Date of Issue: January 25, 1994

Y/DV-1272

**CONSOLIDATION OF ZIRCALOY-4 END CROPS
BY INDUCTION MELTING**

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December 1993

Prepared by the
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P.O. Box 2009, Oak Ridge, Tennessee 37831-8169
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

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SUMMARY

The Oak Ridge Y-12 Plant is investigating the use of induction melting as a method of consolidating Zircaloy-4, a zirconium alloy used in the fabrication of submarine nuclear reactor cores. Knolls Atomic Power Laboratory (KAPL) furnished about 4000 lb of typical core material, also known as hardware, for use in evaluating induction melting as a method of consolidation. Three ingots were produced by the induction melting of hardware in a graphite crucible that was protected by a laminated coating specifically developed for this application. This report includes a description of both the equipment and the crucible coating materials used for this project, a discussion of results, and a production assessment of using this technique for full-scale consolidation.

INTRODUCTION

In March 1991, representatives from the Y-12 Plant, KAPL, and Babcock & Wilcox met for discussions regarding the consolidation of submarine nuclear reactor core hardware, referred to as end-crops. This hardware, supplied as Government-Furnished Material (GFM), may contain stray radioactive particles. KAPL is faced with the disposition of a large (over 200 tons) inventory of hardware material and is interested in finding or developing the most practical and/or economical method for its disposition.

Consolidation is favored over burial because melting will declassify the shapes and result in an overall reduction in material volume. The ideal scenario is to recycle the consolidated material for resale. The standard industrial practice of large-scale consolidation would require that these end-crops be welded together to form an electrode that can then be arc melted; however, consolidation by arc melting is very expensive and labor intensive. Consequently, the Y-12 Plant Development Organization suggested using induction melting for consolidation.

The most significant technical barrier was potential contamination and/or reaction of the molten zirconium with the graphite crucible used in the Y-12 Plant induction melting operations. Of specific concern was preventing the possible contamination of ingots with materials spalling from the graphite crucible. A protective coating system, referred to as SLAMVIM (Super Laminate for Active Metals Vacuum Induction Melting) and developed at the Y-12 Plant, has proved very successful in preventing adverse reactions between the graphite crucible and molten zirconium.^{1,2} After development of this coating, the Y-12 Plant began taking steps to transfer the technology to full-scale operations in large casting furnaces.

KAPL prepared a specification whereby the Y-12 Plant was to supply 14- to 16-in.-diam consolidated ingots, each weighing at least 500 lb. Specifications also included the chemistry and characterization of the ingot material. A primary interest lay in the steps taken by the Y-12 Plant to prevent reaction with the graphite crucible and/or carbide contamination of the zirconium ingots.

PRESENTATION OF EXPERIMENTAL WORK

The most practical method for accomplishing full-scale consolidation appeared to require loading the end-crops into a coated graphite crucible, raising the temperature to 1950°C, and pouring the molten metal into a coated mold. For the initial full-scale experiment, the crucible and the mold (schematically shown in Figs. 1 and 2, respectively) were shipped to Applied Coatings, Inc., in Columbus, Ohio, where each piece received three plasma-spray-coated layers of SLAMVIM coating (shown in Fig. 3). The three layers were composed of the following materials:

1. 45 mils of molybdenum metal,
2. 10 mils of a 50/50 blend by weight of molybdenum- and calcium oxide (CaO)-stabilized zirconia, and
3. 15 mils of CaO-stabilized zirconia.

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Fig. 1. Schematic of plasma-coated graphite crucible.

Notes: All measurements are in inches unless otherwise noted. Material is graphite CS-312 or equivalent.

Fig. 2. Schematic of plasma-coated graphite mold.

Fig. 3. A cross section of SLAMVIM coating applied to crucible and mold.

