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APPLICATION OF ALPHA CANNING TO PREPARATION OF SLUGS FOR ORNL X-10 GRAPHITE PILE

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APPLICATION OF ALPHA CANNING TO PREPARATION OF SLUGS FOR ORNL X-10 GRAPHITE PILE

E. J. Boyle

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ABSTRACT

Production of aluminum-silicon bonded slugs by the triple-dip process was started. The bonded slugs will replace the unbonded slugs now used in the ORNL graphite-moderated pile. Approximately 20% of the bonded slugs showed diffusion blistering during heat treatment at 400°C, and it was found that localized concentrations of residual tin were associated with the diffusion blisters. In order to avoid the tin bath of the triple-dip process, the alpha-canning technique was adopted.

Difficulties associated with non-wetting of slugs in the alpha-canning process were solved by the use of an aluminum brazing-flux cover on the duplex bath. It was found that a continuous layer of the diffusion-barrier phase, $U(Al,Si)_3$, on the surface of alpha-canned slugs was necessary to avoid diffusion blistering during heat treatment at 400°C. This layer is continuous only when complete wetting of the slug by molten aluminum-silicon alloy is obtained.

A total of approximately 12,000 alpha-canned slugs have been tested by heat treatment of seven days at 400°C with no evidence of diffusion blistering. This compares with a blistering frequency of approximately 20% for triple-dip canned slugs.

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APPLICATION OF ALPHA CANNING TO PREPARATION OF SLUGS FOR ORNL X-10 GRAPHITE PILE

E. J. Boyle

INTRODUCTION

About 100 ruptures of the aluminum-canned, unbonded fuel slugs have occurred since the start of the Oak Ridge National Laboratory air-cooled graphite-moderated pile. These ruptures are a direct result of air gaining access to the uranium slug through a break in the aluminum can. The reactor operates with a maximum slug-surface temperature of 250°C, and therefore the oxidation of the uranium core proceeds at a rapid rate and results in swelling and tearing of the aluminum can. In several ruptures, the swelling resulted in blockage of the slug channels, which caused overheating of the remainder of the slugs in that channel and failure of the entire line of slugs.

In a previous report[(1)] data on the causes and solution of the slug rupture problem were presented. This work has shown that the major cause of slug failure was faulty welds at the end-cap closure. A secondary, but equally important, cause of failure was the penetration of the aluminum can by interdiffusion of uranium and aluminum. The recommended solution to this problem was the use of aluminum-silicon bonded slugs, for the following reasons:

1. The welding closure is structurally sounder, since there is a double protection against air leakage into the uranium core by virtue of the fact that there is an aluminum-silicon layer present between the core and the inert gas, arc-weld bead on the end cap.

2. The uranium-rich compound layer formed on the surface of the uranium core when in contact with molten aluminum-silicon acts as an effective diffusion barrier between the core and the aluminum can.

CONCLUSIONS

On the basis of the experimental work carried out in connection with this problem, the following conclusions appear to be justified:

1. The compound layer, $U(Al, Si)_3$, formed on the surface of uranium when in contact with molten aluminum-silicon, is an effective diffusion barrier between uranium and aluminum-silicon or aluminum at 400°C.

2. Slugs canned by the standard triple-dip process, as used at Hanford and duplicated in the present work at Y-12, show a diffusion-blistering frequency of 15 to 20% when heated at 400°C. The diffusion blisters are invariably associated with localized concentrations of tin in the bonding layers. It is thought that localized tin concentrations prevent contact of molten aluminum-silicon with the uranium and result in discontinuities in the $U(Al, Si)_3$ diffusion barrier.

3. Gas blistering will occur in triple-dip, canned slugs heated to 400°C when the aluminum-silicon layer contains dissolved hydrogen. This defect may be avoided by careful attention to preventing moisture from entering the aluminum-silicon baths and by "aging" of the bath for 24 hr prior to the start of canning.

4. The use of a flux on the surface of the duplex bath in the alpha-canning process ensures complete wetting of the uranium surface by molten aluminum-silicon. This complete wetting is very important in ensuring that the

(1) R. O. Williams, *Interim Report on Clinton Slug Ruptures – Causes and Prevention*, ORNL-269, July 14, 1949.

