Electrodeposited Copper Coatings for Used Fuel Containers

Peter Keech[1], Peter Lin[2], Neil Mahalanobis[2],

[1] Nuclear Waste Management Organization, Toronto, Ontario, Canada

(pkeech@nwmo.ca)

[2] Integran Technologies Inc, Mississauga ON, Canada

Abstract

Recently, copper coating of used fuel containers (UFCs) has been an area of research at the Nuclear Waste Management Organization, as copper offers a means of protecting steel UFCs from corrosion within a deep geological repository. The design is based on the application of a high purity copper coating directly to the surface of the UFC structural core. In the proposed fabrication sequence, vessel components would be delivered to the Used Fuel Packing Plant pre-coated with copper. Electrodeposition has been identified as a particularly adaptable method for this purpose; this paper will present applied research in this area.

1. Introduction

The Nuclear Waste Management Organization (NWMO) was established in 2002 in accordance with the Nuclear Fuel Waste Act to assume responsibility for the long-term management of Canada's used nuclear fuel. The program, Adaptive Phase Management, will include used fuel retrieval from reactor sites and placement in an underground Deep Geological Repository (DGR), including all transportation and repackaging required (NWMO, 2010). Figure 1 illustrates the conceptual DGR, including the most recent used fuel container (UFC) and emplacement designs. This facility will be sited at a willing host community in Canada, in a suitable geological environment, at a reference depth of approximately 500 m; NWMO siting has been underway since 2010.

In 2012, the NWMO undertook an optimization study to look at both the design and manufacture of its engineered barriers for the DGR. The UFC was assessed in terms of design options available specific to CANDU fuel bundles which are smaller (0.5 m in length) and lighter (25 kg) than PWR/BWR fuel bundles. From this study, a UFC design (the "Mark II") consisting of a 2.7 tonne used fuel container (~2.5 m length x 0.57 m Ø) with a carbon-steel core, copper-coated surface and welded spherical heads was selected for development and testing. The copper coating is applied to the steel as a corrosion barrier for which thermodynamically favourable corrosion processes are few in the DGR. The design thickness of 3mm is >100% larger than the ~1.3 mm corrosion allowance predicted for one million years[2]. The copper coating will be conducted in two stages:

- The container head and body will be copper coated and inspected in a factory prior to arrival at the radiologically active Used Fuel Packaging Plant. A narrow zone will be left uncoated where the container weld will be performed;

- A container that has been filled with used fuel and welded shut will have the weld zone copper coated within the radiologically active used fuel packaging plant.

Owing to the large difference in industrial processes required (i.e. radiologically active vs. conventional industrial processes), two coating applications are being considered. The current reference process for the weld zone is cold spray, while for the head and body, electrodeposition is planned. In principle, the absence of radiation during fabrication simplifies the electrodeposition operations; however, the shape and quality of the copper coating required have required innovation to produce material satisfying the required mechanical/metallurgical/quality requirements. This paper will outline the research work to date that has been undertaken as part of a multi-phase program of technology development and application demonstration through the fabrication and testing of electrodeposited coupons and UFC vessel components.

