

Mechanism and Inhibition of Preferential Corrosion of Cold-Sprayed Copper in Dilute Nitric Acid

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Abstract

Cold-sprayed copper is a promising additive manufacturing material for a range of applications, including used nuclear fuel containers. Under aggressive dilute nitric acid conditions, it exhibits preferential corrosion associated with the oxide network incorporated during fabrication, a phenomenon that remains poorly understood. Here, we systematically investigate the mechanism of this preferential corrosion by varying the presence of dissolved oxygen and the concentrations of copper ions and chloride. By exploiting the inhibitive effect of chloride on nitrate reduction, we show that nitrate reduction is necessary before the initiation of preferential attack at the oxide-rich particle-particle boundaries can occur. In addition, dissolved copper ions substantially accelerate corrosion, providing direct experimental evidence for their proposed catalytic role. Material loss is ultimately dominated by particle detachment following preferential dissolution along the oxide network. These findings provide new insight into the corrosion mechanism of cold-sprayed copper in dilute nitric acid and indicate that preferential corrosion is specific to nitrate-containing, chloride-free environments.

Highlights

- Cold-sprayed copper exhibits minor preferential corrosion in deaerated, 0.1 M HNO₃
- Presence of copper ions promotes preferential corrosion in deaerated, 0.1 M HNO₃
- Preferential corrosion is inhibited in 0.1 M HNO₃ + 4 mM HCl with O₂, Cu, or NO
- Initiation of preferential corrosion is attributed to local nitrate reduction
- Chloride protects the particle-particle boundaries from accelerated dissolution

1. Introduction

Copper exhibits high electrical conductivity, antimicrobial activity, and corrosion resistance, making it a good material for electronics, medical devices, and structural components[1–4]. Moreover, copper coating technologies, e.g., electrodeposition, vapor deposition, thermal spray, and cold spray are attractive methods for producing thin copper coatings with these desired properties[5–7]. Cold-sprayed copper, in particular, has attracted significant attention as an additive manufacturing method due to its versatile implementation for critical repairs, intricate substrate fabrication, and alloy/composite coatings fabrication[8–10]. Due to the relatively low oxygen incorporation and mild structural alterations during the coating process, cold-sprayed copper often exhibits good performance, although post-fabrication treatment may be needed[9, 11, 12]. For this reason, copper cold spray is being considered by Canada's Nuclear Waste Management Organization (NWMO) as a potential coating material for nuclear waste packages[13].

While copper materials are generally thermodynamically immune to corrosion by pure water under anoxic conditions, they are susceptible to corrosion in the presence of strong oxidants, such as oxygen,

hydrogen peroxide, and nitric acid. Cold-sprayed copper often has a corrosion behavior similar to that of more common copper materials, such as electrodeposited and wrought copper[14, 15]. However, several studies of cold-sprayed copper corrosion have recently found that under specific conditions, such as aerated dilute nitric acid, cold-sprayed copper exhibits preferential corrosion, particularly at particle-particle boundaries [16]. Recent work has shown a clear relationship between this preferential corrosion and the distribution of oxide inclusions in the cold-sprayed copper[17]. These oxides are presumed to be incorporated at the particle-particle boundaries during the fabrication process, arising from the oxide film on the feedstock copper particles, and the particle-particle boundaries form a network within the cold-sprayed copper. Upon exposure to aggressive conditions, dissolution of the particle-particle network accelerates. The resultant copper substrate is left with a network of grooves extending into the depth of the material, and previous work has found that these grooves are close to 100 μm in depth. At this time, there have been no quantitative studies on the effect of preferential corrosion on the overall corrosion damage; however, some qualitative studies show that it can be impeded by increased annealing temperatures to coalesce the oxide network [17].

