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# **Chop-Leach Fuel Bundle Residues Densification by Melting**

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November 1976

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**Battelle**

Pacific Northwest Laboratories

BNWL-2132



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CHOP-LEACH FUEL BUNDLE RESIDUES  
DENSIFICATION BY MELTING

by

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November 1976

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## SUMMARY

Two melting processes were investigated for the densification of fuel bundle residues: Industoslag melting and graphite crucible melting. The Industoslag process, with prior decontamination and sorting, can produce ingots of Zircaloy, stainless steel and Inconel of a quality suitable for refabrication and reuse. The process can also melt oxidized mixtures of fuel bundle residues for direct storage. Eutectic mixtures of these materials can be melted in graphite at temperatures of 1300°C. Hydrogen absorption experiments with the zirconium-rich alloys show the alloys to be potential tritium reservoirs.

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## THEORY

The theory of the present experiment is based on the fact that the rate of change of the concentration of a substance in a solution is proportional to the concentration of the substance itself.

Let  $C$  be the concentration of the substance at time  $t$ . Then the rate of change of  $C$  with respect to  $t$  is given by  $\frac{dC}{dt}$ . According to the theory,  $\frac{dC}{dt} = -kC$ , where  $k$  is a constant.

Integrating both sides of the equation, we get  $\ln C = -kt + \ln C_0$ , where  $C_0$  is the initial concentration.

Thus,  $\ln C = -kt + \ln C_0$ . This equation can be used to determine the value of  $k$  from experimental data.

Let  $C_1$  and  $C_2$  be the concentrations of the substance at times  $t_1$  and  $t_2$  respectively. Then

$$\ln C_1 = -kt_1 + \ln C_0 \quad \text{and} \quad \ln C_2 = -kt_2 + \ln C_0$$

$$\text{Subtracting the two equations, we get } \ln \frac{C_1}{C_2} = k(t_2 - t_1)$$

$$\text{Thus, } k = \frac{\ln \frac{C_1}{C_2}}{t_2 - t_1}$$

$$\text{The value of } k \text{ can be determined from experimental data by plotting } \ln C \text{ against } t.$$

$$\text{The slope of the line is } -k, \text{ and the intercept on the } \ln C \text{ axis is } \ln C_0.$$

$$\text{Thus, the value of } k \text{ can be determined from the slope of the line.$$

$$\text{The value of } k \text{ can also be determined from the intercept on the } \ln C \text{ axis.$$

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$$\text{Thus, the value of } k \text{ can be determined from experimental data.$$



## CHOP-LEACH FUEL BUNDLE RESIDUES DENSIFICATION BY MELTING

### INTRODUCTION

In current LWR fuel reprocessing technology, fuel bundles are sheared in short lengths for acid leach of the fuel pellets. The residues from the acid leach include short lengths of fuel cladding, massive end fittings, fuel spacer grids, assorted springs, guide thimbles and flow channels. These residues constitute a high volume waste, amounting in weight to about 22% of the fuel bundle. Without densification they constitute a substantially higher volume than the high level transuranic (TRU) calcines or glasses. Densification by melting will reduce this volume by a factor of 6. These materials have a bulk density of about 1.1 kg/l. As recovered from the dissolver these hardware residues represent about 325 kg/MT of uranium, and consist of 70 to 80 wt% Zircaloy, 12 to 22 wt% stainless steel (SS) and 8 wt% Inconel.

PNL is evaluating the decontamination and melt densification of the chop-leach fuel bundle residues to minimize waste storage. Decontamination of the residues prior to melting to remove TRU element contamination is being developed to qualify the treated metals for simpler, less expensive waste disposal categories. The results of two melting processes for the densification of unirradiated fuel bundle hardware materials will be discussed in the following text.

### DESCRIPTION OF THE CHOP-LEACH FUEL BUNDLE RESIDUES

The head end of the fuel reprocessing stream consists of short pieces of fuel element cladding together with the end hardware and spacers, etc., which have been neutron irradiated. The principal activation products remaining in the Zircaloy after 5 and 100 years cooling, as calculated by ORIGEN code, are:  $^{60}\text{Co}$ ,  $^{55}\text{Fe}$ ,  $^{125}\text{Sb}$ ,  $^{63}\text{Ni}$ , and  $^{125\text{m}}\text{Te}$ . The total activity is 900  $\mu\text{Ci/g}$  zirconium (Zr) after 5 years and 18  $\mu\text{Ci/g}$  after 100 years.

Zircaloy-2 and -4 usually contain trace uranium ( $\sim 1$  ppm) which will transmute to TRU elements or fission during the irradiation. Calculations by ORIGEN code of the expected TRU contamination, uniformly dispersed in the metal from 1 ppm natural uranium contamination (irradiated in a typical fuel exposure), indicate the principal isotopes would be about 85 nCi/g of  $^{241}\text{Pu}$  and 2 nCi/g  $^{244}\text{Cm}$  in the Zircaloy after 5 years cooling. The balance of the transuranics would be less than 3 nCi/g total.<sup>(1)</sup> Higher levels of TRU elements would be present if irradiated longer. A similar calculation of the transuranics generated in the Inconel and stainless steel parts could be made; however, a satisfactory estimate of the uranium and thorium impurities in these alloys has not yet been obtained. The Zr cladding has been estimated to contain 100 to 150 ppm hydrogen of which about 0.03 wt% is fission product tritium.<sup>(2,3)</sup>

LWR fuel elements might have a corrosion product layer up to 50  $\mu$  thick in locations of maximum corrosion.<sup>(4)</sup> Impurities (crud) circulating in the reactor deposit on fuel surfaces and can contain transuranics if the coolant is contaminated with uranium or plutonium from fuel ruptures. The internal surface of the Zircaloy-clad fuel develops an oxide layer of a few microns in thickness.<sup>(4)</sup> The  $(\text{U}, \text{Pu})\text{O}_2$  fuel has been observed to adhere and possibly react with this oxide layer.<sup>(5)</sup> Estimates of residual  $(\text{U}, \text{Pu})\text{O}_2$  associated with the fuel cladding after leaching are usually stated as less than 0.1 wt% of the uranium charged.<sup>(6,7,8)</sup> Analysis of two irradiated leached fuel cladding pieces has shown considerably less than 0.1 wt% residual fuel, but with much higher than expected  $^{137}\text{Cs}$ .<sup>(9,10)</sup>

### CONCLUSIONS

The Inductoslag process can produce, with prior decontamination and sorting, Zircaloy, stainless steel, and Inconel ingots of a quality suitable for refabrication and reuse. Prior surface preparation is not necessary to produce ingots of these materials and their mixtures for direct storage. Zr-containing ingots can also be used as tritium reservoirs. The melting system is nearly free of refractories and crucible life is exceptionally long. Although the  $\text{CaF}_2$  or  $\text{CaF}_2\text{-MgF}_2$  slag will result in a waste stream, it can be recycled.

The graphite crucible eutectic process can melt alloys of Zircaloy, stainless steel, and Inconel in the range of 80 to 85 wt% Zircaloy at temperatures of 1300°C. Decontamination prior to melting could result in a low volume, low radioactive waste form for direct storage. These alloys could also be used as storage reservoirs for tritium. The percentage of Zircaloy in the chop-leach hulls is conveniently near the desired eutectic composition, thus eliminating the need to melt at the high melting point of Zr, ~1850°C. Spent crucibles could be burned to an ash to reduce the waste stream. Crucible life will probably be less than that of cold crucibles and refabrication of the ingot would not be possible.

## MELT DENSIFICATION PROCESSES

Two melting processes have been investigated for the densification of fuel bundle residues: 1) Inductoslag melting and 2) graphite crucible melting. Decontamination of the melt stock prior to melting can enhance melting characteristics and result in ingots with storage and transportation requirements that are less costly. Sorting by alloy grade could result in metal suitable for reuse in a nuclear facility when melted by the Inductoslag process.

