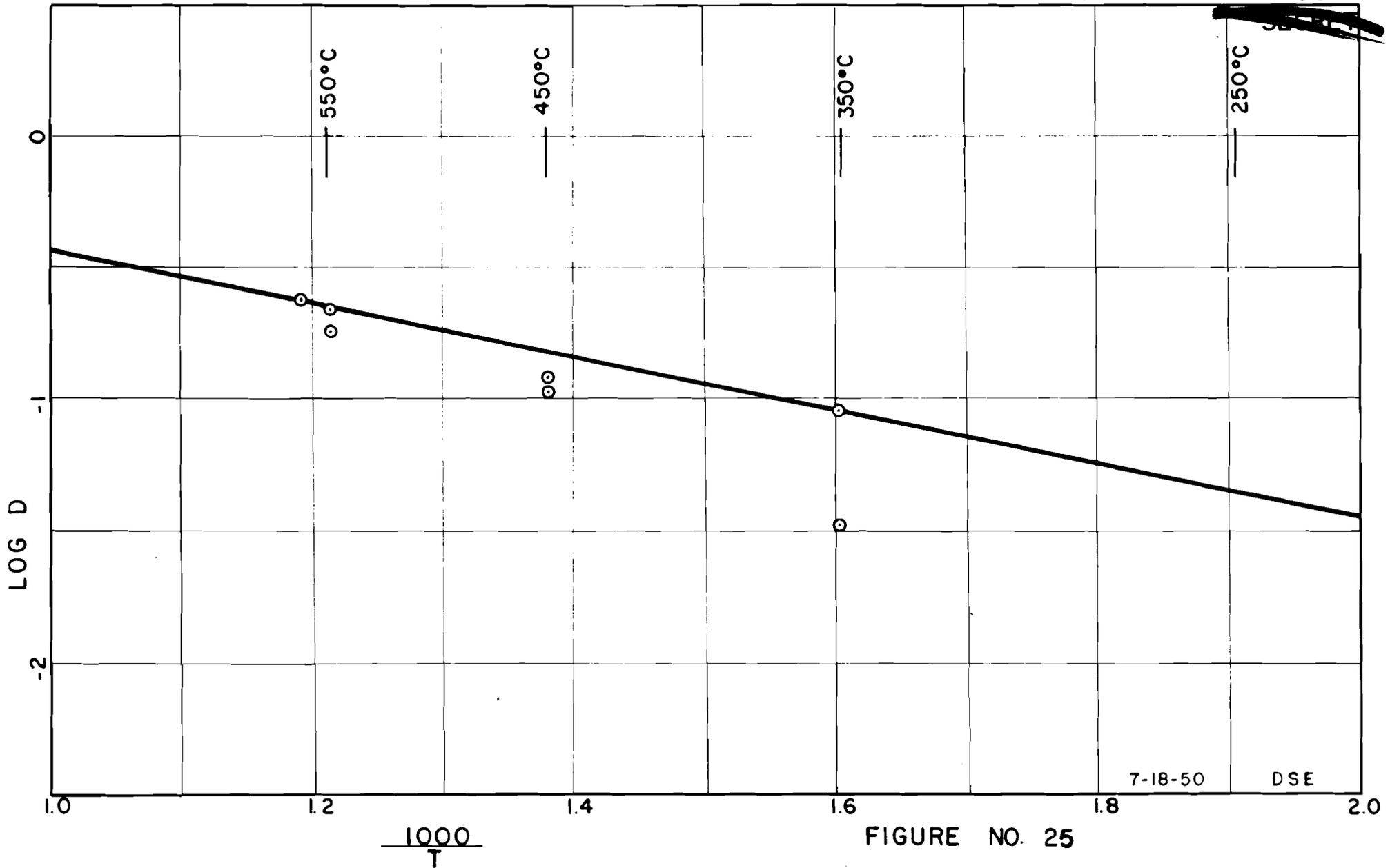


DIFFUSION OF 25 ALUMINUM & URANIUM

FIGURE NO. 24

7-18-50

DSE



DIFFUSION OF 4.88% BI-ALUMINUM ALLOY & URANIUM

of 10,000 for the time to penetrate a given thickness. Since it is known that poor preparation reduces diffusion rates, it was generally assumed that the highest points which were obtained would be most nearly correct. There would, however, be scattering about the correct values because of composition variations. The magnesium distribution in the uranium is not known; and the peaks were measured for determination of the maximum rates; so it is very difficult to evaluate the scattered points. With the early procedure it was easier to get more reproducible results at higher temperatures; however, with the more refined procedures the lower temperatures were feasible except that they required longer times. Original plans called for extrapolating the data from the higher temperatures to 250 C for the determination of diffusion rates under pile conditions. By the examination of the graphs, however, it is seen that the inaccuracies at the higher temperatures are greatly increased by extrapolation to a lower temperature. So, the D for 2S aluminum at 250 C is almost certainly not known by better than a factor of two. This represents a factor of four in time to failure for a slug.

The two other graphs show results from high-purity aluminum and a 4.88% bismuth-aluminum alloy. A tabulation of the data is contained in Appendix II. Since the results on the bismuth alloy fall so far below the results for 2S and high-purity aluminum, there can be no question that the diffusion rates are greatly reduced.