While these studies provide an additional understanding of how material fabrication and treatment parameters affect localized corrosion of cold-spray copper, the mechanism and role of solution parameters are not fully understood. It has been shown that the corrosion mechanism of copper in nitric acid is autocatalytic, with the corrosion products (copper ions, nitrite, nitrogen monoxide, etc.) acting as corrosion accelerators[18]. In dilute nitric acid, autocatalytic behavior has been proposed to be mostly driven by copper ions in solution. This claim is based on the large difference in the corrosion rates of wrought copper observed under deaerated and aerated conditions (where corrosion due to oxygen produces copper ions), and on electrochemical measurements[19–21]. However, direct evidence of a catalytic effect of copper ions on corrosion behavior has yet to be demonstrated. The relative roles of nitrate reduction, oxygen reduction, and copper-ion-mediated catalysis also remain unresolved. A better understanding of the corrosion mechanism of copper in dilute nitric acid would provide insights into the extent of preferential corrosion in cold-sprayed copper coatings possible under various conditions. More specifically, the NWMO may need to weigh this information during its future design updates of the container.

Herein, we assess the overall corrosion damage from preferential corrosion and evaluate the corrosion mechanism of cold-sprayed copper in dilute nitric acid by tuning solution parameters. We added copper ions to the solution to provide direct experimental evaluation of their proposed catalytic effect on (preferential) corrosion. Moreover, we performed experiments with and without small amounts of chloride present to inhibit nitrate reduction, the main cathodic reaction, to evaluate its role in the corrosion behavior. *Ex-situ* surface characterization of corrosion morphology was done by scanning electron microscopy (SEM), atomic force microscopy (AFM), and stylus profilometry, while electrochemical methods were used to examine the electrochemical reactions contributing to corrosion.

2. Materials and Methods

2.1. Materials

In this work, 4-mm-thick cold-sprayed copper coatings were deposited by a cold-spray system (Plasma Giken PCS-800), using N₂ carrier gas at 800°C and 4.9 MPa. The specimens were annealed in air at 350°C for 1 h. Artificially high oxygen-containing cold-sprayed copper was fabricated by pre-oxidizing the feedstock particles in air before cold-spray deposition. The oxygen levels were 123 ppm and approximately 693 ppm for standard cold-sprayed copper and high-oxygen cold-sprayed copper, respectively, as determined by inert gas fusion (Canmet, Canada). Electrodeposited copper was fabricated using a pulse-current plating method in a pyrophosphate electroplating bath. Cold-sprayed and electrodeposited copper were provided by the NWMO. Additional information on the materials characterization and fabrication has been published in detail elsewhere[16, 17, 22]. Oxygen-free, phosphorus-doped (30–100 wt. ppm) wrought copper (Cu-OFP) was supplied by Svensk Kärnbränslehantering AB (SKB, Sweden).

The copper materials were cut into 6 mm cubes with one side drilled, tapped, threaded, and fitted with a steel rod. Specimens for surface analysis were ground to a final grit level of P4000 before being sonicated in methanol and polished with a 1 µm diamond suspension (Struers, Denmark), rinsed with ultrapure water, sonicated again in methanol, and then blow-dried under argon. Specimens for electrochemical measurements were mounted in STYCAST HD 3561 (10:1.5 v/v epoxy/hardener) epoxy and ground to a final grit level of P1200 SiC (Buehler, US).

Nitric acid (ACS plus grade) was obtained from Thermo Fisher Scientific (US) and used as received. Fine Cu₂O powder was used for preparing Cu₂O-containing mixtures. Mixtures were stirred carefully after powder addition to ensure that the Cu₂O was properly dissolved before copper specimens were added[23].

2.2. Surface Characterization

SEM was carried out using a Hitachi SU3500 variable pressure scanning electron microscope. The working distance was approximately 10 mm, and the imaging accelerating voltage was 10–20 keV. Stylus profilometry was carried out with a KLA-Tencor profilometer (P-17, KLA, US) equipped with a diamond probe having a nominal radius of 2 µm. AFM topography imaging was carried out in tapping mode using an XE-100 Park atomic force microscope (Park Systems, South Korea) with a HQ:NSC15/no Al cantilever (MikroMasch, Bulgaria) having a nominal spring constant of 40 N/m, resonant frequency of 325 kHz, and tip radius of 10 nm. Slope correction of AFM and profilometry data was performed using flattening in Gwyddion software.