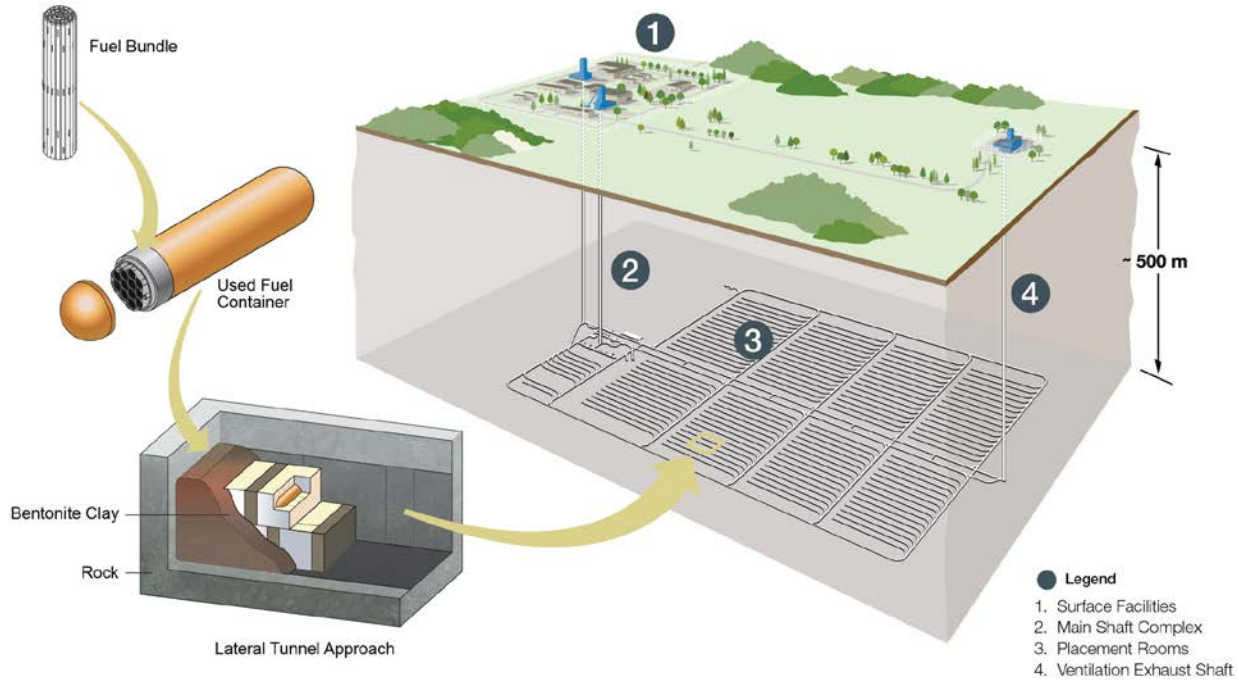


Figure 1: Schematic view of the deep geological repository concept for Mark II containers

2. Electrodeposited Coating Requirements

Based on structural analysis, a preliminary mechanical property requirement for copper coatings has been set at a minimum ductility of 10% (as measured via tensile elongation prior to fracturing). In

addition, a minimum for adhesion strength of 20 MPa is required. In aid of coating parameter development, values of 15% elongation and 60 MPa adhesion strength were set as a target to achieve sufficient margin. Addition metallurgical /chemical requirements are as stated below.

Table 1: Physical and Chemical Electrodeposited Copper Coating Requirements

Criteria	Test Description	Requirement/Result
Copper Purity (quantitative)	Elemental Analysis for Sulphur	< 10 ppm
	Elemental Analysis for Carbon	< 10 ppm
	Elemental Analysis for Oxygen	< 50 ppm
	Elemental Analysis for Copper	>99.9%
Copper Purity (qualitative)	Microscopic inspection following Heat Treatment to 800°C for 1 h	Micrographs showing low levels of porosity as a result of oxygen desorption at high temperature
Adhesion Strength (Quantitative)	As measured in Modified Tensile Test ASTM E-8	>60 MPa Adhesive strength
Adhesion Strength (Qualitative)	Optical/microscopic inspection following Bend Testing	No delamination along coating-substrate interface and no cracking of coating
Hardness	Microhardness (through thickness)	100-200 VHN_{50}
Ductility	Elongation via Tensile Test ASTM E-8	> 15% Elongation
Metallographic Record	Microscopic inspection of etched samples demonstrating coating microstructure	Clear evidence of grain recrystallization within micrographs (indicates high-purity copper by absence of grain boundary pinning)
Thickness	Microscopic inspection (test coupon) or NDE (UFC components)	Achieve thickness requirement of 3 mm - 0/+1mm

3. Electrodeposition Process

Prior to electroplating parts, it is necessary to prepare the steel substrate in a manner that leaves the steel smooth and clean, so that the copper can adhere appropriately. The specific intellectual property is protected; however, a general scheme follows.

- To accomplish good substrate properties, the steel was machined to a roughness of 3.2µm (R_a), and then coated in machining oil for storage until the initiation of the coating process.

- Prior to the application of the coating, the oil was removed with degreaser, and the substrates underwent cleaning and activation steps. These steps included cleaning with alkaline solution, rinsing, acid activation, and rinsing, prior to immersion into the electrodeposition strike solution.

- The strike solution was based on copper cyanide chemistry, and was applied via DC plating for a few minutes.

- Following subsequent rinsing, the main coating was applied in a copper pyrophosphate bath via pulsed plating. In this case, the coating was applied for several days to achieve the required thickness (i.e. > 4 mm).

- To achieve a smooth coating, the coating underwent post-deposition machining to produce a final coating 3 mm thick, with a roughness of approximately 1.6 µm (R_a).