Although detailed descriptions of decontamination processes are outside the scope of this report, the development of decontamination processes is a parallel effort of this program. Because decontamination methods for nickel and iron base alloys have been established, initial efforts have been directed to the more difficult task of decontaminating Zircaloy surfaces with minimum loss of metal. The most promising process investigated to date has been treatment of the  $ZrO_2$  corrosion films in Hf-Argon gas at 550 to 650°C which produces films that are removable in a dilute aqueous reagent developed by Meservey.<sup>(11)</sup> The Hf-Argon gas-treated residues are heated at 90°C for 1 to 2 hr in this solution which consists of 0.4M ammonium oxalate, 0.16M ammonium citrate, 0.1M ammonium fluoride and 0.3M hydrogen peroxide. Technology such as distillation, pyrohydrolysis and calcination exists for treating or recycling of waste side streams. TRU element decontamination factors of about  $10^4$  will be necessary to reduce transuranics to <10 nCi/g.

### INDUCTOSLAG MELTING

The chemical activity of Zr at its melting point ( $\sim 1850^\circ\text{C}$ ) requires that it be melted in vacuum or inert atmosphere. Conventional crucible materials react vigorously with molten Zr. For example, Zr melted in graphite crucibles picks up excessive carbon. Consequently, cold crucible processes were developed for producing Zr.<sup>(12)</sup> These processes have also been used for remelting iron, nickel, and cobalt alloys. Alternate cold crucible melting techniques have been evaluated in the context of fuel bundle

residue densification.<sup>(13)</sup> Conclusions from this evaluation resulted in selecting the Inductoslag process as the most promising process for this application.

The Inductoslag melting process (Figure 1), developed by Clites and Beall<sup>(14,15)</sup> of the U.S. Bureau of Mines in Albany, Oregon, uses induction-heating. The melt is insulated from a split, water-cooled crucible by a layer of frozen slag. Melting takes place in static, one-third atmospheric pressure helium. A pool of Zircaloy-4 and  $\text{CaF}_2$  is melted on a "starting stub" and subsequent charge material vibratorily fed into the top of the crucible as the ingot is extracted out the bottom of the crucible.

Zircaloy-4 fuel cladding chopped into 2.5-cm pieces and etched by the ammonium oxalate, citrate, fluoride, peroxide bath similar to that used in the decontamination process was used as feed material to the Inductoslag process to produce an ingot 10-cm diameter x 75-cm long and weighing 41 kg.<sup>(16)</sup> The scalloped appearance of the ingot sidewall shown in Figure 2 is a result of the split copper crucible design. The fine grained area at the top of the longitudinal cross section is the last metal to freeze and represents the extent of the molten pool during the melting process. Power input during melting was 95 kW, resulting in a melting rate of 19 kg/hr.

Chemical analyses and hardness testing of the ingot showed it to be within nuclear grade specification. Carbon and hydrogen did not increase. Nitrogen increased  $\sim 30$  ppm and oxygen  $\sim 300$  ppm. Fluorine increased  $\sim 16$  ppm; no calcium increase was detected. The average hardness was 180 Brinell.

Portions of the ingot were extruded and refabricated by a commercial cladding tube manufacturer into a cladding tube size of 11.2 mm OD x 0.74 mm wall. Standard autoclave testing of the refabricated cladding tube showed normal weight gain and black lustrous surfaces.<sup>(9,16)</sup>

Clean 304 SS, Inconel 718, and a 2:1 by weight mixture of 304 SS and Inconel have been melted by the Inductoslag process. Successive 10-kg melts were made one on top of the other to form a three-component ingot. Because of the lower melting range of these materials, a eutectic mixture of 48 wt%  $\text{CaF}_2$ -52 wt%  $\text{MgF}_2$  is used as the slag. The eutectic melts at

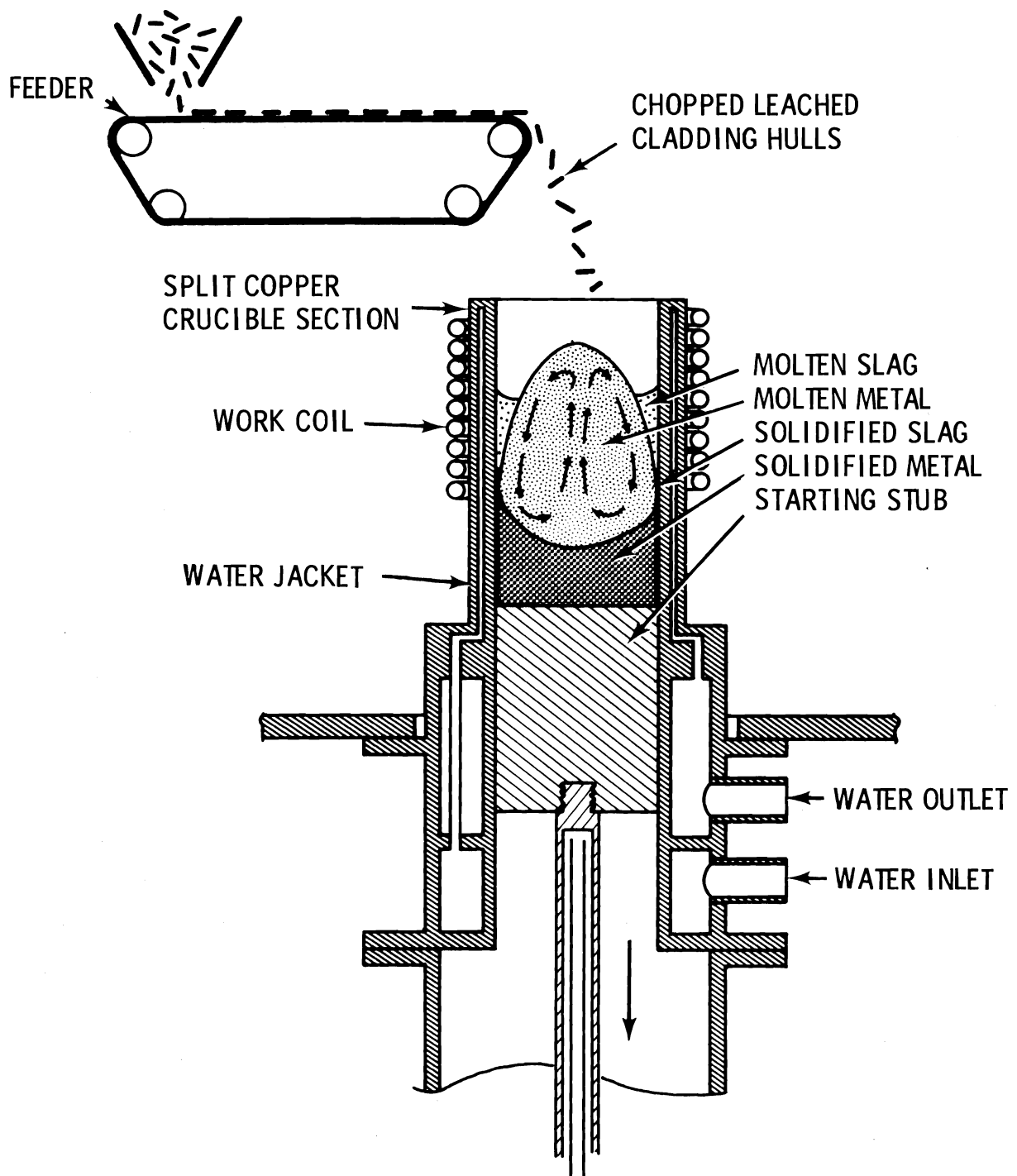
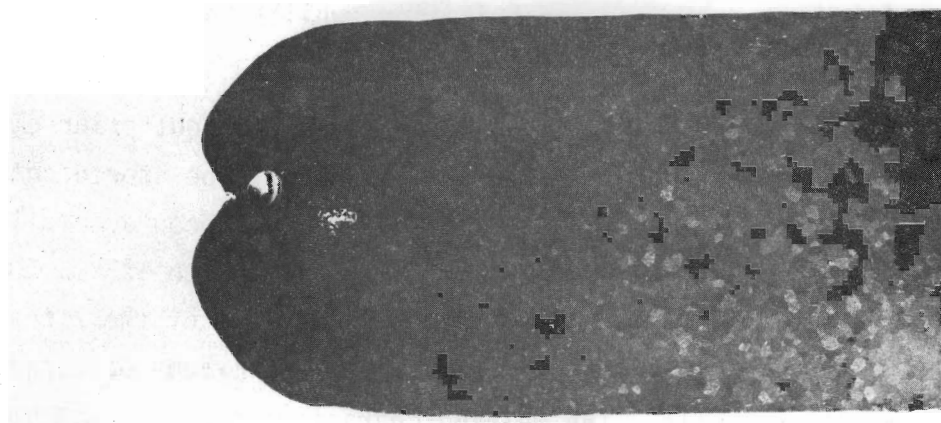
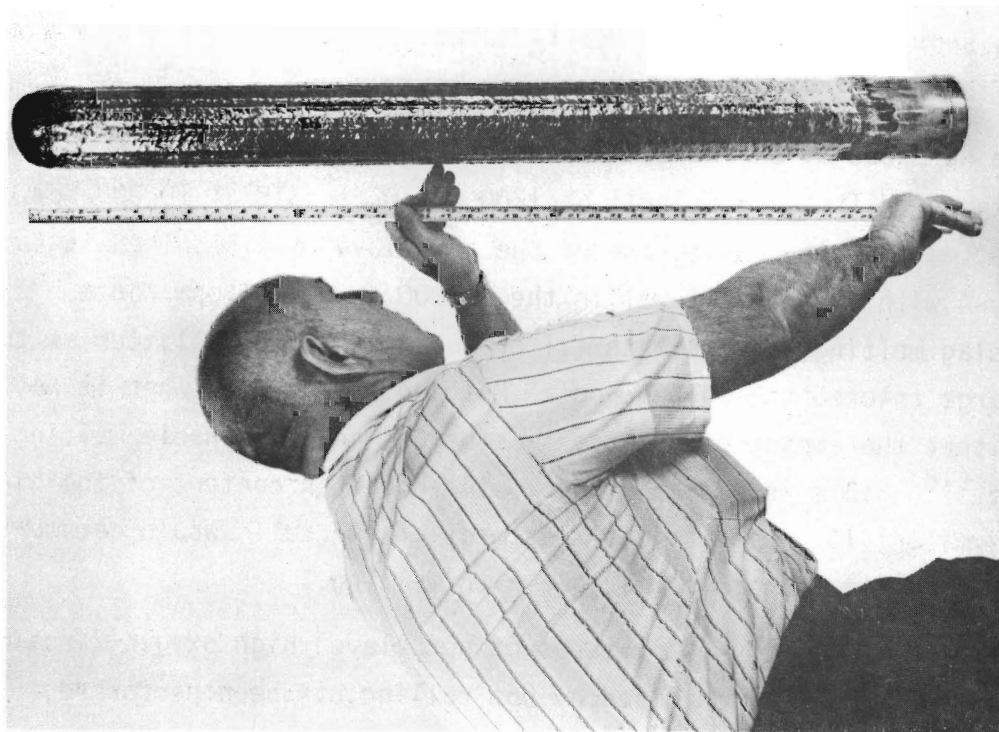