2.3. Electrochemical Measurements

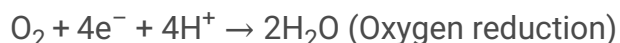
Electrochemical measurements were carried out with a Modulab XM ECS (AMETEK, US) potentiostat in a custom-made, three-electrode electrochemical cell with a final solution volume of 600–700 mL. All reference potentials were obtained from an in-house-fabricated double-junction Ag/AgCl reference

electrode that was used in all experiments. The Ag/AgCl reference electrode was calibrated versus a commercial saturated calomel electrode (SCE) prior to all measurements. A Pt wire or mesh was used as the counter electrode. All electrochemical measurements were carried out with a potential sweep sequence after 2 h under open-circuit conditions to allow the system to achieve a steady state (Supporting Information, Figure S1). All scans were started from E_{corr} with a scan rate of 2 mV/s. No iR -compensation was used.

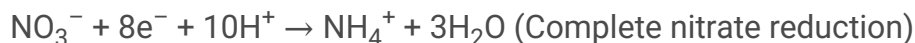
3. Results

3.1. Corrosion of Cold-Spray and Electrodeposited Copper in Deaerated, Dilute Nitric Acid

Preferential corrosion of cold-sprayed copper has been shown to occur in aerated 0.1 M HNO₃[16]. Under such conditions, two cathodic reactions, oxygen and nitrate reduction, are possible:

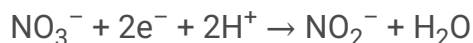


Equation 1



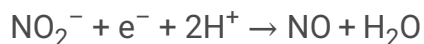
Equation 2

The first step in nitrate reduction is the formation of NO₂[−], which is the rate-limiting step[24]:



Equation 3

This is followed by the more rapid reduction of NO₂[−] to NO[25, 26], which is the main end product observed under cathodic polarization:



Equation 4

During copper corrosion in dilute nitric acid, N₂O has been observed in previous reports, but it is presently unclear whether it is formed from NO reduction or by vapor-phase reactions[17].

To better understand the dominant reactions involved in the preferential corrosion of cold-sprayed copper, immersion experiments were carried out in deaerated 0.1 M HNO₃, where only nitrate (and nitrite) reduction can occur. The corrosion morphology of cold-sprayed copper after 72 h of immersion is

displayed in Fig. 1A, showing that corrosion is substantially less severe than reported for aerated conditions (shown in Fig. 3A for comparison). However, the morphology image reveals that corrosion occurs preferentially at the oxide inclusions, the network of oxides originating from the native oxide present on the feedstock particles[17, 27]. Preferential corrosion at these locations was also confirmed by quantitative AFM topography measurements (Supporting Information, Figure S2). No significant dissolution of the oxide network was seen in non-oxidizing acid (H_2SO_4 at the same pH, Supporting Information, Figure S3). These results show that preferential corrosion can be initiated in the absence of molecular oxygen, but with the overall corrosion being much less severe. The preferential attack at the particle-particle boundaries is possibly related to an increase in the local electrochemical activity of copper oxides towards nitrate reduction[28, 29], and/or that the copper ions that are released from/at the oxide inclusions can act as homogeneous solution catalysts[17, 19], either through solution reactions or by modulating the electrochemical activity[21].