$U(Al,Si)_3$ diffusion-barrier layer is continuous over the entire slug surface.

5. There have been no definite cases of diffusion blistering during heating at 400°C of slugs canned by the alpha-canning method with a flux on the duplex bath. All blisters and ruptures examined to date appear to be associated with leaks in the weld closures or porosity in the end caps.

EXPERIMENTAL PROCEDURE

Triple-Dip Canning.[2] In line with the recommendation presented, the decision was made to replace the slugs now in the pile with aluminum-silicon bonded, triple-dip slugs canned according to standard Hanford technique. All production was carried out in the Chemical Department at the Y-12 Plant.

The standard triple-dip canning procedure, as practiced at Hanford and used at Y-12 in the present work, consists of the following steps:

1. *Bronze Bath.* The machined and etched uranium slugs are immersed in a bronze bath for a period of 44 sec at a temperature of 725°C.

2. *Tin Bath.* Slugs from the bronze bath are quenched into molten tin at a temperature of 600°C and are held for a period of 40 seconds.

3. *Centrifuge.* From the tin bath the slugs are transferred directly to a centrifuge and spun at 650 rpm for a period of 6 seconds.

4. *Aluminum-Silicon Dip Bath.* After centrifuging, the slugs are immersed in an aluminum-silicon (11.2% silicon) bath at 600°C and are held for a period of 8 seconds.

5. *Aluminum-Silicon Canning Bath.* After the slugs have been wet with aluminum-silicon in the dip bath, they are transferred to the canning bath where they are inserted into a preheated aluminum can inside of a steel sleeve. Just prior to insertion, the aluminum can is filled with aluminum-silicon by lowering the mouth below the surface of the bath. The final operations are to insert a preheated aluminum cap, prewet with aluminum-silicon, into the end of the can and quench the entire assembly into water.

6. *Welding.* After cutting end caps to proper length, a weld is made at the end cap-can interface with inert-gas, shielded-arc welding.

Two of the standard Hanford inspection tests – i.e., visual inspection and autoclaving – were used. A third Hanford test, the frost test, was eliminated. Finally, a test consisting of holding the slugs for one week at 400°C was employed to determine whether diffusion between the uranium core and the aluminum can would occur.

Alpha Canning.[3] Because of difficulties (to be discussed later) associated with the triple-dip canning process, it was decided to use the alpha-canning process. This process, so named because all canning operations are carried out at temperatures below the alpha-beta transformation temperature in uranium, consists of the following steps:

1. *Beta Heat Treatment.* This step, considered a preliminary step prior to canning, is carried out by immersing slugs in a salt bath at 720 to 740°C for a period of 3 minutes. The salt used is Houghton's Liquid Heat No. 980. Slugs machined to size prior to the salt-bath treatment were used because they had already been machined for the triple-dip process. If the Y-12 Canning

(2) E. A. Smith, *Operating Process for Canning 4-in. Slugs*, HW-9401, April 15, 1948.

(3) E. A. Smith, *Development of Lead-Dip Canning Process – Interim Report on Production Test*, HW-8694, Jan. 29, 1948.

Group were starting anew, the salt-bath treatment would be carried out prior to machining because some pitting of the slugs occurs during the salt-bath treatment.

2. *Duplex Bath.* After chemical cleaning (50% nitric acid) following the salt-bath treatment, the slugs are immersed in a duplex bath consisting of a 10-in.-thick lead layer at the bottom and a 15-in.-thick aluminum-silicon layer at the top. A cover of Eutector 190 flux (manufactured by Eutectic Welding Company) is kept on top of the aluminum-silicon layer. The slugs are held for 35 sec in the lead layer at 600°C, and then raised into the aluminum-silicon layer and held for 5 sec at 600°C.

3. *Aluminum-Silicon Dip Bath.* Slugs are transferred from the duplex bath to the dip bath where they are held for 13 sec at 600°C.

4. *Aluminum-Silicon Canning Bath.* The time, temperature, and procedure here are exactly the same as for the triple-dip process.

