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OAK RIDGE Y-12 PLANT

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DEVELOPMENT OF A PLASMA COATING SYSTEM FOR INDUCTION MELTING ZIRCONIUM IN A GRAPHITE CRUCIBLE

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DEVELOPMENT OF A PLASMA COATING SYSTEM FOR INDUCTION MELTING ZIRCONIUM IN A GRAPHITE CRUCIBLE

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SUMMARY

A plasma coating system has been developed for induction melting zirconium at 1900°C using a graphite crucible. This laminated coating system consists of plasma spraying the following materials onto the graphite: (1) molybdenum or tungsten, (2) a 50% blend by weight of the metal powder and calcia-stabilized zirconium oxide, and (3) calcia-stabilized zirconia followed by painting a final coating of nonstabilized zirconia on top of the plasma-sprayed coating system. Zirconium was melted in argon using both laminating systems without any degradation of the graphite crucible and with only a minimal amount of carbon absorption. This novel approach that is being proposed as an alternative method of melting zirconium alloys offers substantial cost savings over the standard practice of electric arc melting using a consumable electrode.

INTRODUCTION

In March 1991, personnel of the Oak Ridge Y-12 Plant entered into discussions with a customer who was interested in disposing ~400,000 lb of obsolete Zircaloy® reactor core end crops for recycle applications. Disposal options presented in the briefing were burial, which is an unpopular position, and consolidation and recycle. These end crops are classified shapes that may contain isolated stray uranium oxides with radioactive readings up to 1.2 pCi²³⁵U/g. The primary method of consolidation discussed at the meeting would require that an electrode be assembled by welding the individual end crops together and shipping the electrode to the Y-12 Plant for electric arc melting using the production skull caster. Consolidation of these end crops by arc melting electrodes made by the customer appeared to be very costly and labor intensive. Consequently, an alternative method of consolidation by induction melting was proposed by Y-12.

The primary concerns about induction melting zirconium in a graphite system included finding a furnace that could perform the melt at 1900°C, which is much higher than the typical uranium melting temperature, and developing a coating system that could prevent carbon contamination of the melt primarily in the form of large carbides. A feasibility study was conducted in Development whereby various materials and designs were investigated. The results of those experiments indicated that melting zirconium in a plasma spray-coated graphite crucible was feasible, but further proof, especially in the area of carbon contamination, was needed. Based on those initial studies, the most promising coating system appeared to be a trilayered laminate of plasma-sprayed metal (molybdenum or tungsten), cermet, and refractory oxide (zirconia). A final wash coating using nonstabilized zirconia was added to provide a release mechanism and to minimize calcium contamination. Induction melting of zirconium in the plasma-sprayed molybdenum and tungsten coating system is the focus of this report. This coating system is referred to as Super Laminate for Active Metals Vacuum Induction Melting (SLAM VIM).

PRIOR WORK

The initial report of the investigation of a laminated plasma spray system for high temperature melting applications is found in Ref. 1. To the authors' knowledge, induction melting of zirconium in a graphite system has never been accomplished.

PRESENTATION OF EXPERIMENTAL WORK

Two 5-in.-diam. crucibles made from Grade CS graphite were plasma sprayed using the coating scheme shown in Fig. 1. In the first experimental coating system, molybdenum was used as the metallic layer, whereas tungsten was used for the other application. Coating thicknesses for the metal/cermet/zirconia were ~ 0.045 , 0.007 to 0.010, and 0.015 in., respectively. Lids, used to protect the molten zirconium from carbon monoxide in the furnace atmosphere, were plasma sprayed with zirconia. In addition, a wash coating of nonstabilized zirconia was painted onto the existing plasma-sprayed coating. Both plasma-sprayed crucibles, each of which contained ~ 5 kg of zirconium plate stock, were heated to $\sim 1900^\circ\text{C}$ in an argon-purged furnace in the Development Division.

RESULTS AND DISCUSSION

After the melting run was completed, the crucibles were removed from the furnace, the lids were removed, and, photographically, the results are shown in Fig. 2. The crucible in Fig. 2(a) represents the molybdenum coating system, whereas the crucible in Fig. 2(b) represents the tungsten coating system. Both systems produced "clean" melts with large grain structures caused by the slow cooling of the molten zirconium metal. Because of the customer's concern that induction melting in a graphite crucible might lead to spalling or degradation of the crucible, the coating system was removed from the crucible so that the interior surface of the graphite crucible could be examined. Figure 3 shows that the interior surface of the graphite crucible used in the molybdenum coating experiment showed no evidence of degradation. The other graphite crucible revealed similar results.

