

Cold Spray Copper Corrosion in the Presence of Humidified Gas

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The long-term disposal plan of high-level nuclear waste in Canada, involves emplacement of radioactive materials within a deep geological repository (DGR), providing multi barrier environmental protection for 1 million years. Waste materials will be sealed in copper-coated steel containers (used fuel containers, UFCs), providing a combination of mechanical strength and corrosion resistance. Cold spray copper coating is proposed as an additive manufacturing thermal spray process to protect the weld region between the body and the head of the of the UFC after fuel has been loaded into the container. This technique relies on the acceleration of fine copper particles (20-53 μm) toward the exposed weld region, where they plastically deform on impact and adhere. This produces a controlled layer by layer deposition of copper on the container surface and is used to seal the corrosion resistant copper envelope of the UFC.

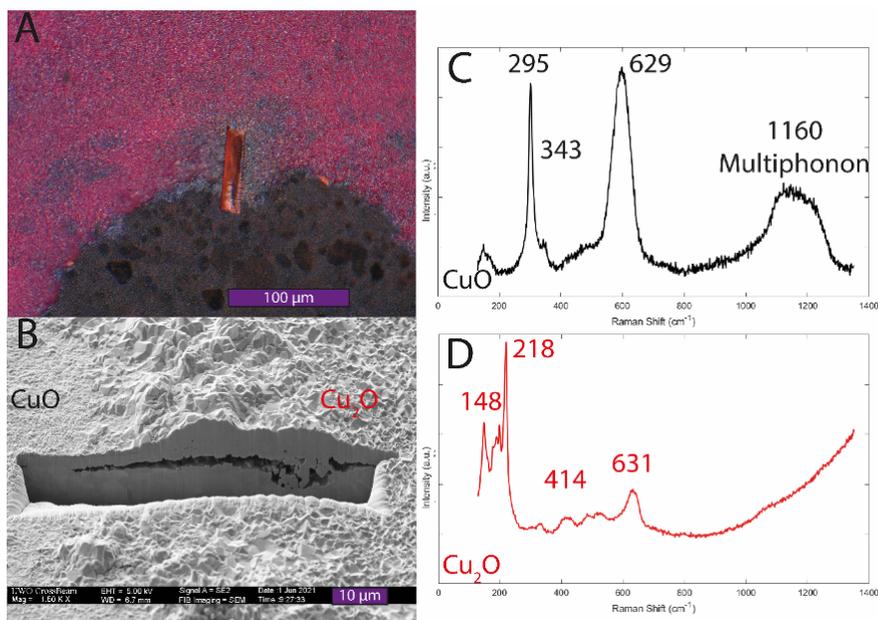


Figure 1 - NaCl coated cold spray copper.

(a) Optical image of CuO and Cu₂O oxide transition on surface of material. (b) FIB cross section of oxide films. (c) Raman spectra of predominantly CuO oxide. (d) Raman spectra of predominantly Cu₂O oxide.

During the early stages of emplacement, conditions in the DGR are expected to be humid, warm, and aerated. These conditions allow for possible corrosion conditions as water deliquesces on the material surface. Cold spray copper samples were prepared for 1-month humidity chamber experiments (RH 70% at 75°C for 31 days). Samples were prepared in both an as-polished state, as well as in a salt coated (NaCl) state. Through the use of inkjet printing, highly controllable salt films can be deposited on the material surface prior to exposure to the humidified atmosphere of the chamber. Salt exposed samples were observed to form both CuO and Cu₂O oxides on the surface of the cold spray material (Figure 1a). Focused ion beam (FIB) cross sections of the transition regions between these two oxides showed predominantly Cu₂O in contact with the bulk cold spray copper, and CuO layers formed on top of this lower layer. Voids and small regions of partial delamination were also common along the oxide metal interface (Figure 1b). Raman spectra of the oxides confirmed sites of predominantly black CuO and red Cu₂O species on the copper material (Figure 1c,d respectively).

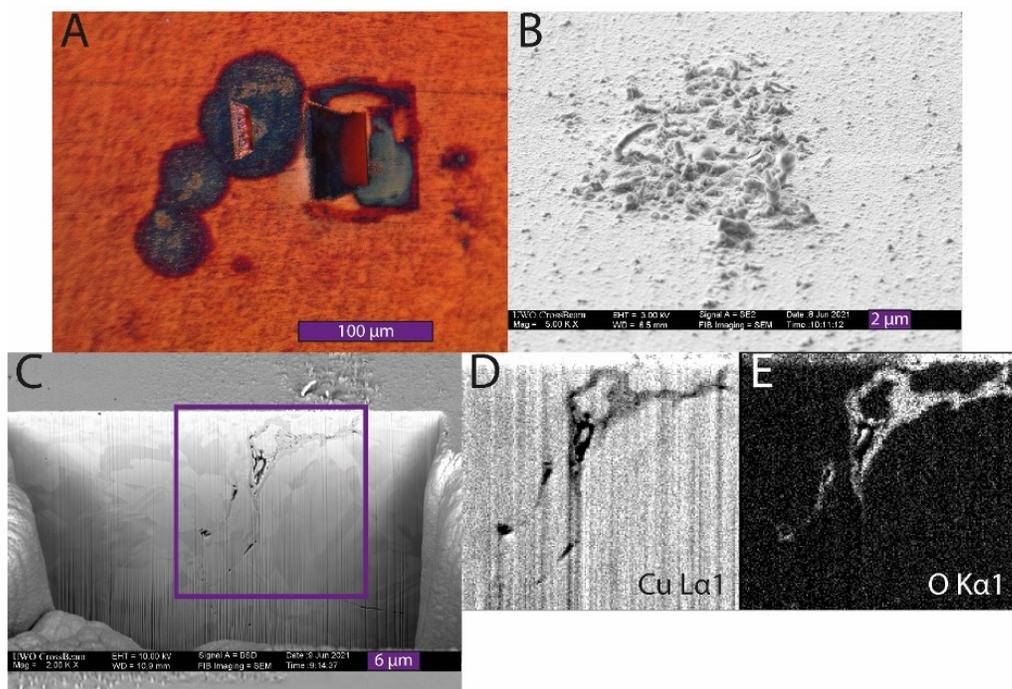


Figure 2 – As polished 31-day humidity chamber sample.

(a) Optical Image of blue corrosion product on cold spray copper. (b) SEM of CuO corrosion product above subsurface void. (c) SEM image of subsurface void structure. (d,e) EDX mapping of Cu La1 and O Ka1 respectively.

As-polished cold spray copper samples exposed to humidified conditions over the 31-day period exhibited the formation of a thin (50-65 nm) Cu₂O oxide film across the surface of the samples. These samples did however have occasional sites where a blue/purple corrosion product could be seen (Figure 2a). These sites often had a small black CuO oxide observed in the centre. The 3D structure of this corrosion product becomes visible by SEM (Figure 2b). Performing a FIB cross section of one of these sites exposed the presence of a subsurface void defect structure in the cold spray copper, where access to the humidified atmosphere at the surface was possible (Figure 2c). EDX imaging indicated the presence of copper oxide on the interior of the subsurface voids, and connecting many of these voids to each other along the particle splat boundaries (Figure 2d,e).

These techniques are being used to characterize the influence of material impurities in cold spray copper on the long-term viability of the corrosion barrier of the UFC container for the safe permanent disposal of nuclear waste in Canada.

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