5. *Welding.* The same procedure is followed as for triple-dip, canned slugs.

The same inspection techniques – i.e., visual, autoclave, and heat treatment for one week at 400°C – are used as for triple-dip, canned slugs.

An electrical resistance furnace with a graphite crucible for the salt bath and Ajax-Wyatt low-frequency, induction furnaces with rammed linings for the duplex bath, dip bath, and canning bath are used in the canning line.

RESULTS AND DISCUSSIONS

Triple-Dip Canning. The production of triple-dip, bonded slugs was begun in the Chemical Department at Y-12 in June 1951. Testing of the first 5886 slugs for one week at 400°C resulted in diffusion blistering of 18.6%. The external appearance of a typical blistered slug is shown in Fig. 1. The microstructure at the area of a diffusion blister is shown in Fig. 2.

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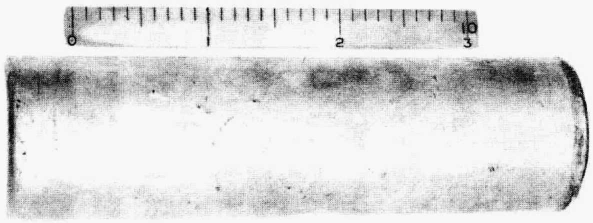

Fig. 1. Typical Diffusion Blisters on Triple-Dip Slug.

The structure at the can-slug interface in Fig. 2 shows that there is a layer of UAl_3 between the aluminum-silicon and uranium. It will be noted that there is no uranium-rich compound; i.e., $U(Al, Si)_3$, at the uranium surface. The absence of this layer, which acts as a diffusion barrier, has led to interdiffusion between the aluminum-silicon and/or aluminum layer and uranium to form the UAl_3 layer. The formation of UAl_3 results in an increase in volume and, hence, blister formation. This diffusion can lead to penetration of the can and rapid oxidation of the uranium to form a ruptured area, as shown in Fig. 3.

In the course of investigating the cause of the diffusion blisters in triple-dip, canned slugs, it was found that the tin content at the bonding layers had a very significant effect on diffusion-blister formation. Two slugs that showed diffusion blistering after heat treatment for one week at 400°C were sectioned, and the bond layers were submitted for examination by spectrographic analysis. Both blistered and blister-free areas were examined. It was found in every case where a blister had formed that a high concentration of tin was present, but