When the crucible and the mold were returned to the Y-12 Plant in September 1992, the crucible contained an aluminum plug in the pour hole. The plug was inserted during the

plasma-spray process to facilitate application of the coating. Attempts to remove the plug cracked the coating in the area surrounding the pour hole. While discussing the use of a crucible having a damaged coating, the author loaded approximately 325 lb of end-crops into the coated mold for melting in the medium-size 16S casting furnace.

Furnace 16S is capable of a power output of 250 kW; however, it was operated at approximately 220 kW for the zirconium alloy melts. The vacuum was $<250\text{ }\mu\text{m}$ with a leak rate of $<500\text{ }\mu\text{m}$ over a 5-min period. The material appeared molten at 1860°C , but when the mold cooled, portions of end-crops within the solidified melt were not completely melted. This partially melted material could not be removed. The partially filled mold was then transferred to a different furnace, 18S, which is referred to as our high-temperature furnace. Enough material was added to produce an ingot weighing approximately 500 lb.

Furnace 18S does not have pouring capability but was designed and insulated to operate at higher temperatures than furnace 16S. Furnace 18S was operated at approximately 190 kW using an argon flow rate of $1.5\text{ ft}^3/\text{min}$. On December 12, 1992, the first ingot was successfully produced but could be removed only by breaking the mold. Figure 4 is a photograph of the first ingot, a quiescent or "dud" melt.

Fig. 4. Ingot 1, composed of consolidated Zircaloy-4 end-crops produced by a quiescent melt in furnace 18S.

The damaged coating of the crucible was patched with Zicar cement so that a melt-and-pour run could be attempted. Because the original coated mold was broken in removing the first ingot, another mold was prepared by lining its interior with Grafoil® and then painting wash coatings of TiN and zirconia onto the Grafoil® surface.

The standard operational practice for releasing a melt is to insert a rod down and through the molten pool, pushing the rod nose against a rupture disk until it breaks, thus

allowing the molten metal to flow into a mold directly below the crucible. On December 15, 1992, the material in the patched crucible was heated to 1950°C using furnace 16S; however, the pour rod was not successfully engaged. Because the rupture disk was not broken, the melt failed to pour. A second effort later in the day was successful after the third attempt broke the rupture disk, producing the first melt-and-pour ingot, shown in Fig. 5.

Fig. 5. Ingot 2, the first Zircaloy-4 ingot produced by melt-and-pour techniques in furnace 16S.

In the following weeks, a larger crucible and a tapered mold were designed (shown schematically in Figs. 6 and 7). Both were made, but only the crucible was plasma-spray coated with the same SLAMVIM materials used earlier. The mold was coated using a TiN wash coating and a zirconia wash coating. On February 25, 1993, a melt-and-pour run was attempted with a 700-lb charge but was unsuccessful when the operator had trouble locating and striking the pour hole rupture disk.

During this attempt, the stainless steel adaptor began to melt, and the operator was instructed to raise the pour rod. The graphite pour rod became disengaged from the adaptor and fell into the molten metal.

On March 4, 1993, another 73 lb of material was added to the large crucible, and a technique using a zirconium melt-out plug was attempted. The plug did not melt and release the molten metal. After a review of the situation, the crucible was raised 2 in. higher in the furnace in an attempt to better locate the effective heat zone. The charge was held at ~1950° to 2000°C for several hours but again failed to release. In an effort to raise the charge even higher into the effective heat zone, ~10 in. of the top of the crucible was sawed off. Another melt was attempted but did not pour. Plans for future melts using the large crucible were placed on hold.

1. **Material:** High-quality, mold-grade graphite meeting the requirements of GP-PP-00/24, Section 4.0.

2. Mark parts by mechanically engraving:
Manufacturer's ID: xxx
Unique serial: xxxxx
3. All dimensional features as flagged by this note are designated as critical; 100% inspection required for all parts. All other features must be dimensionally sampled per MIL-STD-1050: 1.5 AQL level II normal inspection or approved equal.