The data on the binary aluminum alloys are contained in Table VI, while those on the commercial alloys are in Table VII. When incomplete results are listed under four temperatures, this is an indication that the data were insufficiently accurate to permit  $\log B^{\frac{1}{2}}$  and Q values. When  $\log B^{\frac{1}{2}}$  and Q values are given, the D values are selected to fit equation 3 and are not

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TABLE VI

RESULTS OF DIFFUSION STUDIES OF BINARY ALUMINUM ALLOYS AND URANIUM

<u>Atomic Number</u>	<u>Element</u>	<u>Alloy Number</u>	<u>Concen- tration, %</u>	<u>Cross Section, Barns</u>	<u>Log B<sup>1/2</sup></u>	<u>Q</u>	<u>D, 0.001" x (Hours)<sup>-1/2</sup></u>			
							<u>250</u>	<u>350</u>	<u>450</u>	<u>550</u>
		A1	99.9	0.24	3.88	18,200	1.25	5	14	30
		2S	99.0		4.43	24,000	.30	1.7	6.8	19
4	Be	A-43	1.7	0.01				0.12	0.48	.36
12	Mg	A-23	1.23	0.35	3.64	16,700	1.5	5.6	14	28
		A-24	2.10		3.99	16,700	2.7	10	25	52
14	Si	A-9	1.02	0.22	2.37	14,600	0.22	0.68	1.5	2.8
		A-8	2.35		2.53	15,900	.17	.56	1.35	2.54
		A-7	7.62						1.3	1.6
		11.5 Si	11.84					.68	2.2	
20	Ca	A-19	1.59	0.45					2.4	10
		A-20	4.42					.80	6.7	10

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TABLE VI (cont'd.)

<u>Atomic Number</u>	<u>Element</u>	<u>Alloy Number</u>	<u>Concen- tration, %</u>	<u>Cross Section, Barns</u>	<u>Log B<sup>1/2</sup></u>	<u>Q</u>	<u>D, 0.001" x (Hours)<sup>-1/2</sup></u>			
							<u>250</u>	<u>350</u>	<u>450</u>	<u>550</u>
22	Ti	A-41	2.46	5.5				.07	.13	1.8
23	V	A-40	0.79	6	4.14	21,000	0.6	3.0	10	24.0
27	Co	A-21	0.42	30						1.8
		A-31	1.35							
28	Ni	A-30	4.53	5				0.19	0.26	0.35
29	Cu	A-1	1.1	3.5	4.57	25,700	.166	1.26	5.2	15
		A-2	3.3		4.43	25,100	0.165	1.12	4.5	13
30	Zn	A-4	1.88	1.2	4.83	27,000	0.15	1.2	5	21
		A-5	5.19		4.41	25,000	0.15	1	4.2	12
		A-11	6.66		4.87	28,000	0.14	1.0	5	16.5
		A-3	14.72		5.37	29,000	0.17	1.6	8.5	30
38	Sr	A-37	9.10	1.5				0.032		.59
40	Zr	A-35	1.11	3.5	3.52	18,400	0.5	2.0	5.0	12

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TABLE VI (cont'd.)