FIGURE 1. Inductoslag Melting Process. Clites and Beall, Albany Metallurgical Research Center, U.S. Bureau of Mines, Albany, Oregon. (15)





HEAT NO.  
USBM 431

FIGURE 2. Inductoslag Remelted Chopped Leached Cladding Hulls, Zircaloy-4 (16)

1000°C, while the  $\text{CaF}_2$  alone melts at 1360°C. Eighty-five to 95 kW produced a melting rate of 28 kg/hr for the 304 SS and 15 kg/hr for the 2:1 mixture and the pure Inconel 718.<sup>(9)</sup> Figure 3 shows transverse etched ingot sections of these materials. The 304 SS and Inconel ingots are of a quality that is suitable for direct storage or refabrication, while the mixture with unmelted 304 SS is suitable for direct storage only.

Consolidation by melting of fuel bundle residues without prior cleaning or decontamination may be desirable for materials to be stored only. Inductoslag melting of oxidized fuel bundle residues has been accomplished. Zircaloy-4 cladding has been oxidized by autoclave at 500 to 525°C, 200 psi for 40 to 48 hr. This resulted in a total oxygen content of the Zircaloy ranging from 1200 to 10,000 ppm, an oxygen content estimated to be present in full-term irradiated hulls. The melting characteristics of this material appeared to be nearly identical to those of clean hulls. The high (10,000 ppm) oxygen material produced some splattering and smoke during melting, but melting was not inhibited. Melting at 85 kW resulted in a melting rate of 20 kg/hr.<sup>(17)</sup> The external appearance and the etched sections shown in Figure 4 are nearly identical to those of the low oxygen ingot (Figure 2).

The hardness of Zr increases with increased oxygen content. This material ranged from 175 Brinell at 1200 ppm  $\text{O}_2$  to 375 at 10,000 ppm. Equipment malfunction during one of the autoclave runs resulted in some Zircaloy-4 with an oxygen level in the 20,000 to 40,000 ppm range. Inductoslag melting of this material produced excessive splatter as the cold charge entered the molten pool. Melting was stopped when it was evident that the amount of splatter was beyond any reasonable melting practice.<sup>(18)</sup> This is probably due to the hydrogen content of the highly oxidized material. Premelt heat treatment of the hulls would reduce the hydrogen level to a range compatible with melting.

Inductoslag melting of mixtures of autoclaved high oxygen Zircaloy with 304 SS and Inconel oxidized by hot rolling has been performed. These compositions consisted of:

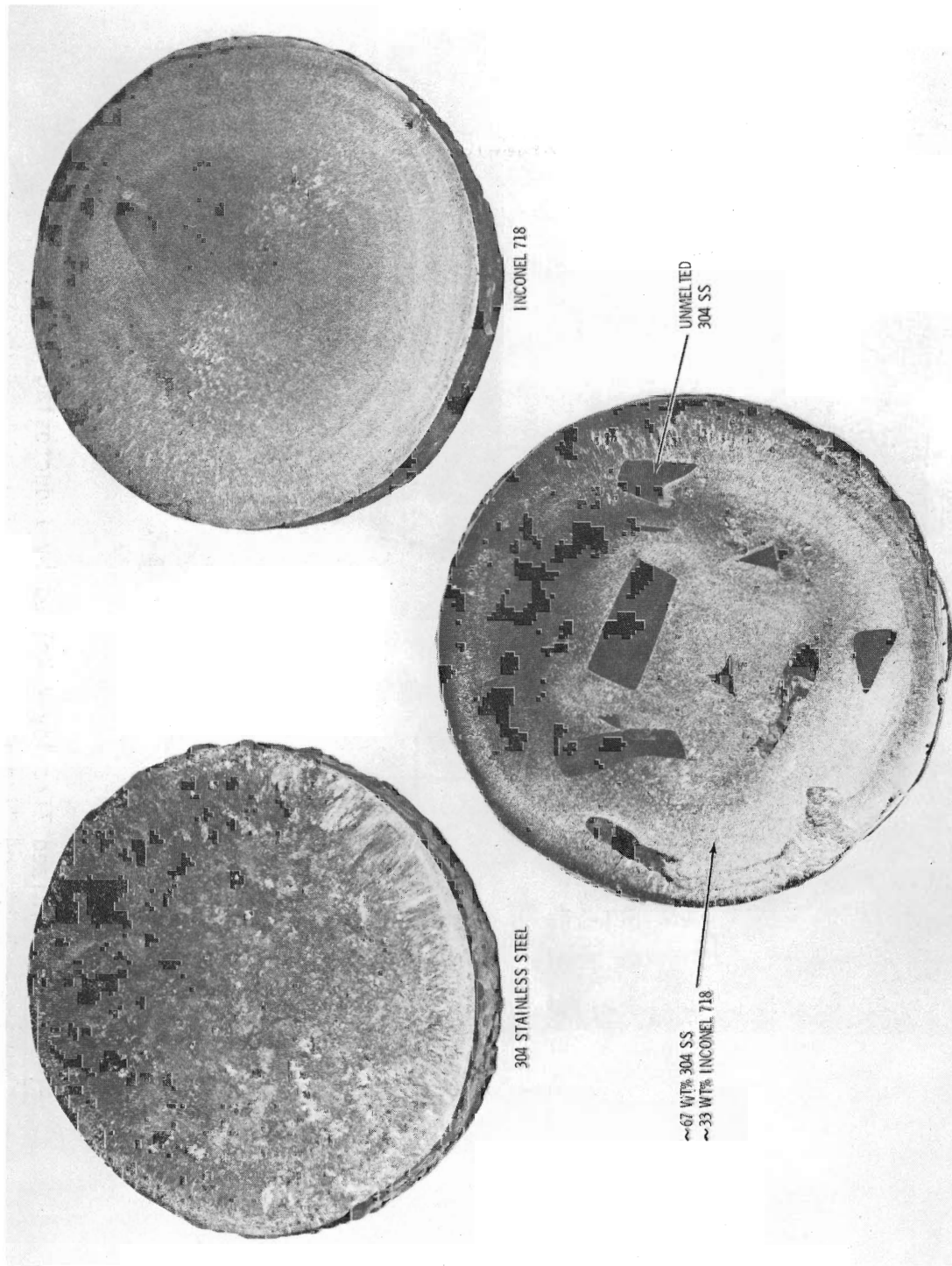
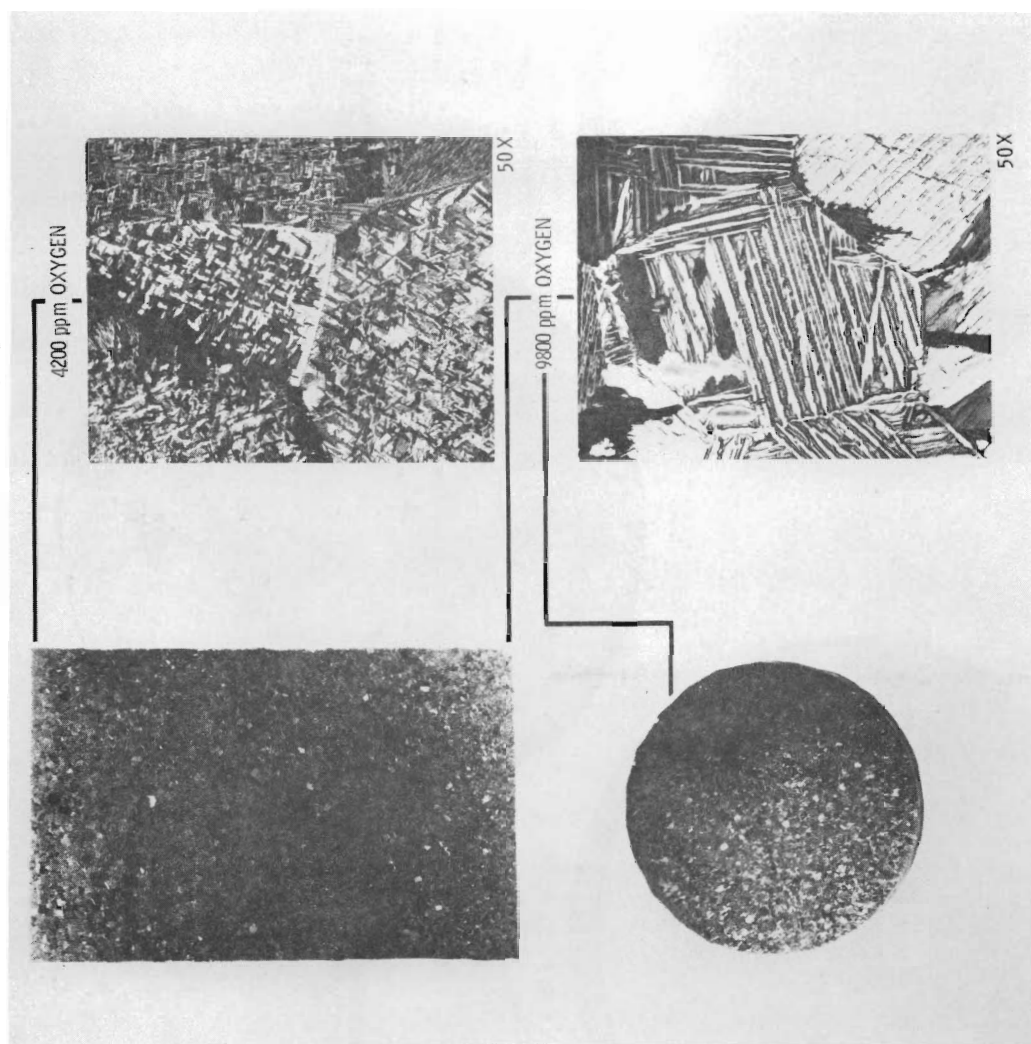


FIGURE 3. Transverse Sections of 10 cm Diameter Inductoslag Ingot (Heat No. USBM 460)<sup>(9)</sup>



**FIGURE 4.** Oxidized Zircaloy-4 Melted by Inductoslag USBM 529<sup>(17)</sup>

1. Zircaloy-4 with 3000 to 8000 ppm  $O_2$  with 4 wt% oxidized Inconel 718
2. Zircaloy-4 with 3000 to 8000 ppm  $O_2$  with 10 wt% oxidized Inconel 718
3. Zircaloy-4 with 3000 to 8000 ppm  $O_2$  with 10 wt% oxidized 304 SS and 5 wt% oxidized Inconel 718.

These mixtures represent a range of partially segregated fuel bundle residues and were melted using 48 wt%  $CaF_2$ -52 wt%  $MgF_2$  slag. The mixtures form the low melting eutectic and result in unmelted metal potted in the eutectic matrix. Figures 5 and 6 are typical of these alloys. The ingots are free of voids and suitable for direct storage; however, they are subject to cracking induced by severe thermal gradients.<sup>(17)</sup>

The low temperature molten pool is slow in dissolving the feed material, causing excessively slow melting rates. A power input of 85 kW results in melting rates of 5 to 8 kg/hr. Efforts are currently under way to increase the melt rate of these alloys.

Aluminum oxide pellets have been added to these materials during melting to simulate the insulator pellets in the fuel bundle residues. They do not interfere with melting and occur as "potted" unreacted inclusions in the ingot.

#### GRAPHITE CRUCIBLE MELTING

Graphite crucible melting, although not as versatile as Inductoslag melting, gave good results. While Zr melts at  $\sim 1850^\circ C$ , binary mixtures of Zr with iron, nickel and chromium form low melting eutectics that can lead to simplified melting processes.<sup>(19)</sup> Figure 7 shows the binary equilibrium diagrams of Zr with iron, nickel, and chromium. Fortunately the low melting eutectics occur at the approximate composition of the fuel bundle residues. Decontamination of the residues prior to melting will provide clean metallic surfaces for diffusion, resulting in liquid formation.