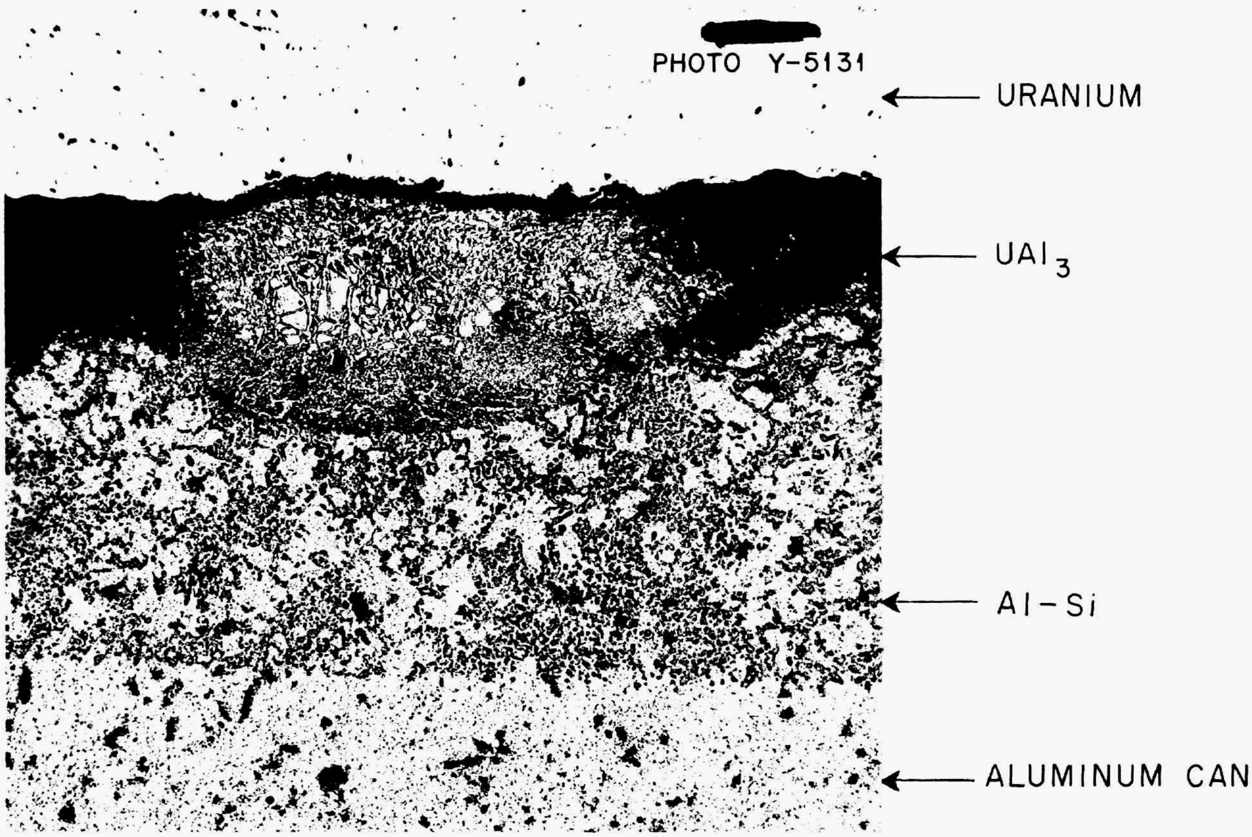

Fig. 2. Center Section of Typical Diffusion Blister. 100X.

no detectable amounts of tin were observed in blister-free areas. In order to obtain a more quantitative idea of the amounts of tin present in blistered slugs as compared with blister-free slugs, the cans were stripped from five slugs that had blistered in the seven-day heat treatment at 400°C and five that did not blister and the bonding layers were removed by filing. Chemical analyses of these samples revealed that the blistered slugs contained from 75 to 300 mg of tin, whereas nonblistered slugs contained less than 1 mg of tin.

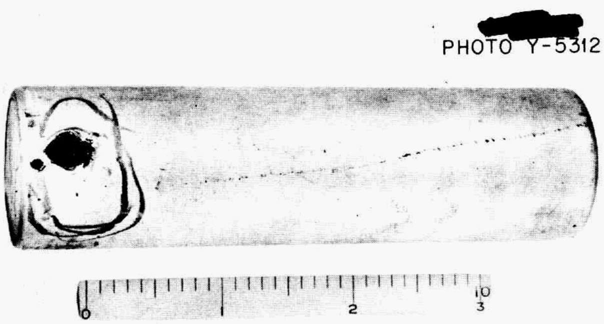

Fig. 3. Can Rupture Caused by a Diffusion Blister.

Since it appeared that localized concentrations of tin were associated with the blistering problem in triple-dip, canned slugs,[4] various techniques were employed to eliminate residual tin on the slugs. These techniques were as follows:

1. Lowering the bronze-bath temperature from 720 to 710°C,

2. Increasing the time of slug immersion in the aluminum-silicon dip bath from 6 to 12 seconds,

(4) Although no direct evidence was obtained about the mechanism involved, it was felt that localized concentrations of tin probably represented nonwet areas on the slug. These areas would, therefore, not have a barrier layer of $U(Al, Si)_3$ present, and blister formation would result from diffusion.

3. Redesigning the fixture which held the slug during centrifuging to permit point contact only between the slug and fixture.

When these changes were incorporated, one at a time, a significant decrease was noted in the number of slugs that blistered during the standard heat treatment of one week at 400°C. However, when a production lot of 550 slugs was made by using the first two techniques but not the last one, 25% of the slugs blistered during the seven-day heat treatment at 400°C. The results of this test made it apparent that the tin content in triple-dip slugs could not be controlled sufficiently well during production runs to ensure complete freedom from blistering difficulties. At this point in the experimental work it was decided to abandon the triple-dip canning technique and explore the possibilities of using the alpha-canning technique, which completely eliminates the use of tin.