<u>Atomic Number</u>	<u>Element</u>	<u>Alloy Number</u>	<u>Concen- tration, %</u>	<u>Cross Section, Barns</u>	<u>Log B<sup>1/2</sup></u>	<u>Q</u>	<u>D, 0.001" x (Hours)<sup>-1/2</sup></u>			
							<u>250</u>	<u>350</u>	<u>450</u>	<u>550</u>
41	Cb	A-38	1.14					1.0		
42	Mo	A-36	1.51	3.0	2.36	14,000	0.3	0.85	1.86	3.3
51	Sb	A-16	1.66	6.0				.26		1.4
		A-28	4.62		5.23	34,000	.019	.23	1.35	5.9
52	Te	A-17	0.81	4	2.59	16,800	.13	.48	1.2	2.4
74	W	A-42	1.95	15	2.32	15,600	.11	.38	0.9	1.8
82	Pb	A-6	1.06	0.18	3.54	20,800	.16	.76	2.0	5.9
		A-32	1.22		3.46	18,400	0.38	1.6	4.5	10
83	Bi	A-18	1.82	0.016						1.0
		A-29	4.88		.57	9,200	.043	0.09	.15	.21
90	Th	A-44	20	8				0.6	2.1	2.1

TABLE VII

RESULTS OF DIFFUSION STUDIES OF COMMERCIAL ALUMINUM ALLOYS AND URANIUM

Alloy Number	Composition						Log $B^{\frac{1}{2}}$	Q	D, 0.001" x (Hours) $^{-\frac{1}{2}}$			
	Cu	Si	Mn	Mg	Zn	Cr			250	350	450	550
2S							4.43	24,000	.30	1.7	6.8	19
3S			1.2				3.84	21,500	0.24	1.2	4.0	10
4S			1.2	1.0			4.87	28,000	0.85	3.7	10.6	23.5
14S	4.4	0.8	0.8	0.4			4.26	23,200	.27	1.6	5.9	16
52S				2.5		0.25	3.42	15,300	3.3	7.2	15	27
61S	0.25	0.6		1.0		0.25	3.03	12,600		6.6		22.4
75S	1.6			2.5	5.6	0.3	5.11	27,500	0.25	2.0	9.3	30
Mg							6.12	35,500	0.052	.79	5.8	26

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necessarily experimentally determined. No values of D below 350 C were experimentally determined.

In calculating the times for failure from the D values given, the thicknesses used should be 1.55 times that of the aluminum since the uranium contributes to the thickness. Using a can thickness of 0.030" and the D values listed in the tables, the time for can penetration at 250 C for 99.9% aluminum, 2S and 4.88% bismuth-aluminum alloy are, respectively, 57, 1000, and 49,000 days while at 550 C the times are 0.1, 0.25, and 2000 days. It is believed that the true difference between the 2S and 99.9% aluminum at 250 C is considerably less than shown, the discrepancy resulting from inaccurate data. The rates for aluminum are rather high in contrast to the low rates for the bismuth alloy. Based on these results, the relative effect of the bismuth improves with increased temperatures.