Of note, the coatings have been produced without using organic levellers, as these have been known to be co-deposited with the metallic species. While this is not a universal phenomenon, to date the use of levellers has been avoided to ensure an absence of coating contamination and achieve a copper purity >99.9%. A leveller free chemistry results in surface asperities (nodules) to which post-deposition machining is required; the coating deposit is however, fully dense.

4. Coating Development

4.1 Coupons and Small Samples for Electrodeposited Copper Coatings

As noted above, the electrodeposition program has been conducted over a series of phases, which have focussed on increasingly complex geometries and larger substrates. Some coatings have included free-standing materials, which were deposited on titanium, on which there is no adhesion; these are convenient for assessing coating properties in the absence of the steel substrate. Figure 2 depicts typical results from phase 1 as bent coupons for freestanding copper and copper plated on steel.

(A) (B)

Figure 2: Electrodeposited copper bend test coupons showing (a) freestanding copper and (b) copper plated on steel

Coupons of this type have been extensively characterized by physical means: bend testing shown in Figure 2 as per ASTM E290-09 [1]; tensile testing[2] (for ductility/elongation); microhardness[3], as well as by spectroscopy/image analysis and by chemical analysis. zTensile testing, shown in Figure 3 reveals both high ductility of 40% and a high ultimate tensile strength (UTS) of > 300 MPa; the latter is particularly impressive, as high purity, wrought polycrystalline (copper has a UTS on the order of 200 MPa[4]. The electrodepostited material is also harder than wrought copper, with typical values of 105±10 VHN_{50} vs. SKB copper's value of 81±4 VHN_{50}[4]. This combination of high tensile strength, hardness and elongation displayed by the electrodeposited copper is an effect of the fine grained microstructure.

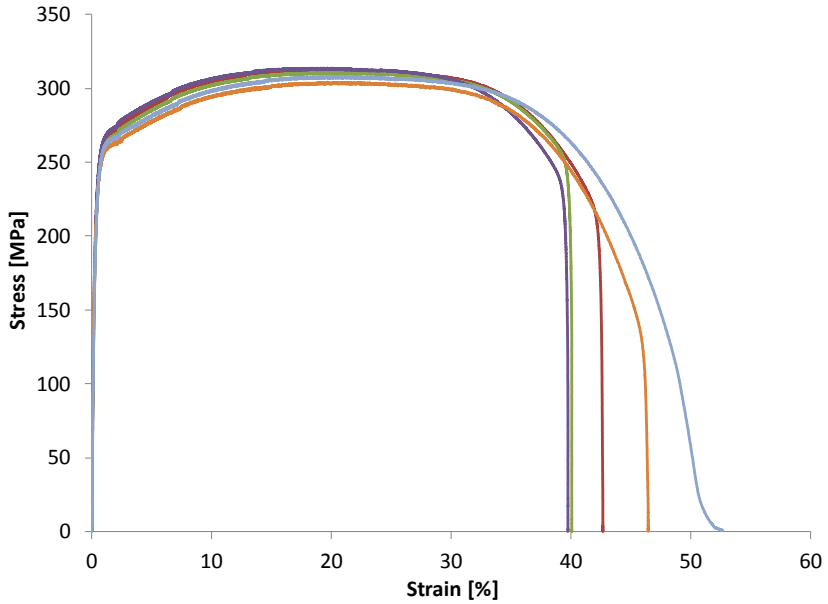
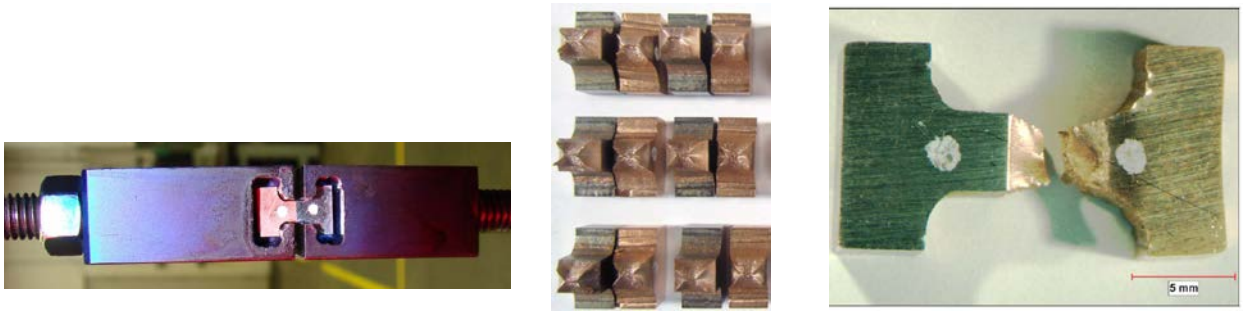