The disc-shaped zirconium castings were sectioned, as shown in Fig. 4, for metallographic and scanning electron microscopy (SEM) evaluation. The nonmetallic portion of the sectioned zirconium represents the portion of the plasma-sprayed zirconia layer that adhered to the casting. Except for some minor isolated fissuring near the metal/coating interface, the structural integrity of the casting was sound. The microstructures were also examined by metallography and SEM for carbides, most likely in the form of Mo_2C found in Ref. 2. Although a small number of carbides were detected in the zirconium cast in the tungsten-coated graphite, the relative size and distribution of the carbides were deemed insignificant. Carbides were not readily apparent in the zirconium section cast in the molybdenum-coated graphite crucible. Carbon analyses of each casting revealed an average of 311 ppm for the tungsten system and 283 ppm for the molybdenum system. Carbon analysis of the rolled zirconium plate stock, which was used as charge material, was ~ 50 ppm.

Figure 5 shows a portion of the molybdenum coating system. The left portion of the molybdenum layer, which was the surface in direct contact with the molten zirconium, was examined with SEM to characterize the degree of carbon diffusion into the metal. The slightly darker layer that extends vertically along the photomicrograph in Fig. 6 was identified as a carbon-rich zone indicative of carburization. The depth of carbon diffusion is $\sim 100\text{ }\mu\text{m}$.

PLASMA-SPRAY LAMINATED COATING SYSTEM FOR FINAL EXPERIMENTS

Y-GA 92-862 lhm

Fig. 1. Schematic of SLAM VIM used to melt zirconium.

Fig. 2. Crucible containing zirconium melted with molybdenum-laminated coating.
(a) Molybdenum-laminated coating and (b) tungsten-laminated coating.

(a)

(b)

Fig. 2. Crucible containing zirconium melted with molybdenum-laminated coating.
(a) Molybdenum-laminated coating and (b) tungsten-laminated coating.

Fig. 3. Interior surface of graphite crucible used to melt zirconium.
Note that no attack or degradation has occurred.

CROSS SECTIONS OF Zr MELT USING PLASMA SPRAYED LAMINATED COATING

Mo

W

Fig. 4. Cross sections of zirconium melted in tungsten-laminated coating and molybdenum-laminated coating.

Fig. 5. SEM view of primarily the molybdenum layer of the SLAM VIM coating. Note the gray zone on the left portion of the coating.

Fig. 6. Gray region from Fig. 5 that was identified as a carbon-rich zone indicative of depth of carbon diffusion through the molybdenum layer.

CONCLUSIONS

Induction melting of zirconium in a plasma-sprayed graphite system is feasible. Indeed, Induction melting of zirconium plate stock at 1900°C in argon has been demonstrated in Development using a plasma spray-laminated system consisting of a metal/cermet/refractory oxide. Although both molybdenum and tungsten were successful as the metallic layer, molybdenum appears to be more effective as a barrier to potential carbon contamination. One of the primary concerns of the customer was that pieces of the graphite crucible would spall or chip off into the melt, but this did not occur. The interior surface of the graphite crucible remained intact with no evidence of degradation. Although there was a slight increase in the carbon chemistry of the melt, the increase in carbon meets the customer's current requirement. More importantly, SLAM VIM produced a casting that was structurally sound and void of discernible carbides. The depth of the carbon-rich zone indicated that the plasma spray-laminated system using molybdenum as the metallic layer was very effective in impeding carbon diffusion. Using the results from this study, one could expect at least 11 more runs before the molybdenum layer would become completely saturated with carbon. In fact, at a constant temperature, the rate of carbon diffusion diminishes over time, as in the casting of steels (Ref. 3), so it is quite possible that the number of runs could be extended even further.

FUTURE WORK

SLAM VIM is being scaled up for casting in the medium-size, high temperature furnace in the H-1 Foundry. The customer has requested the Y-12 Plant produce five ingots weighing at least 500 lb each and will furnish about 4000 lb of end-crop hardware to evaluate the applicability of induction melting for consolidation of Zircaloy® for recycle options. Plasma spray activities are being performed by Y-12 Plasma Spray Group and Applied Coatings International in Columbus, Ohio. Applied Coatings International is scheduled to plasma spray the molybdenum/cermet/zirconia laminate on a graphite crucible that is 22 in. diam x 24 in. long, mold that is 18 in. diam x 32 in. long, and lid for the crucible.

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