No conclusions can be reached as to how the values of D are affected by the concentration of the element added. It is believed that the presence of relatively small amounts of magnesium increase the diffusion rate of 2S as shown by the results on magnesium-bearing alloys, both binary and commercial. The data for high-purity aluminum fall too close to that of magnesium-bearing alloys to allow any conclusion. For silicon-bearing alloys the results have been too erratic to allow comparison over a range of temperatures; however, at elevated temperatures a decided effect can be seen. If similar Q values are assumed, this advantage would be maintained at lower temperatures. Most of the results on the binary alloys suggest slight improvement in resistance to diffusion; however, the most promising alloy additions would seem to be beryllium, antimony, and bismuth. Bismuth would seem to be especially recommended because of its low cross section and low solubility in aluminum.

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Also, its high density would mean that appreciable amounts of this second phase would not drastically alter the properties of the aluminum. Beryllium and antimony would be similarly recommended except that beryllium has a low density, and antimony forms a compound with resulting loss in density and amount of free aluminum. There were no experimental results, however, to support these conclusions relative to the change of physical properties of the aluminum.

The approximate composition of the diffusion layers as determined by X-ray diffraction work is given in Table VIII. The fraction of compound was determined as previously described earlier in the report. The only sample in which the compound  $UAl_4$  could be definitely identified was a 2% magnesium-aluminum alloy which gave a maximum diffusion rate. Even then, the amount was very small, estimated to be less than 1%. The second run, XR-2, had identical treatment but failed to diffuse in so great amounts. This was assumed a result of an interference layer initially between the aluminum and uranium. If it is assumed that this resistance layer always remained next to the aluminum and the aluminum atoms pass through, then it is clear that no  $UAl_4$  should be found, but that approximately the same total amount of  $UAl_2$  would be found provided some  $UAl_3$  was present. From the thicknesses obtained, this is seen to be approximately the case. In the next sample, XR-4, the diffusion rate again was low; and  $UAl_4$  would not be expected. In the last two runs there was more than enough silicon present so that the formation of  $UAl_4$  would be completely suppressed, and only  $UAl_3$  and  $UAl_2$  should be found. It would seem that the higher concentration of silicon increased the ratio of  $UAl_2$  to  $UAl_3$ .

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TABLE VIII

COMPOSITION OF DIFFUSION LAYERS BETWEEN  
URANIUM AND ALUMINUM OR ALUMINUM ALLOYS FORMED AT 450 C

<u>Run</u>	<u>Alloy No.</u>	<u>Comp.</u>	<u>Time Hrs.</u>	<u>Thickness</u>		<u>D 0.001<sup>m</sup> T<sup>-1/2</sup></u>	<u>Fraction of Compound</u>		
				<u>Ave.</u>	<u>0.001<sup>m</sup> Max.</u>		<u>UAl<sub>4</sub></u>	<u>UAl<sub>3</sub></u>	<u>UAl<sub>2</sub></u>
XR-1	A-24	2.1 Mg	22	110	118	25.1	0.81	97.8	0.8
XR-2	A-24	2.1 Mg	22	8	12	2.56		78.0	22.0
XR-4	A-1	99.9 Al	97	9.5	12	1.22		89.7	10.3
XR-5	A-7	7.62 Si	97	10.5	13	1.32		87.2	12.8
XR-6	Al-Si	11.85 Si	97	22	27	2.74		80.3	19.7

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### CONCLUSIONS

This investigation has not made it possible to distinguish clearly between slug failures by diffusion and those connected with the welds. Very little is known about the length of time which a faulty slug can stay intact in the pile or the exact nature of the failure. Also, no really reliable data are available on the minimum times for failure by diffusion at 250 C and lower and the frequency of expected failures after this time.

As proposed previously, the best solution would seem to be the use of slugs which are bonded by the Hanford method.<sup>4</sup> This conclusion is based upon the fact that the diffusion rates are reduced and that weld failures are not expected. No exact prediction can be given as to the expected increase in life of a slug. Since plans call for operating the pile at 350 C, once bonded slugs are placed in use, the problem of life at this temperature could be important. There is insufficient evidence to predict beforehand the expected life at this temperature. It is thought that bonded slugs will require at least as much time to fail by diffusion at 350 C as do regular slugs at 250 C. The short-time failures resulting from holes in the welds are not expected.