A second type of blistering occured during the heat treatment of the lot of 550 slugs described previously. As may be seen from Figs. 4 and 5, these blisters do not contain diffusion

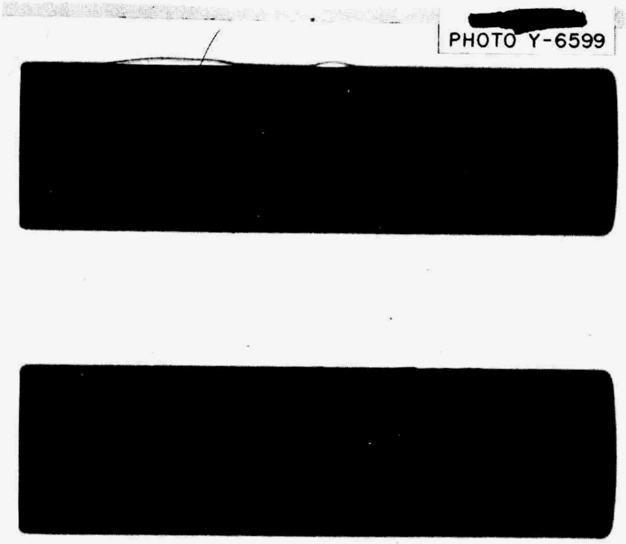

Fig. 4. Radiograph of Slugs with Typical Gas Blisters (top) and Diffusion Blisters (bottom).

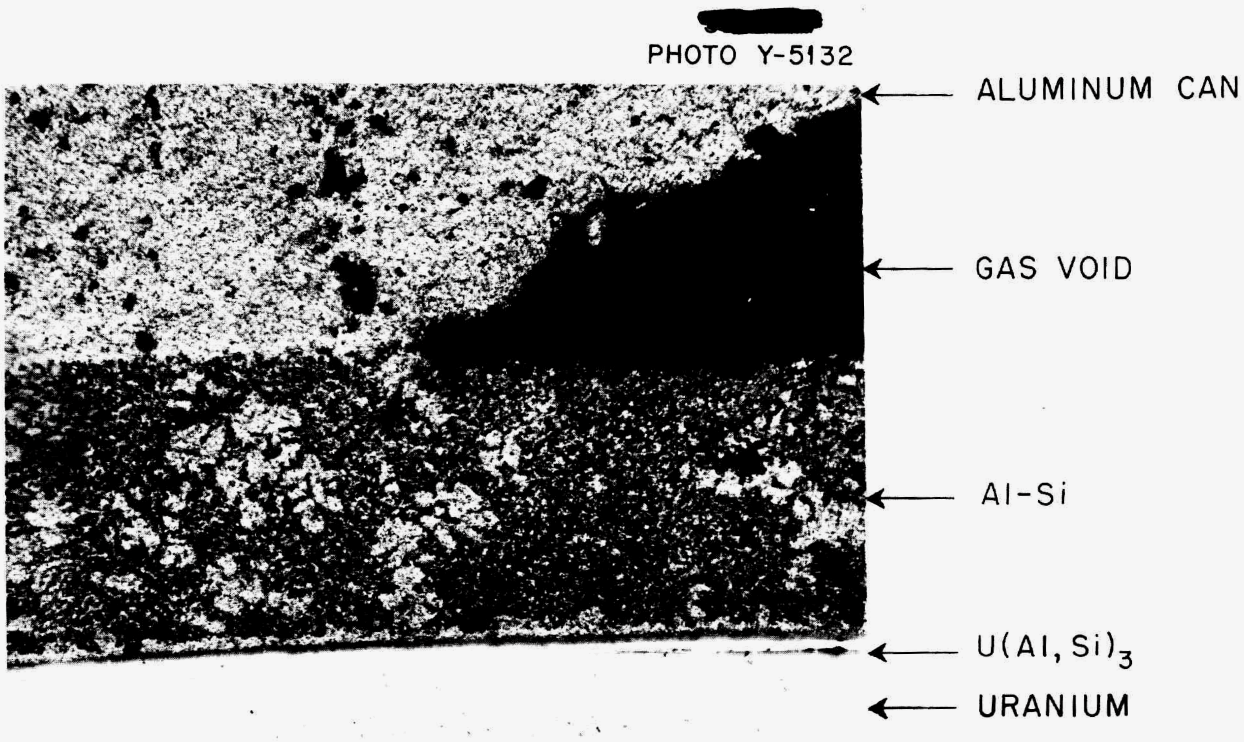

Fig. 5. Edge of Gas Blister Between Aluminum-Silicon Layer and Aluminum Can. 100X.