Melting point determinations were made on pre-alloyed 150 g ingots of Zircaloy-2 with 10, 15 and 20 wt% 316 SS. These were performed under vacuum in graphite crucibles heated by a tungsten resistance element. All three

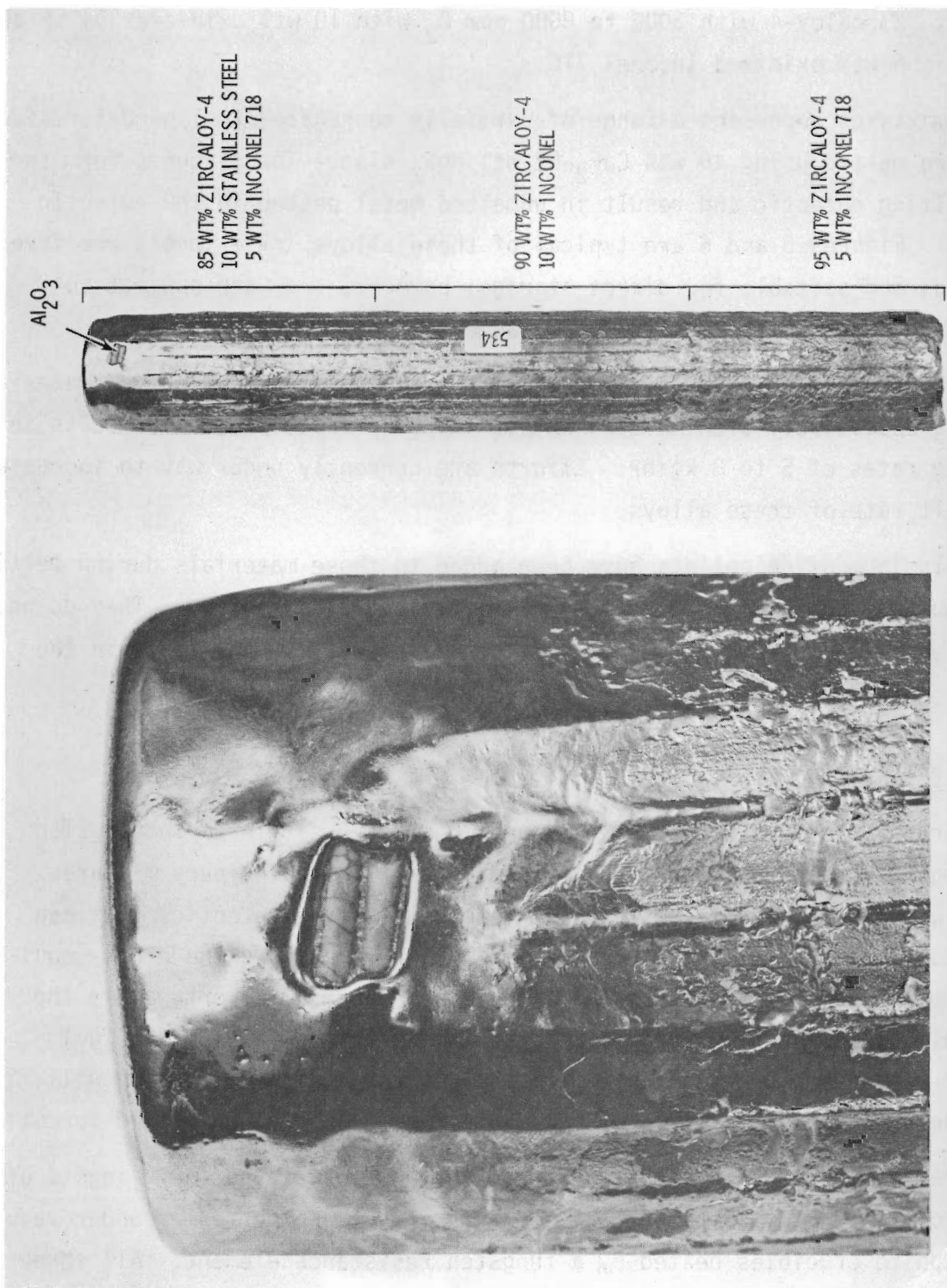


FIGURE 5. Oxidized Zircaloy, Stainless Steel, Inconel Alloys Melted by Inductoslag USBM 534 (18)



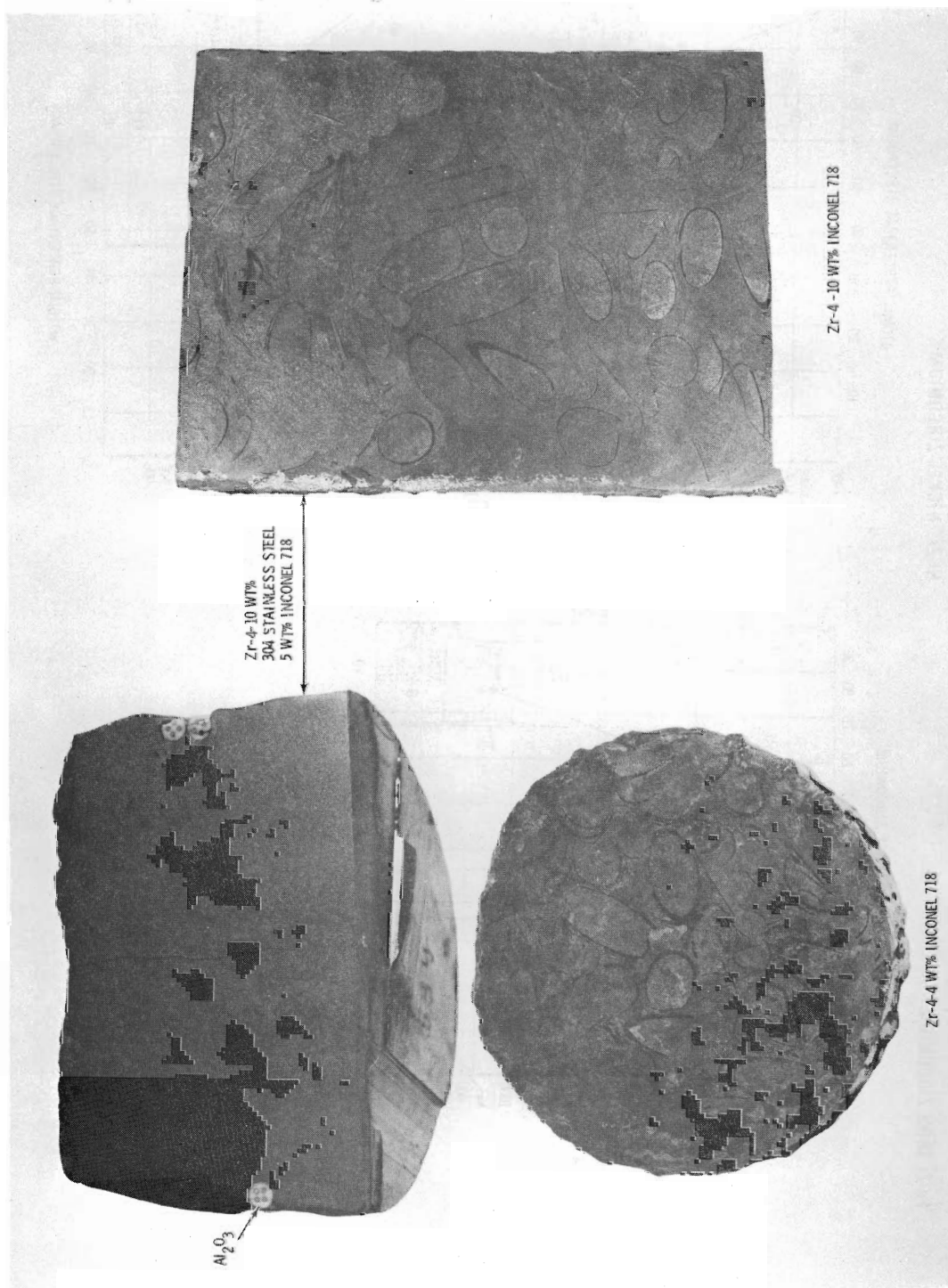


FIGURE 6. Oxidized Mixtures of Zircaloy-4 with Inconel 718 and 304 Stainless Steel Melted by Inductoslag (18)