There are indications that the presence of magnesium will increase the rate of diffusion. This may be the result from the formation of  $Mg_2Si$ . Then, too, it was found that good preparation was not so necessary for the diffusion of magnesium-bearing alloys. It has been shown that the magnesium content of uranium will vary and reach 0.2% at points.<sup>9</sup> It is assumed without definite experimental basis that the effect of magnesium in the uranium would be about the same as if it were in the aluminum.

As far as the effectiveness of the reduction of diffusion rates is concerned, there are several other elements which appear to be considerably more

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effective than silicon. The most effective one seems to be bismuth which has good nuclear properties and would seem to alloy well with aluminum in small concentrations which would be effective.

Very little is known about the mechanism by which the alloying additions reduce the diffusion rate. In the case of silicon it is known that silicon has a tendency to replace aluminum in  $UAl_3$  out of proportion to its concentration and completely prevents the formation of  $UAl_4$  when in relatively small concentrations.

On the basis of what is now known, the use of bonded slugs is the best solution to the problem and is a step which certainly seems warranted. There are facilities existing with trained personnel now which could, with possible additions, perform the job. All results obtained to this time indicate that the change would improve the operation of the pile. There is no apparent objection to the step except the slightly increased costs of manufacture. On the basis of present knowledge, it is believed that the use of bonded slugs in the pile at 350 C will result in not more than 50% of the present rate of failure. The use of unbonded slugs at 350 C could possibly increase the rate by about 20 times.

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REFERENCES

1. C. D. Cagle, L. B. Emlet: "Slug Ruptures in the Oak Ridge National Laboratory Pile". ORNL 170
2. H. S. Arms, P. Fortescue: "Consumption of Air by Uranium". AERE E/R 279
3. M. E. Ramsey, E. J. Witkowski, A. F. Rupp, J. A. Cox, L. B. Emlet: "Monthly Report for Month Ending December 31, 1949 - Operations Division". ORNL 584
4. R. O. Williams: "Interim Report on Clinton Slug Ruptures - Causes and Preventions". ORNL 269
5. W. S. Pellini: "Resume of Clinton Slug Cycling Experiments - ORNL". 48-10-148
6. E. J. Field, Jr.: "Progress Report of Brookhaven Work Being Carried Out at M.I.T.". BNL-Log No. C-2330
7. A. H. Snell: "Quarterly Progress Report for Period Ending March 15, 1950 - Physics Division". ORNL 693
8. Frederick N. Rhines: "Diffusion Coatings on Metals". Surface Treatments of Metals - ASM
9. W. T. Kattner: "Investigation of Low Canned Slug Reactivity in Test Pile". HW-11061

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BIBLIOGRAPHY

Report from Cooperating Laboratories for Month Ending July 1, 1944 C. M. Cooper, J. Chipman, A. B. Greninger	CT-1938
Studies of the Aluminum-Uranium Alloying Reaction D. W. Bareis	BNL-Log No. R-8210
Diffusion in Solid Metals R. F. Mehl	Trans. v. 122, AIME 1936
File Characteristics and Design (Project Handbook, Chapter VIII) M. C. Leverett	CL-697
Metallurgy (Project Handbook, Chapter IX) J. C. Warner	CL-697
Progress Report of Brookhaven Work Being Carried Out at M.I.T. E. J. Field, Jr.	BNL-Log No. C-2330
Information Which Has Been Developed for Us at M.I.T. D. H. Gurinsky	BNL-Log No. C-2489
Progress Report of Brookhaven Work Being Carried Out at M.I.T. E. J. Field, Jr., G. Snyder	BNL-Log No. C-1729
Preliminary Report on Experiment Uranium Cartridges for Graphite Piles - Dependence of Slug Temperature upon Pressure of Gas in Slug-Can Gap G. W. K. Ford, D. W. J. Loveday	AERE E/R 280
Consumption of Air by Uranium H. S. Arms, P. Fortescue	AERE E/R 279
Resume of Clinton Slug Cycling Experiments - ORNL W. S. Pellini	48-10-148
Technical Cooperation Program Report of Visit of Drs. Finniston and Bauer to Brookhaven National Laboratory on December 20 - 21, 1948 Lyle B. Borst	TID-210
Journal of Metallurgy and Ceramics, Issue No. 1 U.S.A.E.C.	TID 65
Quarterly Progress Report for Period Ending March 15, 1950 - Physics Division A. H. Snell	ORNL 693