products and may be ascribed to gas formation. It was noted that the aluminum-silicon baths used for preparation of this lot of slugs were made up from virgin ingot that was not preheated prior to melting. Also, the incidence of blisters from heat treatment decreased markedly in the last slugs canned as compared with the first. It was concluded that the trouble arose from hydrogen absorption in the aluminum-silicon baths. This gas was released on heating of the slugs and caused the blisters. The well-known techniques for eliminating hydrogen from molten aluminum – i.e., flushing the melt with either nitrogen or chlorine – were employed in several tests and found to be effective in removing the absorbed hydrogen. The simpler techniques, however, of preventing moisture from entering the bath by preheating the charge and also allowing the bath to stand for a period of approximately 24 hr prior to the start of canning to allow any absorbed hydrogen to diffuse out were equally effective and are used at present.

Alpha Canning. As pointed out previously, the decision to investigate alpha canning was made when it was found impossible to control, at a low level, the tin content of triple-dip, canned slugs. A lot of 553 slugs was canned by the alpha process under the following conditions:

1. Beta heat treatment for 3 min at 730°C in Houghton's Liquid Heat No. 980,
2. Cleaning with nitric acid (50%) etch,
3. Aluminum-silicon duplex bath – 35 sec in lead bath, 5 sec in aluminum-silicon, no flux on bath,
4. Aluminum-silicon dip bath and canning bath using the standard procedure.

After heat treatment for seven days at 400°C, 14.6% of these slugs showed diffusion blisters. It was noted during the canning and when the as-canned slugs were stripped that the major difficulty was nonwetting of the slugs by aluminum-silicon in the duplex bath. When blistered slugs from the seven-day heat treatment at 400°C were stripped, it was found that the diffusion blisters were invariably associated with nonwet areas on the slug surface. As pointed out previously, the absence of the $U(Al, Si)_3$ compound layer on the uranium surface as a result of nonwetting by aluminum-silicon invariably leads to diffusion blistering during heat treatment at 400°C.

Various attempts were made to ensure that a clean, nonoxidized uranium surface was presented to the aluminum-silicon layer in the duplex bath. The following methods were tried:

1. *Electrolytic Etching Following the Salt-Bath Treatment.* The slugs that were beta heat treated and quenched in water, show a stained surface that could not be completely cleaned by a nitric acid etch. Electrolytic etching was found to improve this situation markedly.

2. *Flowing Water Quench.* If slugs from the salt-bath treatment are quenched in static water, considerable pitting of the surface by corrosion from the water-soluble salt results. The use of flowing water alleviated this behavior.

3. *Redesign of Handling Tools.* The first tools used had a large contact area with the slugs during canning. It was found that the use of point contacts eliminated the oxidation and consequent nonwetting of the slugs in the duplex bath. The oxidation occurred when the slugs were put into the hot tongs prior to dipping in the aluminum-silicon bath.

4. *Use of Flux on Duplex Bath.* This change, which was the most

important one made, completely solved the nonwetting problem. Eutector 190 aluminum brazing flux (made by Eutectic Welding Company) was employed as a cover on the aluminum-silicon layer of the duplex bath. This flux, composed of sodium, lithium, potassium, and aluminum chlorides and/or fluorides, cleans the uranium surface when the slug is immersed in the duplex bath and results in complete wetting of the slug by the aluminum-silicon. Large numbers of slugs canned with this technique have been stripped and examined for nonwetting; no cases of nonwetting have been observed.