4. Minor fabrication and handling defects (i.e., scratches, nicks, gouges, chips, toolmarks, etc.) on noncritical features will be accepted within the limits of good handling and machining practices for graphite components. Any part exhibiting defects on critical features as designated by flag note No. 3 will be rejected. Inspection for defects will be performed on all manufactured parts.
5. Surface finish: 125 F.A.O.
6. All measurements are in inches unless otherwise marked.

Fig. 6. Schematic of large plasma-coated graphite crucible.

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Notes: All measurements are in inches unless otherwise noted. Material is graphite CS-312 or equivalent.

Fig. 7. Schematic of large, tapered graphite mold used to produce large Zircaloy-4 ingots.

The original crucible was reloaded with scrap material, and another melt-and-pour run was attempted on March 31, 1993, using a zirconium plate as a melt plug. Although the plug melted, the pool of molten metal did not pour. A dark gray, crust-like material was observed on the surface of the shiny zirconium metal. The crusty material was analyzed by the Plant Laboratory, which determined that it was a zirconia oxide with a structure or compositional phase different from that of the wash coating and, more importantly, a melting point greater than that of Zircaloy-4. The zirconia oxide crust was chipped away from the solidified contents at the pour hole, and the freshly exposed surface of the zirconium was painted with TiN only. On May 18, 1993, the charge was reheated in furnace 16S, reached 1950°C in ~4 h, and self-poured after 20 min at temperature, thus producing the third consolidated ingot. Figure 8 shows this ingot.

Chemistry results were obtained using spectrophotographic analysis of chips produced by drilling a hole in the ingot. Such chips are not normally used for gas analysis, so the data reported for the first two ingots may be suspect. A standard gas sample specimen, which is disk-like in shape, was machined from the third ingot and analyzed for oxygen and nitrogen.

Fig. 8. Ingot 3, the first Zircaloy-4 ingot produced using the self-pouring technique.

RESULTS AND DISCUSSION

The SLAMVIM coating appeared to have remained intact despite being subjected to extended periods at temperatures of from 1900° to 2000°C. Degradation and/or spalling of the graphite crucibles and molds did not occur. In fact, the SLAMVIM coating appeared to get stronger with each additional run. Ingots produced from each of the runs were somewhat less than ideal because of the problems encountered with the cracked coating and unforeseen difficulties experienced in attempting to scale the developmental work into a full-scale production mode, specifically the melt-and-pour process. The three ingots produced from consolidation of the end-crops were made using the original crucible that was damaged while the aluminum plug was being removed. The larger crucible, designed to facilitate application of the plasma-spray coating and to hold enough material to produce an 800-lb ingot, was unsuccessful because

1. the rupture disk knock-out capability was weakened when the stainless steel adaptor began to melt, allowing the rod to become disengaged;
2. the large radius of the inner contour of the lower portion of the crucible gives it a thicker graphite wall, which may fail to heat effectively within the induction field; and/or
3. free oxygen, generated by the long-term, high-temperature exposure of the zirconia wash coating and in-leakage of the furnace, resulted in the formation of a high-temperature zirconia oxide with a melting point in excess of 2000°C, inhibiting the liquid metal from flowing into the mold.

Despite design and operational difficulties, chemistry results and characterization of the three ingots were obtained. Table 1 provides the chemistry results. The first ingot, a quiescent melt, was sectioned for metallography. Figure 9 shows a representative area of the microstructure for Ingot 1. The matrix contained zirconium carbides that appeared as stringers selectively "highlighted" by the polishing solution (125 mL H₂O, 11 mL HNO₃, and 1.5 mL HF). These carbides, shown in Fig. 10, are more evident at higher magnification because the effects of the etchant were milder. Figure 11 shows the microstructure from Ingot 2, the first melt-and-pour ingot, which is in the fully etched condition. The etching solution is stronger than the polishing solution and consists of 45 mL H₂O, 45 mL HNO₃, and 10 mL HF. The microstructure representative of Ingot 3 (Fig. 12) appears to contain fewer carbides than Ingot 2. The reduction in carbides is consistent with the reduction in bulk carbon reported in the chemistry results in Table 1.