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Monthly Report for Month Ending December 31, 1949 - ORNL 584  
Operations Division  
M. E. Ramsey, E. J. Witkowski, A. F. Rupp,  
J. A. Cox, L. B. Emlet

Monthly Report for Month Ending February 28, 1949 - ORNL 320  
Operations Division  
M. E. Ramsey, E. J. Witkowski, A. F. Rupp,  
J. A. Cox, L. B. Emlet

Interim Report on Clinton Slug Ruptures - Causes and ORNL 269  
Preventions  
R. O. Williams

Investigation of Low Canned Slug Reactivity in Test HW-11061  
File  
W. T. Kattner

Slug Ruptures in the Oak Ridge National Laboratory File ORNL 170  
C. D. Cagle, L. B. Emlet

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APPENDIX I

RESULTS OF TESTING OF CLINTON SLUGS AT 250 C

<u>Number</u>	<u>Slug No.</u>	<u>Type of Slug</u>	<u>Time, Hours</u>	<u>Results</u>
1	CBS-1	Bonded	876	Furnace overheated; hence, the failure is meaningless.
2	CBS-2	Bonded	876	Furnace overheated; hence, the failure is meaningless.
3	CS-67	Unknown	5,780	Impossible to tell why slug failed.
4	CS-157	Leaky	8,040	This slug was rejected from leak test, but it is believed that it was sound with possibly a lid slightly bulged; however, this was not due to oxide as was shown by radiographs. Slug failed when the furnace overheated.
5	CS-51	Class 1	9,024	Furnace overheated to cause failure.

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RESULTS OF TESTING CLINTON SLUGS AT 350 C

<u>Number</u>	<u>Slug No.</u>	<u>Type of Slug</u>	<u>Time, Hours</u>	<u>Results</u>
1	CBS-3	Bonded	6,360	No external change
2	CBS-4	Bonded	6,360	No external change
3	CS-18	Class 1	14,560	No external change. Limited diffusion and slug bright.
4	CS-20	Class 1	14,560	No external change, but one of few points of diffusion was about 95% through.
5	CS-21	Class 1	14,560	Several points of diffusion but not over 0.015" thick. Slug bright.
6	CS-54	Class 1	14,560	Limited diffusion with a small blister on bottom of slug. Blister reported in 10 months.

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RESULTS OF TESTING OF CLINTON SLUGS AT 550 C

<u>Number</u>	<u>Slug No.</u>	<u>Type of Slug</u>	<u>Time, Hours</u>	<u>Results</u>
1	CS-246	Slightly oxidized	21	Ruptured at weld probably from bad weld.
2	CS-245	Slightly oxidized	45	Ruptured near weld and presumably from leak in it.
3	CS-271	Class 1, flux coated	48	Ruptured at weld but had been dropped.
4	CS-266	Class 1	96	Had just failed at a blister. Only a small amount of diffusion and blistering. Blisters in 2 days.
5	CS-267	Class 1	96	Several small blisters. Blisters in 2 days.
6	CS-268	Class 1	96	Had just failed at a blister. No other diffusion.
7	CS-269	Class 1, flux coated	96	About 10% diffusion mostly resulting in blisters covering only 1 ridge.
8	CS-270	Class 1, flux coated	96	Slug bright with diffusion on top of ridges. Blisters in area where dropped.
9	CS-220	Brookhaven	117	Can had bulged but did not fail.
10	CBS-14	Bonded	120	Furnace overheated, and slug showed incipient fusion where it failed.
11	CBS-16	Bonded	120	Same as CBS-14.
12	CS-272	Class 1	192	Slug bright but only very limited area of diffusion not higher than 0.008".
13	CS-265	Class 1	596	No change.
14	CS-264	Class 1	648	No change.