Figure 3 Electrodeposited copper coatings stress strain curves indicating high ductility (~40%) and high ultimate tensile strength (~300 MPa)

Regarding adhesion, physical testing (i.e. bending, chiseling) has been conducted for qualitative evaluation, and significant work has been applied to quantify the copper-to-steel adhesion strength directly. In these cases, very thick coatings must be applied, and small bi-metallic coupons must be machined out to conduct pull tests as per a modified ASTM E08 tensile test[2]. Figure 4A illustrates the copper-steel composite "dog-bone" coupon in the testing rig. A total of 15 miniature bi-metal dog-bone coupons were fabricated and evaluated. The average yield and ultimate strengths were 242±4 MPa and 271±3 MPa, respectively. Collectively, all 15 samples failed within the copper region exhibiting ductile failure with an average of 33±7% elongation to fracture. Most significantly, there was no evidence of interfacial delamination at the copper-steel interface (Figure 4 B and C), indicating exceptional adhesion strength was achieved.

Chemical analysis and embrittlement of the coating were used to assess coating purity, and residual oxygen, respectively. Greater than 99.9% copper was obtained in all samples. The (embrittlement testing) heating of the copper sample to 900 °C did not reveal any porosity in the subsequent surface analysis; this would indicate that oxygen comprises < 50 ppm of the coating. These results were useful, along with those above, in proceeding to subsequent electrodeposition programs.



(A) (B) (C)

Figure 4: (A) Bi-metallic (copper-steel) E08 coupon for adhesion test in test rig and typical adhesion results (B) end-on view and (C) side-on view.

4.2 Arc/cylindrical samples, Container Geometries for Electrodeposited Copper Coatings

Subsequent coatings were applied to more realistic substrates to validate the amenability of this method to UFC fabrication. Samples included arc materials, which were cut from near full sized UFC cylinders, as well as miniature UFC mock-ups, Figure 5 and Figure 6, respectively.

(A)

(B)

(C)

Figure 5 Images of 20" NPS schedule 120 pipe (A) as-received; and after application of copper to a target thickness of 3 mm to an arc segment 46 cm x 46 cm projection (b) facing view and (c) cross-sectional view (right).

(A)

(B)

(C)

(D)

(E)

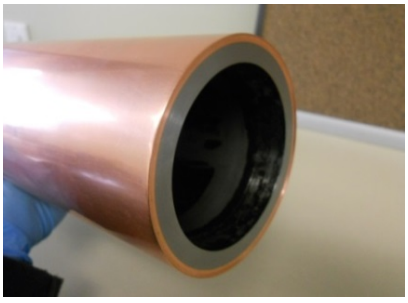


Figure 6: Images of small cylinder - 4"OD x 0.3" Wall x 12" Length – (A) uncoated with hemihead; and after application of copper to a target thickness of 3 mm: (b) as-deposited; as-machined showing (c) the full length; (d) the hemispherical portion and (e) the base.

As above, these components were extensively characterized via surface analysis, mechanical/chemical testing protocols; in some cases (i.e. where flat substrates are required), companion coupons produced

within the same baths were selected for assessment. Within Figure 6, the nodularity that occurs during the coating process is evident in (B); as noted above, the nodules are fully dense, and readily machineable Figure 6 (C)-(E). To account for nodularity, the components are slightly overplated to approximately 3.5 mm; this allows for a small amount of excess material to be removed, while maintaining a minimum thickness of 3 mm for the coating.

4.3 Full Sized Container Components for Electrodeposited Copper Coatings

Prior to production of large scale parts, it was necessary to increase the capacity of the electrodeposition cells, such that the large areas could be accommodated. Equipment such as voltage sources, substrate supports and the tanks themselves were scaled up, and some rudimentary current flow distributions were modelled using finite element methods. Subsequently, full scale hemispherical heads were coated, as shown in Figure 7; within this figure, the as-deposited coating (A) and the as-machined coating (B) can be observed. A shortened version of the full container was also fabricated and coated, as shown in Figure 8; (A) and (B) illustrate the steel only and coated part, respectively. The shortened container has also undergone machining operations (not shown).