Some difficulty was encountered with crucible erosion at the flux line. The original clay-graphite crucibles had a relatively short life of two to three weeks. Low carbon steel crucibles were tried but gave poor service because of reaction with the aluminum-silicon and contamination of the flux cover. However, the rammed linings in the low-frequency, induction furnaces used at present give very satisfactory service. These furnaces have now been in service for several months and have shown no observable attack from the flux.

The success obtained with the solution of the problem of obtaining complete wetting of the uranium by aluminum-silicon prompted using this technique for a trial production run of 1000 slugs. A heat treatment of these slugs for three weeks at 400°C resulted in a single blister on one slug. A photomicrograph of this blister is shown in Fig. 6. There is some doubt about the cause of this blister, but it appears to be a result of oxidation from a leak in the can or cap rather than diffusion. Figure 7 shows the structure at the bonding layer of a typical alpha-canned slug. It can be noted that the compound layer is cracked and separated, and there is a layer of aluminum-silicon between the separation. This condition is typical of alpha-canned slugs but apparently does not lead to diffusion blistering during heat treatment at

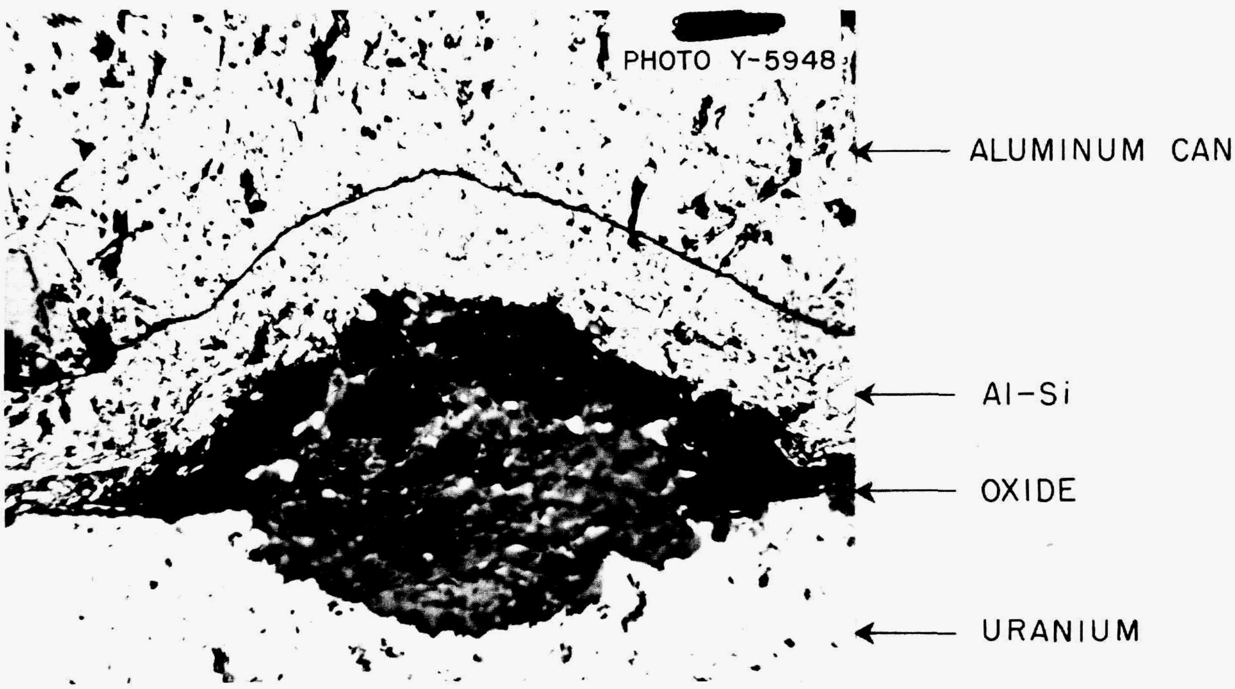

Fig. 6. Oxidation Blister on Alpha-Canned Slug. 150X.

400°C, since there is always a continuous layer of $U(Al,Si)_3$ compound at the uranium surface.