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TESTING AT 550 C (cont'd.)

<u>Number</u>	<u>Slug No.</u>	<u>Type of Slug</u>	<u>Time, Hours</u>	<u>Results</u>
15	CBS-11	Bonded	1,102	Furnace overheated to cause failure.
16	CBS-15	Bonded	1,272	No external change.
17	CS-248	Slightly oxidized	1,296	No external change.
18	CS-249	Al-Si coated	1,320	No external change.
19	CS-250	Al-Si coated	1,320	No external change.
20	CBS-10	Bonded	1,824	No external change. Used for metallographic studies.
21	CBS-13	Bonded	1,848	The furnace overheated and caused the can to fail. The coating was partly protecting.
22	CBS-12	Bonded	3,960	This slug apparently had failed at 550 C but had been overheated on 2 previous occasions.

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RESULTS OF TESTING OF CLINTON SLUGS AT 450 C

<u>Number</u>	<u>Slug No.</u>	<u>Type of Slug</u>	<u>Time, Hours</u>	<u>Results</u>
1	CS-276	Class 1	24	This slug was used to sample the gas in a slug before diffusion. Examination revealed no diffusion and dark slug.
2	CS-275	Class 1	96	Rupture started at a point of diffusion where there appeared to have a blister. Blisters reported in 2 days.
3	CS-280	Class 1	120	About 5% area diffused and resulted mostly in blisters. About 50% penetration.
4	CS-282	Class 1	144	This slug had some 10 blisters and saved for any future gas analysis. Blisters in 3 days.
5	CS-273	Class 1	162	It appeared that the rupture started at a blister.
6	CS-274	Class 1	162	Rather limited diffusion with two blisters.
7	CS-279	Class 1	264	Had about 10 to 20 blisters and was used for gas analysis. Blisters reported in 7 days.
8	CS-283	Class 1	336	Slug blistered extensively, and the can was stripped with NaOH for a picture.
9	CS-277	Class 1	360	Slug was fairly bright with a few points of diffusion. Two small blisters.
10	CS-278	Class 1	360	Very limited diffusion with only about 0.015" penetration. Slug has blue oxide coating.
11	CS-281	Class 1	480	Had about 10 blisters appearing first in 3 days. Slug saved for gas analysis.
12	CS-262	Class 1	648	Slug ruptured and was completely lost to oxide. It appeared that diffusion had occurred to cause the failure.

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TESTING AT 450 C (cont'd.)

<u>Number</u>	<u>Slug No.</u>	<u>Type of Slug</u>	<u>Time, Hours</u>	<u>Results</u>
13	CS-263	Class 1	648	Only a few small blisters were found on the surface.
14	CS-247	Slightly oxidized	792	No change as observed from the outside.
15	CS-251	Coated Al-Si	792	No change.
16	CBS-5	Bonded	4,752	Furnace overheated and caused the slug to fail.
17	CBS-6	Bonded	4,752	Furnace overheated and caused the slug to fail.
18	CBS-7	Bonded	4,752	Furnace overheated and caused the slug to fail.