(A) (B)

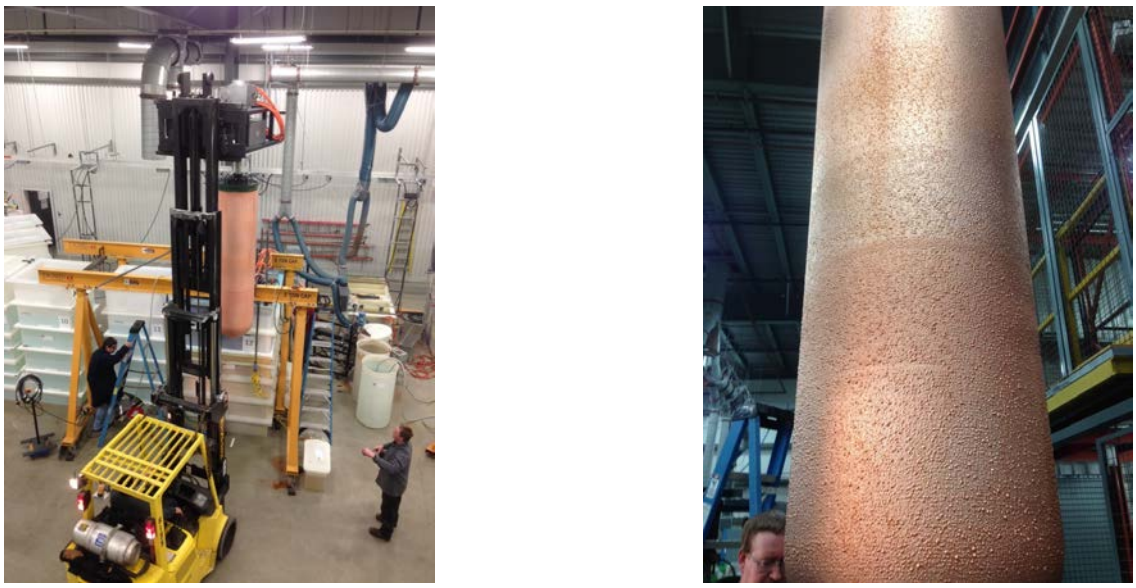
Figure 7: Hemispherical head coated by electrodeposition (a) as deposited and (b) as machined

Witness coupons were produced before and after production runs to validate that the bath chemistry was maintained throughout the processes, such that destructive testing of these samples has not been conducted, as yet. In the future, it is expected that some parts produced in this manner will be destructively examined.

(A) (B)

Figure 8: Short Container (a) prior to and (b) immediately following coating by electrodeposition.

Most recently, electrodeposition has been used to produce a full sized container, as shown in Figure 9, which has concluded the development phase of electrodeposition.



(A) (B)

Figure 9: Full length container following coating by electrodeposition following removal from plating tank illustrating (a) full container and equipment, and (b) closeup of container surface.

Following machining operations, the full sized container will undergo seal welding with a container head (Figure 7) to produce the full container; the sealed container will subsequently be coated over the weld zone via cold spray, such that the entire copper coating operation can be demonstrated.

5. Conclusions and Future Directions

The electrodeposition program to date has focussed on developing full sized parts, through a range of substrate geometries and sizes. The program has followed through activities involving (i) coating initial development, (iii) coating validation, and (iii) scale-up and prototype UFC activities, each of which has proven successful. Full sized parts are now available for testing purposes.

Ongoing efforts are proceeding to produce additional full size UFC vessels for parallel NWMO programs and testing purposes. In addition, the research program will target the development of manufacturing specifications for these items, such that they may be rapidly produced in a production environment. Properties such as bath chemistries, process temperatures, material handling, etc. have all been optimized, but it is necessary to define how wide the optimal operation windows are, to assess coating production when operational windows are exceeded, and to determine process success/failure assessment criteria.

6. References

[1]. ASTM, 2009, Standard Test Methods for Bend Testing of Material for Ductility, ASTM E290-09, ASTM International, West Conshohocken, USA.

[2]. ASTM, 2008, Standard Test Methods for Tension Testing of Metallic Materials, ASTM E8/E8M-08, ASTM International, West Conshohocken, USA.

[3]. ASTM, 2009. Standard Test Method for Microhardness of Electroplated Coatings, ASTM B578-09, ASTM International, West Conshohocken, USA.

[4]. E.T.C. Ho, A.M. Brennenstuhl, 2000. “Characterization of samples from as-received and heat-treated electron beam welded Cu-OFP prototype canister shell material supplied by SKB.” Report No. 06819-REP-01300-10009-R00, Ontario Power Technologies, Toronto ON, Canada.