To better understand the corrosion mechanism, the involvement of dissolved copper ions was evaluated, as they can be easily added to the immersion solution. The corrosion morphology of cold-sprayed copper in 0.1 M HNO_3 , in the presence of Cu^+ (as 1 mM equivalent of Cu_2O powder, which is above saturation), and in the presence of 1 mM Cu^{2+} (as $\text{Cu}(\text{NO}_3)_2$) is shown in Figs. 1B and C, respectively. For both conditions, the characteristic preferential corrosion morphology is dramatically enhanced and is closer to that seen in experiments performed under aerated conditions. These results support previous interpretations and provide direct experimental evidence for a catalytic role of copper ions on corrosion in dilute nitric acid. In contrast, fine-grained electrodeposited copper showed a relatively uniform corrosion morphology under these conditions, but more severe corrosion was also observed when copper ions were present (Fig. 1D-F).

3.2. Effect of Chloride on the Corrosion of Cold-Sprayed and Electrodeposited Copper in Dilute Nitric Acid

Previous studies have shown that when chloride is present in the solution, nitrite reduction is significantly inhibited. We have previously quantified this inhibitory effect during corrosion and found that 0.16 mM chloride inhibits nitrate reduction by approximately 50%, while 4 mM totally inhibits nitrate reduction on Cu-OFP[23]. To better understand the role of nitrate reduction in preferential corrosion and the corrosion-accelerating effect of copper ions on cold-sprayed copper corrosion in dilute nitric acid, we performed immersion experiments in the presence of 4 mM HCl [28, 30, 31]. An SEM image of cold-sprayed copper after 72 hr immersion in 0.1 M HNO_3 + 4 mM HCl is shown in Fig. 2A, confirming that corrosion is almost completely inhibited. The pores seen are intrinsic to the material, and their sharp edges suggest no corrosion occurred in these areas. Areas with no pores showed only mild oxidation and increased surface roughness compared to Cu-OFP under the same conditions[23] (8 nm versus 20 nm, respectively, Supporting Information, Figure S4). However, when copper ions were also present, there was mild corrosion activation, but the corrosion morphology was uniform (Fig. 2B-C). Moreover, electrodeposited copper also showed a uniform corrosion morphology. These results suggest that

preferential particle-particle boundary attack is related to the local nitrate-reduction activity. Moreover, chloride inhibits particle-particle boundary attack even in the presence of dissolved Cu ions, although Cu ions can partially overcome the inhibiting effects of chloride.

To evaluate whether chloride can inhibit particle-particle boundary attack under more aggressive conditions, experiments were carried out in aerated 0.1 M HNO_3 . Preferential corrosion was seen in the absence of chloride, which is in agreement with previous reports (Fig. 3A)[16, 17]. In the presence of 4 mM HCl, a uniform corrosion morphology was seen (Fig. 3B). In fact, even when 1 mM NaNO_2 , another strong oxidant, was additionally added, there was still no evidence of particle-particle boundary attack (Fig. 3C). The inhibition of particle-particle boundary attack under these more aggressive conditions with chloride further supports the involvement of nitrate reduction in the initiation of preferential corrosion. To confirm that particle-particle boundary attack requires the presence of nitrate, the corroded surface of cold-sprayed copper after immersion in aerated 0.05 M H_2SO_4 is given in Fig. 3D/E. The images show a uniform, characteristically grain-dependent (not particle-dependent) corrosion morphology, with indications of minor intergranular attack [16, 23]; no particle-particle boundary attack was observed.

3.3. Relationship Between Preferential Corrosion and Corrosion Damage

To better understand the consequences of preferential corrosion of cold-sprayed copper, the extent of corrosion damage was measured after immersion experiments. For better comparison, cold-sprayed copper specimens with elevated amounts of oxygen were used for these experiments to increase the corrosion rate such that the preferential corrosion morphology was seen under deaerated and aerated conditions. The oxygen contents were 123 and 693 ppm for standard and elevated-oxygen cold-sprayed copper, respectively. The high-oxygen cold-sprayed copper was fabricated by oxidizing the feedstock particles prior to cold-spray deposition.