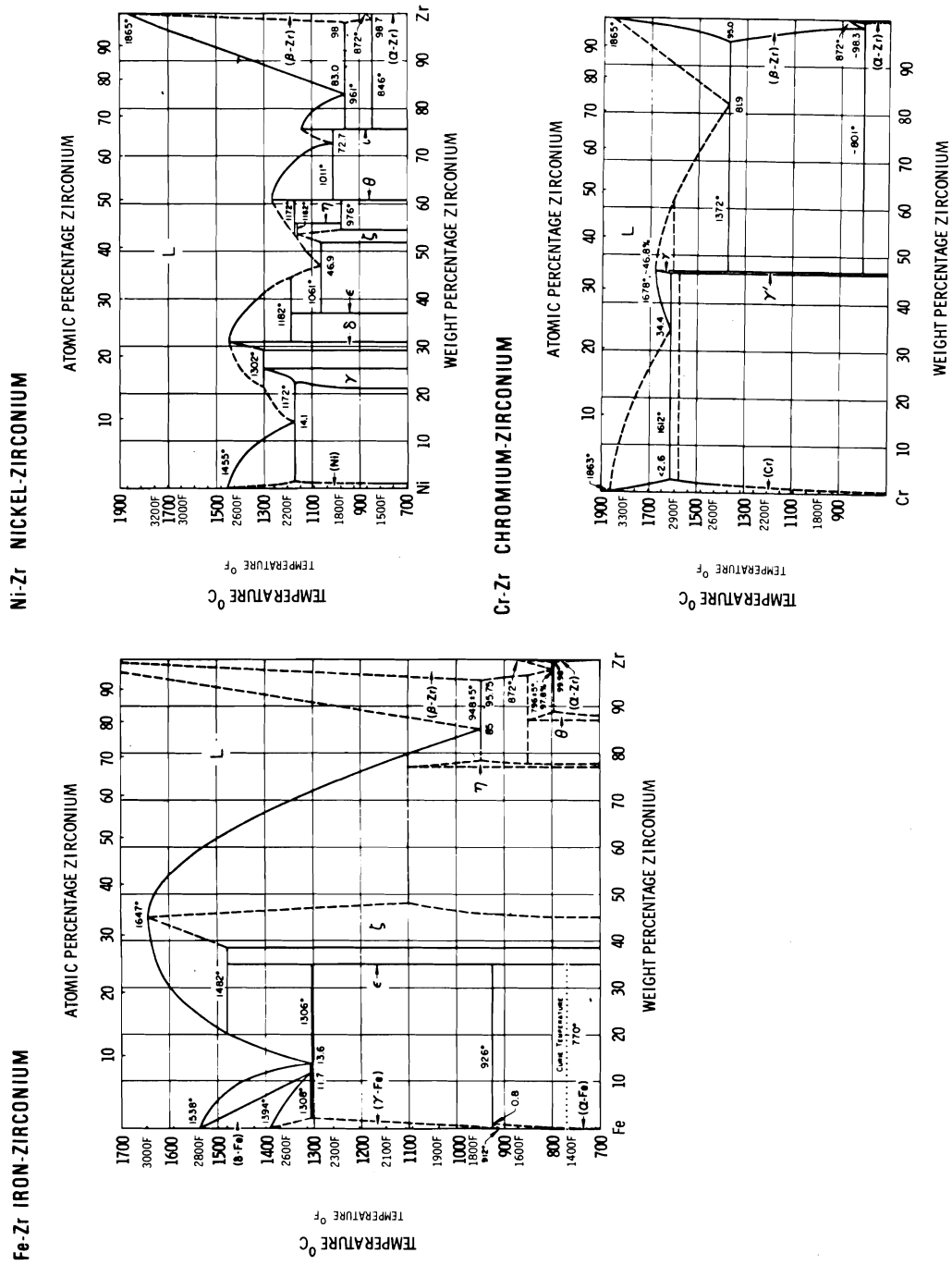


FIGURE 7. Binary Equilibrium Diagrams of Zirconium with Iron, Nickel and Chromium (19)

compositions start melting at about 925°C. The 15 and 20% alloys complete melting at about 1100°C, whereas melting is incomplete for the Zircaloy-2, 10 wt% SS alloy.<sup>(20)</sup>

Scale-up of this work to 8.2 kg heats was performed with a 50 kW, 3000 cycle vacuum induction melting furnace. The crucible and coil assembly are of the tilt type. A graphite susceptor heats an outer graphite crucible which in turn heats the inner or melting crucible. Melting stock was clean sheet chopped into 2.5-cm squares. The 14.0-cm diameter crucible was charged with layers of the 304L SS-Inconel mixture between layers of Zircaloy-2. The heats were started at  $5 \times 10^{-4}$  Torr chamber pressure with a power setting of 5 kW and gradually increased to 10 kW. The pouring temperature was reached in approximately 2.5 to 3 hr, held for 30 min, and poured into an 8.9-cm diameter x 30.5 cm deep split graphite mold. Five 8.2-kg heats made to date have been poured into the same mold and no mold reaction has been observed.<sup>(10,21)</sup>

Figure 8 shows the 85 wt% Zircaloy-2, 10 wt% 304L SS, 5 wt% Inconel 718 ingot that was poured at about 1300°C. A slightly higher pouring temperature or a preheated mold would reduce the skirt at the top of the ingot. A very mild crucible reaction was noted.

A mild crucible reaction was also noted in the 80 wt% Zircaloy-2, 13.4 wt% 304L SS, 6.6 wt% Inconel 718 ingot poured from 1315°C (Figure 9). The ingot had surface cracks. The cracks were eliminated when the melt was allowed to cool in the crucible (Figure 10); however, excessive crucible reaction bonded the ingot to the crucible.

Figure 11 shows the 90 wt% Zircaloy-2, 6.7 wt% 304L SS, 3.3 wt% Inconel 718 ingot poured from ~1415°C. Higher pouring temperatures would be required to successfully pour this composition. A severe crucible reaction was observed.