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APPENDIX II-a

DIFFUSION DATA FOR 2S ALUMINUM WITH URANIUM

<u>Temp.</u> <u>C</u>	<u>Time</u> <u>Hrs.</u>	<u>Thickness</u> <u>0.001"</u>	<u>D</u> <u>0.001" T<sup>-1/2</sup></u>	<u>Log D</u>	<u>Run</u>
550	144	15	1.25	0.0997	D-6
550	144	32	2.66	0.426	D-6
550	144	32	2.66	0.426	D-6
550	114	38	3.56	0.552	D-7
550	124.5	10	0.895	1.952	D-10
405	288	2.5	0.147	1.168	D-11
550	116	45	4.17	0.621	D-2
550	116	2	0.186	1.269	D-2
550	116	3	0.278	1.444	D-2
450	283	62	3.68	0.566	D-1
415	307	6	.342	1.534	D-12
415	307	6	.342	1.534	D-12
415	307	4	.228	1.358	D-12
415	307	6	.342	1.534	D-12
415	307	5	.285	1.454	D-12
450	67.5	2.5	.305	1.484	D-19
550	23.25	38	7.88	0.896	D-30
450	7.5	9	3.28	0.516	D-33
450	7.5	11	4.01	0.604	D-33
550	2.25	28	18.7	1.271	D-34
550	2.25	27	18.0	1.255	D-34
350	52.5	12	1.66	0.222	D-35
350	52.5	13	1.79	0.252	D-35
550	2.25	19	12.7	1.10	D-39
550	2.25	20	13.3	1.124	D-39
450	5	20	8.9	0.952	D-40
450	5	20	8.9	0.952	D-40
350	16	5	1.25	0.096	D-38
350	16	4.5	1.12	0.05	D-38

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APPENDIX II-b

DIFFUSION DATA FOR 99.9% ALUMINUM WITH URANIUM

<u>Temp.</u> C	<u>Time</u> Hrs.	<u>Thickness</u> 0.001"	<u>D</u> 0.001" T <sup>-1/2</sup>	<u>Log D</u>	<u>Run</u>
415	307	29	1.65	0.219	D-12
415	307	27	1.54	0.187	D-12
350	985	3	0.0955	2.982	D-15
565	72	1.5	1.765	0.247	D-13
550	.25	15	30.0	1.476	D-26
550	.25	15	30.0	1.476	D-26
550	.25	20	40.0	1.602	D-26
550	.25	23	46.0	1.662	D-26
550	1.25	33	29.5	1.470	D-24
550	1.25	30	27.8	1.428	D-24
550	1.25	32	28.6	1.456	D-24
550	1.25	39	26.0	1.414	D-24
550	5	32	14.3	1.155	D-27
550	5	32	14.3	1.155	D-27
550	5	34	15.2	1.182	D-27
550	5	34	15.2	1.182	D-27
550	46	50	7.4	0.868	D-29
550	46	30	4.43	0.646	D-29
550	46	50	7.4	0.868	D-29
550	46	45	6.65	0.822	D-29
550	169.3	34	2.69	0.43	D-28
550	408	9	0.445	1.648	D-25
550	408	7	0.346	1.539	D-25
550	408	30	1.48	0.172	D-25
550	408	30	1.48	0.172	D-25
450	97	22	2.23	0.348	D-
450	5	30	13.4	1.137	D-40
450	5	33	14.8	1.17	D-40
550	2.25	32	21.4	1.33	D-39
550	2.25	29	19.3	1.286	D-39
350	16	35	8.7	0.94	D-38
350	16	10	2.5	0.40	D-38

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## APPENDIX II-c

DIFFUSION DATA FOR 4.88% BISMUTH-ALUMINUM ALLOY WITH URANIUM

<u>Temp.</u> <u>C</u>	<u>Time</u> <u>Hrs.</u>	<u>Thickness</u> <u>0.001"</u>	<u>D</u> <u>0.001" T<sup>-1/2</sup></u>	<u>Log D</u>	<u>Run</u>
350	985	1	0.0319	2.504	D-15
565	72	2	0.236	1.372	D-13
450	67.5	1	0.122	1.086	D-19
550	69.5	1.5	0.180	1.256	D-22
350	480	2.0	0.0913	2.960	D-23
450	211	1.5	0.103	1.014	D-14
550	24	1	0.204	1.309	D-37
450	97.5	1	0.101	1.005	D-36
450	97.5	1	0.101	1.005	D-36