The corrosion depth was evaluated by masking parts of the cold-sprayed copper surface and imaging the topography of the transition region using profilometry after immersion in 0.1 M HNO_3 , with and without the presence of oxygen and/or 4 mM HCl (Fig. 4A-B). The corrosion damage was estimated to be 50 μm and 300 μm after exposure to deaerated and aerated 0.1 M HNO_3 , respectively (Fig. 4C). These results demonstrate a quantitative effect of dissolved oxygen, increasing the corrosion damage by a factor of 6 (18 if accounting for the immersion period). For comparison, in 0.1 M HNO_3 , Cu-OFP copper has previously been found to corrode only 3 μm under the same deaerated conditions[23]. Copper particles collected by filtration after immersion experiments under chloride-free conditions were found to be similar in size, around 50 μm , to the feedstock copper particles (Supporting Information, Figure S4) [27]. Therefore, it appears as if the damage to cold-sprayed copper when preferential corrosion becomes significant is caused primarily by particle-particle boundary corrosion, leading to particle detachment.

In the presence of 4 mM HCl, the corrosion damage for aerated and deaerated conditions was only 0.86 μm and 0.85 μm , respectively (Fig. 5C), a substantial reduction compared to the chloride-free conditions, and no copper particles were observed in the immersion solution. These results are particularly interesting because they corroborate the surface morphology findings and demonstrate that when preferential corrosion is inhibited, the corrosion damage is substantially lower. They also show that the presence of oxygen does not cause significant copper oxidation directly, relative to nitrate, but catalyzes nitrate-driven corrosion. However, electrochemical data are needed to evaluate differences in nitrate reduction rates across the conditions and the effect of chloride on oxygen reduction.

Figure 4: A) Scheme showing the methodology for evaluating corrosion damage to high-oxygen cold-sprayed copper. A mask prevents corrosion in a reference area used for topography measurements. B) SEM (top) and topography images (bottom) show the transition from uncorroded to corroded regions in A). C) Topography line profiles across this transition for high-oxygen cold-sprayed copper in 0.1 M HNO_3 with/without aeration and 4 mM HCl: aerated, no HCl, 24 h immersion (red); deaerated, no HCl, 72 h (blue); aerated, 4 mM HCl, 24 h (purple); and deaerated, 4 mM HCl, 72 h (green).

3.4 Evaluation of the Effects of Chloride and Oxygen on the Electrochemical Behavior of Copper Materials in 0.1 M HNO_3

Electrochemical measurements provide additional insights into the accelerated corrosion of cold-sprayed copper. Potentiodynamic polarization curves for electrodeposited, standard cold-sprayed, and oxygen-elevated cold-sprayed copper in deaerated 0.1 M HNO_3 are shown in Fig. 5A. At substantially negative potentials, around -0.35 V vs. SCE, the cathodic current densities are similar and only slightly higher than those measured on Cu-OFP copper (Supporting Information, Figure S6). These results suggest that, at this potential, the surfaces become active toward nitrate reduction, and the differences between them are limited. However, the cathodic current densities close to E_{corr} were in the order: standard cold-sprayed copper < electrodeposited copper < high-oxygen cold-sprayed copper.

To clarify whether these differences were due to nitrate reduction activity, copper ion reduction, or oxide reduction, we conducted experiments in 4 mM HCl, where nitrate reduction is inhibited (Fig. 5B). In the presence of chloride, the cathodic currents were much lower, with a significant increase in the current density associated with nitrate reduction occurring at approximately -0.3 V vs. SCE, due to chloride desorption around this potential[32, 33]. The trend of cathodic current densities in the potential range -0.3 V to -0.2 V vs. SCE was electrodeposited copper < standard cold-sprayed copper < high-oxygen cold-sprayed copper. The linear characteristics and potential-independent current density of this activity are consistent with diffusion-limited copper ion reduction. This suggests that copper ions are slowly released from cold-sprayed copper materials, with the extent increasing with incorporated oxygen content, contributing to the initiation of preferential corrosion in high-oxygen cold-sprayed copper. The higher nitrate reduction activity of electrodeposited copper compared to that of standard cold-sprayed copper close to E_{corr} may be associated with a microstructural effect from differences in grain size and orientation[28].