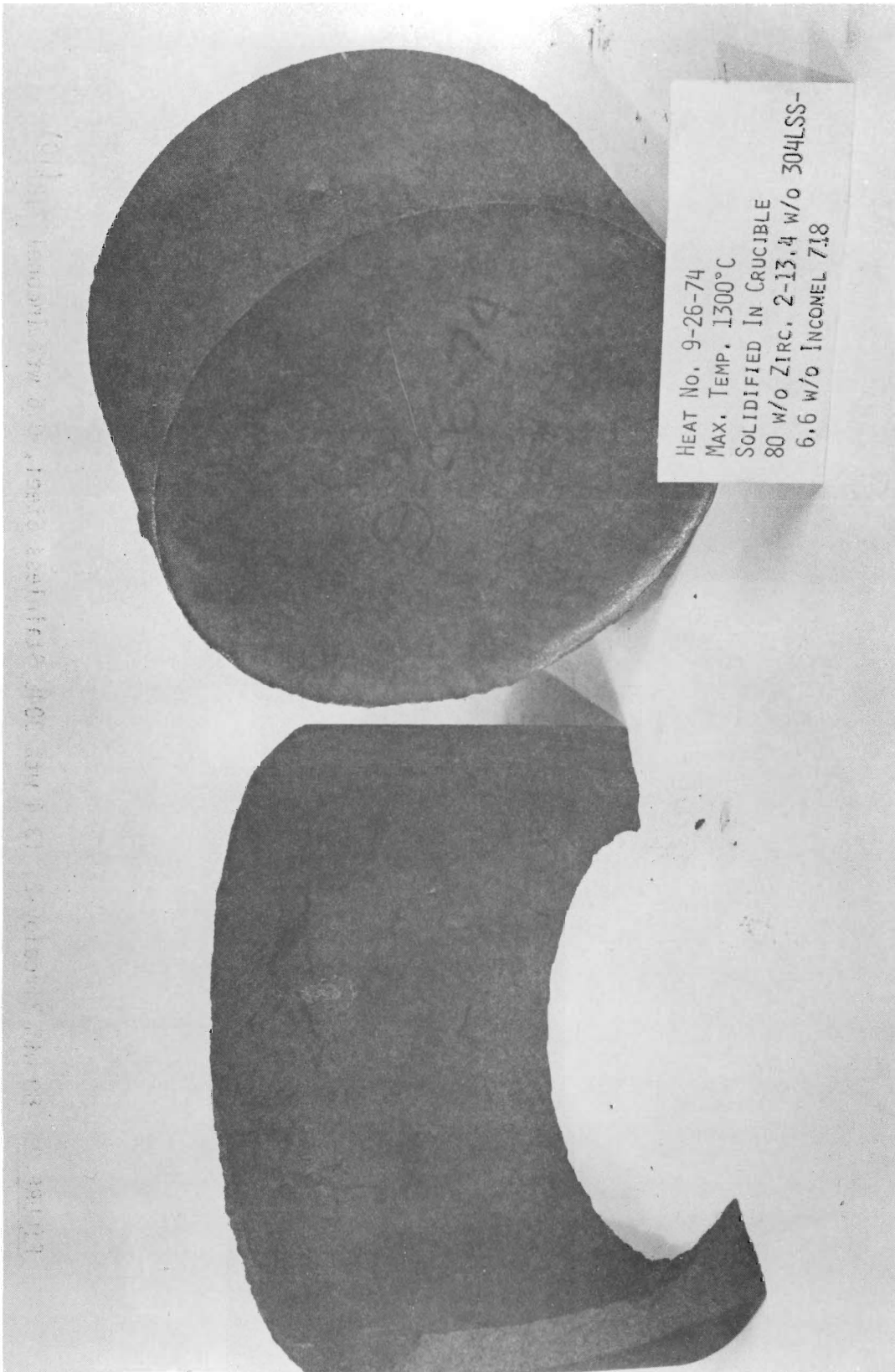
An example of a typical microstructure is given in Figure 12 of the as-polished 85 wt% Zircaloy-2, 10 wt% 304L SS, 5 wt% Inconel 718 alloy showing three major microconstituents and their approximate compositions as determined by microprobe analyses.



FIGURE 8. 85 wt% Zircaloy-2, 10 wt% 304L Stainless Steel,  
5 wt% Inconel 718(21)



FIGURE 9. 80 wt% Zircaloy-2, 13.4 wt% 304L Stainless Steel, 6.6 wt% Inconel 718<sup>(10)</sup>



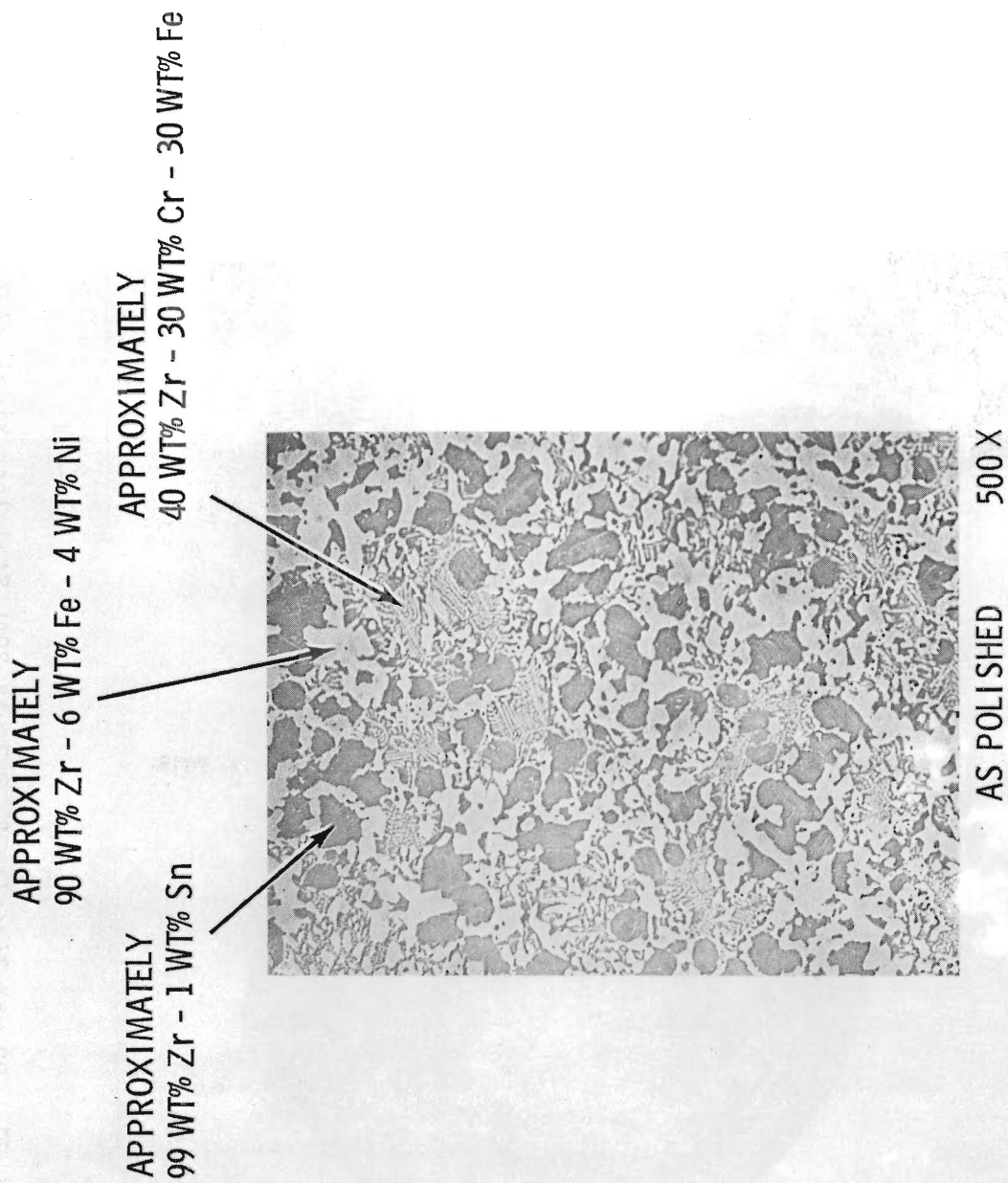
HEAT No. 9-26-74  
MAX. TEMP. 1300°C  
SOLIDIFIED IN CRUCIBLE  
80 w/o ZIRC. 2-13.4 w/o 304LSS-  
6.6 w/o INCONEL 718

FIGURE 10. 80 wt% Zircaloy-2, 13.4 wt% 304L Stainless Steel, 6.6 wt% Inconel 718<sup>(10)</sup>





FIGURE 11. 90 wt% Zircaloy-2, 6.7 wt% 304L Stainless Steel, 3.3 wt% Inconel 718<sup>(10)</sup>



**FIGURE 12.** Microprobe Analyses of As-Cast 85% Zircaloy-2, 10 wt% 304 Stainless Steel, 5 wt% Inconel 718(10)

Concentrations of major metallic elements of these heats agreed reasonably well with the design compositions. Carbon, hydrogen, oxygen and nitrogen values for the melting stock and the resulting heats are listed in Table 1.