The summary listed in Table 1 illustrates the behavior of production lots of alpha-canned material as compared with triple-dip, canned slugs. It can be noted from examination of this table that no cases of diffusion blistering have occurred with slugs prepared by alpha canning with a flux on the duplex bath. All blistering of these slugs was associated with either porosity in the welds or leaks in the end caps. Some end caps were prepared from defective aluminum rod that contained porosity and permitted access of air to the uranium during heat treatment. This situation has been corrected by rigid inspection of end-cap stock.

TABLE 1

Effect of Canning Technique on Blistering of Aluminum-Silicon Bonded Slugs During Heat Treatment at 400°C

METHOD OF CANNING	NO. OF SLUGS TESTED	TIME AT 400°C (days)	BLISTERED SLUGS (%)	REMARKS
Standard triple-dip, canned at Y-12	5886	7	18.6	
Standard triple-dip, canned at Hanford	130	7	13.8	Hanford 4-in. slugs
Alpha-canned, with no flux, at Y-12	648	7	14.6	
Alpha-canned, flux on duplex bath, at Y-12	2288	7	0	Two slugs failed from leaky welds
Retest of 977 of above for additional 2 weeks	977	21	0.1	One slug showed oxidation blister from can leaks
Alpha-canned, flux on duplex bath, at Y-12	8801	7	0.1	Eleven slugs showed oxidation blisters from can leaks

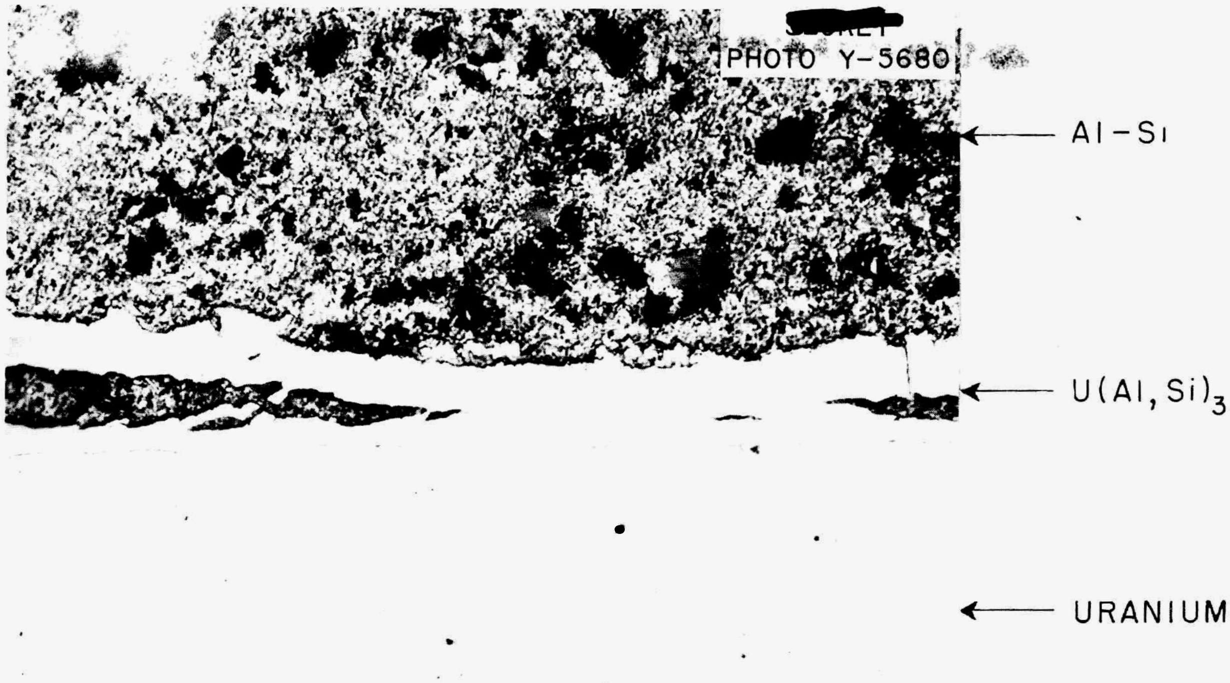

Fig. 7. Structure at Bonding Layer of Typical Alpha-Canned Slug. 250X.