A trend similar to that observed under deaerated conditions was observed under aerated conditions close to E_{corr} , although the cathodic currents were higher due to the additional contribution of oxygen reduction (Fig. 5C). At more negative potentials, where nitrate reduction dominates the current, there was only a minor difference between aerated and deaerated conditions, which suggests that the accelerated nitrate reduction reaction rates are unaffected by the presence of oxygen. Similarly, in the presence of chloride, the voltammograms were very similar, and oxygen reduction dominated the cathodic current densities (Fig. 5D). In order to determine the effect of chloride on oxygen reduction, experiments were carried out with Cu-OFP copper in 0.05 M H_2SO_4 with and without 4 mM HCl to avoid current densities associated with nitrate reduction and copper ion reduction (Supporting Information, Figure S7). Unfortunately, the effect of chloride on “background” current densities, presumably related to oxide film reduction, makes this impossible without a detailed analysis[23].

4. Discussion

In this study, we examine the mechanism of preferential corrosion of cold-sprayed copper in dilute nitric acid by exploring how solution parameters affect electrochemistry and corrosion behavior. Several observations suggest that nitrate reduction drives preferential corrosion of cold-sprayed copper in dilute nitric acid. First, immersion experiments with cold-sprayed copper under deaerated conditions, where nitrate reduction was the only cathodic reaction, showed indications of preferential corrosion. However, it was much less severe than under aerated conditions (due to the catalytic effect of the copper ions produced). Additionally, in the presence of chloride, which inhibits nitrate reduction, preferential corrosion was completely mitigated, even when oxygen and nitrite reduction occurred.

When copper ions and nitrate are present in solution together, the main requirement for the copper-ion oxidation mechanism proposed by Turnbull et al.[20] and supported by Li et al.[17] is fulfilled, where the first step of this reaction sequence is $\text{Cu}^+_{(\text{aq})} + \text{NO}_3^-_{(\text{aq})} \rightarrow \text{NO}_2^-_{(\text{aq})} + \text{Cu}^{2+}_{(\text{aq})}$. However, this does not seem to be the main reaction initiating preferential corrosion, given the strong corrosion inhibition in the presence of chloride and excess copper ions (although mild corrosion reactivation is seen, likely from this mechanism). Additionally, small amounts of chloride do not affect the subsequent nitrite reduction, nor do they completely eliminate $\text{Cu}^+/\text{Cu}^{2+}$ in solution through its favorable complexation. Because Cu^+ and Cu^{2+} are rapidly interconverted under these conditions, their individual contributions cannot be readily distinguished[23]. The copper-ion oxidation mechanism likely contributes to the propagation of preferential corrosion once initiated; however, our results show that copper ions and nitrate alone are insufficient to initiate significant preferential corrosion.

Following this rationale, the evidence points to copper ions catalyzing nitrate reduction directly on the copper surface as a more important driver in preferential corrosion than previously believed. The electrochemical data support this by showing an apparent increase in nitrate reduction activity near E_{corr} at the macroscale for cold-sprayed copper compared with electrodeposited and Cu-OFP copper, which may indicate higher nitrate-reduction activity associated with oxide inclusions in cold-sprayed copper.

One important limitation of the electrochemical results is that under cathodic polarization, when copper ions are reduced, a catalytic effect of dissolved copper ions on nitrate reduction may not be fully captured in the electrochemical data, especially at substantially negative potentials. That said, the electrochemical data indicate release of copper ions from the oxide in the material, which we show acts as a catalyst, and we infer higher nitrate-reduction activity.