Table 1. Chemistry and gas results (ppm)

Source	Nb	Y	O	C	N	W	U _{Total}
Specification (max)	100	100	2000	350	100	100	3.5
Feedstock	<0.4	<0.03	NT	53	NT	NT	6.3
Ingot 1	<0.07	3	3317*	1168	70*	15	0.9
Ingot 2	0.8	22	6690*	1084	189*	16	7
Ingot 3	4	1	3023	701	133	3	0.4

*Results obtained from drilled chips are suspect; normally, these values are obtained from disk-like specimens machined specifically for gas analysis.

NA = Not available at press time.

NT = Not tested.

Fig. 9. The microstructure (at 50X-etched) of Ingot 1 shows stringer-like zirconium inclusions.

Fig. 10. The same microstructure of Ingot 1 as shown in Fig. 9 but at higher magnification (100X) before the effects of the etching solution are far advanced.

Fig. 11. The microstructure (100X) of Ingot 2 shows the spread of carbides throughout the matrix.

Fig. 12. The microstructure (100X) of Ingot 3 shows heavily etched carbides that appear to be an improvement (less carbide) over that shown for Ingot 2 in Fig. 11.

ASSESSMENT AND FUTURE WORK

SLAMVIM is a viable technique for consolidating this material and is less expensive than arc melting electrodes assembled from individual end-crops. Each end-crop weighs ~3 kg (6.6 lb), which equates to a volume reduction of 66% for consolidation for these prove-in runs. Greater reductions in volume can be achieved with larger crucibles/furnaces. In addition, classified shapes are destroyed in the melting process. Some lessons learned from this endeavor include the following.

1. The inability to knock out the rupture disk in the first melt-and-pour attempt is attributed to partial melting of the stainless steel adaptor, thus allowing the graphite rod to become wobbly and/or disengaged. Replacing the stainless steel with niobium should solve this problem.
2. The standard practice of using a knock-out rod requires the operator to be exposed to temperatures much greater than those generated by other melting jobs and may not be the preferred method of releasing a melt. The use of a melt-out plug appears to be an effective alternative method for releasing the molten metal.
3. The large graphite crucible may need to be redesigned so that the wall near the bottom is thinned out, thereby ensuring even heating by the induction field.
4. The effect of these high temperatures on the insulation is difficult to assess because of the extended periods of time spent holding the molten metal at temperature while trying to release the melt. Regardless of the number of runs predicted, even with ideal heat-up times and successful pours, effective insulation and maintenance of the furnace are required.
5. If the overall chemistry requirements, specifically the formation of large carbides, are relaxed and/or omitted, other techniques can be evaluated that would not be as harsh as the one experienced in this study. For example, the plasma-spray laminated coating would not be required, and melts could be consolidated using only furnace 18S, which is better insulated for these temperatures.

If the chemistry requirements specified for this job are maintained, including the ability to prevent the formation of large carbides, the recommended scenario for consolidation will be to use the SLAMVIM coating for the crucible and to coat a tapered mold with TiN. The pour hole will be redesigned and enlarged, making it easier for a niobium adaptor and knock-out rod to locate the hole. A melt-out plug is another option that could serve as the primary method of releasing a melt.

A proposal package is being prepared for future work.

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ACKNOWLEDGMENTS

The author would like to thank the following people for their assistance and input into this project and report.

Mechanical Operations

G. L. Ward

J. E. Thompson, Jr.

L. L. Francis

Program Management

C. W. Coates

A. P. Keller

Y. H. Tracy

W. E. Steinkamp

Development

C. E. Holcombe, Jr.

Knolls Atomic Power Laboratory

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C. D. Montgomery

W. G. Northcutt, Jr.

G. P. Patterson

T. R. Shope

W. E. Steinkamp

C. J. Swindeman

J. E. Thompson

J. E. Thompson, Jr.

Y. H. Tracy

G. L. Ward

Y-12 Central Files (Y-12RC)

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5/19/94

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