TABLE 1. Chemical Analyses of Interstitials<sup>(10)</sup>

| Heat<br>No.      | Composition of Ingots, ppm  |                         |                   |                |         |
|------------------|-----------------------------|-------------------------|-------------------|----------------|---------|
|                  | 85% Zr-2 Alloy              |                         | 90% Zr-2<br>Alloy | 80% Zr-2 Alloy |         |
|                  | 8-29-74                     | 9-5-74                  | 9-12-74           | 9-18-74        | 9-26-74 |
|                  |                             |                         |                   |                |         |
| C                | 100                         | 160                     | 250               | 160            | 90      |
| H                | 24                          | 14                      | 8                 | 60             | 80      |
| O                | 1060                        | 1010                    | 980               | 980            | 870     |
| N                | 380                         | 120                     | 200               | 180            | 70      |
| Brinell Hardness |                             |                         |                   |                |         |
|                  |                             | 357                     | 294               | 377            | 286     |
| Heat<br>No.      | Melt Stock Composition, ppm |                         |                   |                |         |
|                  | Zircaloy-2                  | 304L<br>Stainless Steel | Inconel<br>718    |                |         |
|                  |                             |                         |                   |                |         |
|                  |                             |                         |                   |                |         |
| C                | 100                         | 420                     | 430               |                |         |
| H                | 22                          | 80                      | 17                |                |         |
| O                | 1150                        | 50                      | 10                |                |         |
| N                | 50                          | 350                     | 280               |                |         |

Carbon pickup from melting in the graphite crucible is minimal. The 250 ppm carbon level was the result of a high pouring temperature (1415°C). The melting of pure Zr in graphite at temperatures of 1820 to 1920°C will result in carbon contents as high as 3000 ppm.<sup>(5)</sup> Hydrogen and oxygen showed little or no increase after melting and nitrogen was slightly raised.

Brinell hardness values of the as-cast ingots range from 294 to 377. Ingots have been successfully hack sawed with high speed tool steel blades and water soluble oil coolant.

The melting experiments described above show that mixtures of clean sheet composed of 80 to 85 wt% Zircaloy balance stainless steel and Inconel can be melted and poured at temperatures about 1300°C using graphite crucibles and molds. Although slight crucible reactions do occur, the crucibles are reusable. Ingot surface quality and density appear adequate for direct storage. Controlled mold cooling may be required to eliminate surface cracking of the 80 wt% Zircaloy composition.

#### TRITIUM ABSORPTION AND STORAGE IN ZIRCONIUM ALLOY INGOTS

The melting of fuel hardware into ingots will release absorbed hydrogen and tritium. Consequently 100 to 150 ppm of hydrogen and tritium evolved can be reabsorbed into another ingot. The absorption rate and equilibrium pressure of hydrogen over Zircaloy and Zr-(Fe, Ni, Cr) alloy ingots melted in graphite were investigated at representative gas pressure and concentration (Figure 13). The absorption temperature was fixed high enough (700°C) that Zr would dissolve its own oxides and nitrides which would otherwise impede absorption.<sup>(16)</sup> A large temperature gradient was imposed over the length of the absorption specimen to increase the capacity of the ingot for hydrogen while keeping equilibrium gas pressure down. Absorption rates for Zircaloy-2 and 85% Zircaloy-2, 10% Type 304 SS, 5% Inconel 718 specimens with grit blasted surfaces were compared. In general, the equilibrium pressures were controlled by the Zr concentration. The rate of absorption favored the Zircaloy-2. The re-hydriding of the Zr alloy always resulted in faster subsequent absorption rates even though the hydrogen was removed before the second absorption. This suggests the development of a preferred path for absorption and diffusion. Both the alloy and Zircaloy-2 absorb hydrogen rapidly enough to be useful for storage of the hydrogen and tritium removed from the densified hulls.

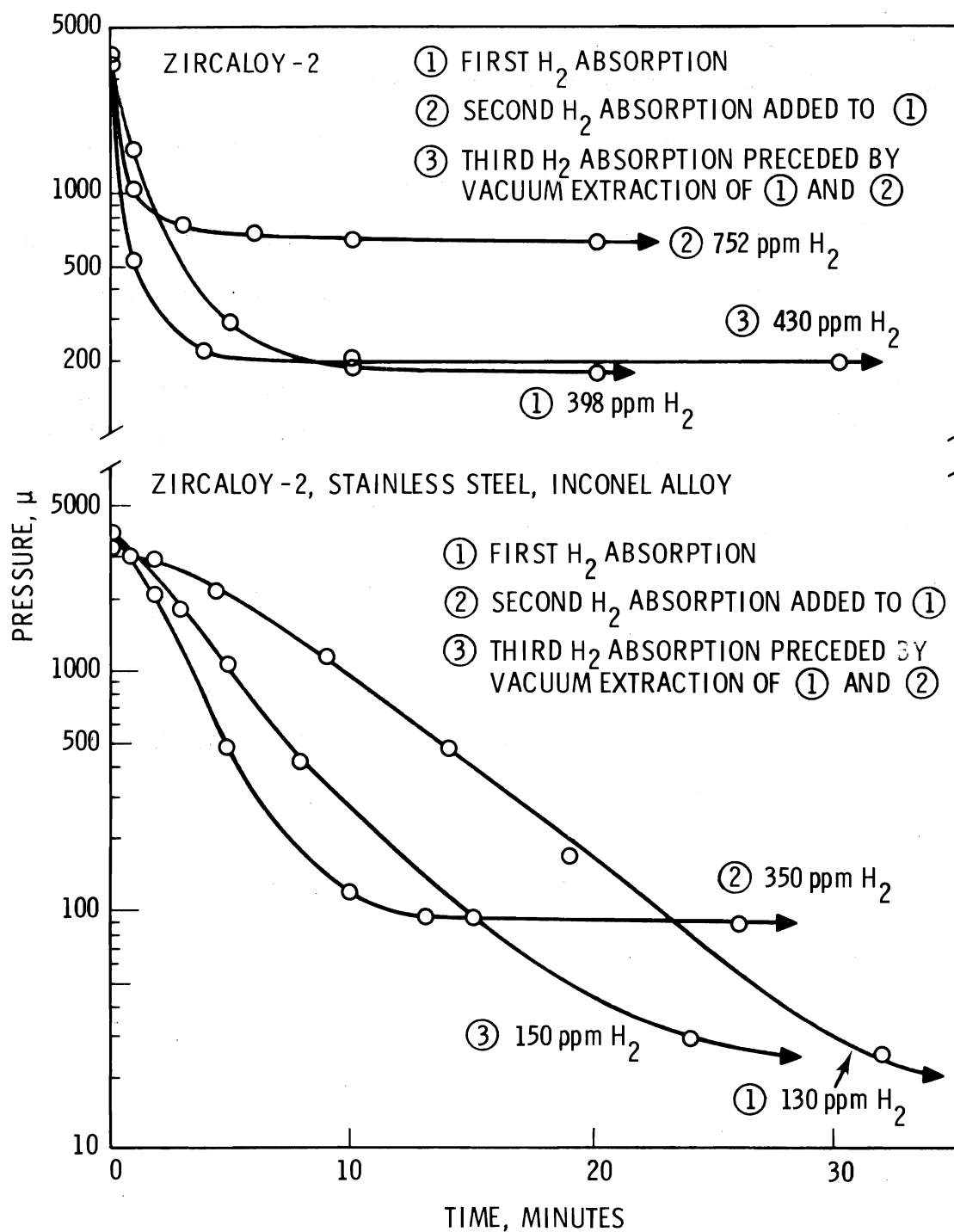


FIGURE 13. Hydrogen Pressure Versus Time at 700°C<sup>(16)</sup>

## FUTURE WORK

Future work will be aimed at the following:

- a) Determine the effectiveness of the graphite crucible eutectic process in melting oxidized material.
- b) Determine mechanical and corrosion properties of the cast materials.
- c) Improve the Inductoslag melting rate of Zr, stainless steel, Inconel alloys.
- d) Melt small samples of irradiated material and determine the extent and mechanism of decontamination, and the effect of the  $\text{CaF}_2$  and  $\text{CaF}_2\text{-MgF}_2$  slags on TRU levels.
- e) Cold mock-up of Inductoslag melting.
- f) In-cell operation of the Inductoslag melting process.
- g) Seek reuse applications in nuclear facilities.
- h) Monitor and compare the economic feasibility of this waste treatment process with other proposed waste treatment methods.



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