However, the most important aspect regarding the effect of preferential corrosion is that the additional material loss from particle detachment only occurs simultaneously with nitrate reduction. One possible explanation is that inhibiting nitrate reduction may prevent the formation of reactive intermediate species that directly attack the particle-particle boundary. Intermediate species from nitrate reduction are known to dissolve copper, even during cathodic corrosion [23]. Moreover, the nitrate reduction pathway is altered in the presence of chloride, as demonstrated under cathodic polarization[28]. We expect this to extend to corrosion conditions because nitrate is reduced to nitrite, and nitrite reduction occurs readily under both conditions. This could mean that reactive intermediates from nitrite reduction differ under chloride-containing versus chloride-free conditions. Alternatively, chloride adsorption on the Cu_2O layer may protect it from accelerated dissolution by reactive intermediates under either condition[34–36].

Alternatively, preferential corrosion could be explained if nitrate reduction occurs locally at oxide inclusions, and nitrite formation and catalytic copper ions drive further particle-particle boundary attack. Electrocatalytic studies have established that an oxidized copper surface has higher nitrate-reduction activity than a bare one, though the active phase on oxidized copper has long been debated[29]. Recently, it has been established that copper oxides are reduced to form nanostructured copper metal during nitrate electroreduction, which is the active phase for nitrate reduction[37]. During copper corrosion in dilute nitric acid, it was deduced that chloride preferentially adsorbs to the metal phase rather than to the Cu_2O due to the lack of competitive adsorption to bulk Cu_2O in solution[23]. These recent studies do not align with the proposal of an elevated nitrate reduction activity directly at the oxide inclusions (nitrate adsorption to Cu_2O and subsequent reduction). Additionally, most copper surfaces have a native oxide film that would cover the entire surface. Therefore, the higher copper ion concentration near the oxide inclusions is more likely responsible for preferential corrosion by catalyzing nitrate reduction. However, localized electrochemical measurements are needed to directly evaluate nitrate-reduction activity near the oxide inclusions and confirm this hypothesis[38].

Conclusions

We studied the mechanism of preferential corrosion of cold-sprayed copper by varying solution parameters, including the presence of oxygen, chloride, and copper ions. We first provide direct experimental evidence for previous proposals of a catalytic effect of copper ions on copper corrosion in dilute nitric acid. We further show that in the presence of small amounts of chloride, all preferential corrosion is inhibited, even in the presence of strong oxidants such as oxygen and nitrite, which suggests that the initiation of preferential corrosion of cold-sprayed copper may be directly linked to

nitrate reduction. Moreover, accelerated dissolution at particle-particle boundaries causes particle detachment, increasing material loss compared with other copper types. This work has important implications for real-world applications of cold-sprayed copper, including nuclear waste management, where chloride is expected, and preferential corrosion is likely to be inhibited under repository-relevant conditions[39]. Moreover, limiting oxygen incorporation, modifying the oxide network through annealing, and reducing particle size and porosity may help mitigate preferential corrosion in cold-sprayed copper materials [17].

Declarations

Declaration of Competing Interests

The authors declare no competing financial interest.

Data Availability

Data will be made available on request.

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CRedit authorship contributions statement

Sebastian A. Skaanvik: Conceptualization, Supervision, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft and Writing – review and editing. **Sherry Cao:** Investigation and Methodology. **Jessica E. M. Winslade:** Investigation and methodology. **Xuejie Li:** Conceptualization and Methodology. **Diego A. Membreno:** Investigation. **Mehran Behazin:** Conceptualization, Resources, Project administration, and Writing – review and editing. **Peter G. Keech:** Conceptualization, Resources, Project administration, and Writing – review and editing. **David W. Shoesmith:** Conceptualization and Writing – review and editing. **James J. Noël:** Conceptualization, Resources, Supervision, Project administration, Funding acquisition and Writing – review and editing.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work, the authors used Grammarly to correct and improve the manuscript text. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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Figures

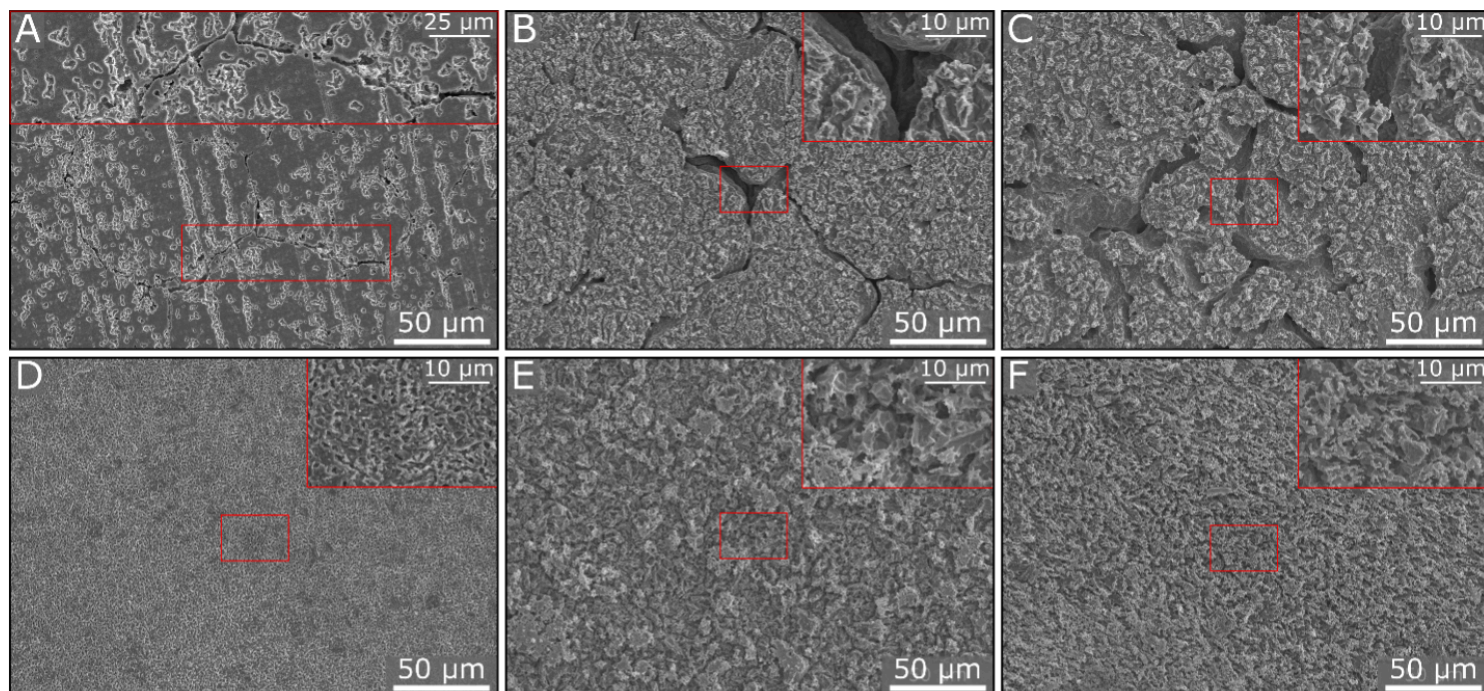


Figure 1

SEM images of cold-spray and electrodeposited copper after 72 h immersion in deaerated: A) 0.1 M HNO_3 (cold-spray); B) 0.1 M HNO_3 + 1 mM Cu_2O (cold-spray); C) 0.1 M HNO_3 + 1 mM $\text{Cu}(\text{NO}_3)_2$ (cold-spray); D) 0.1 M HNO_3 (electrodeposited); E) 0.1 M HNO_3 + 1 mM Cu_2O (electrodeposited); F) 0.1 M HNO_3 + 1 mM $\text{Cu}(\text{NO}_3)_2$ (electrodeposited). Red boxes mark the locations of the inset magnified images.

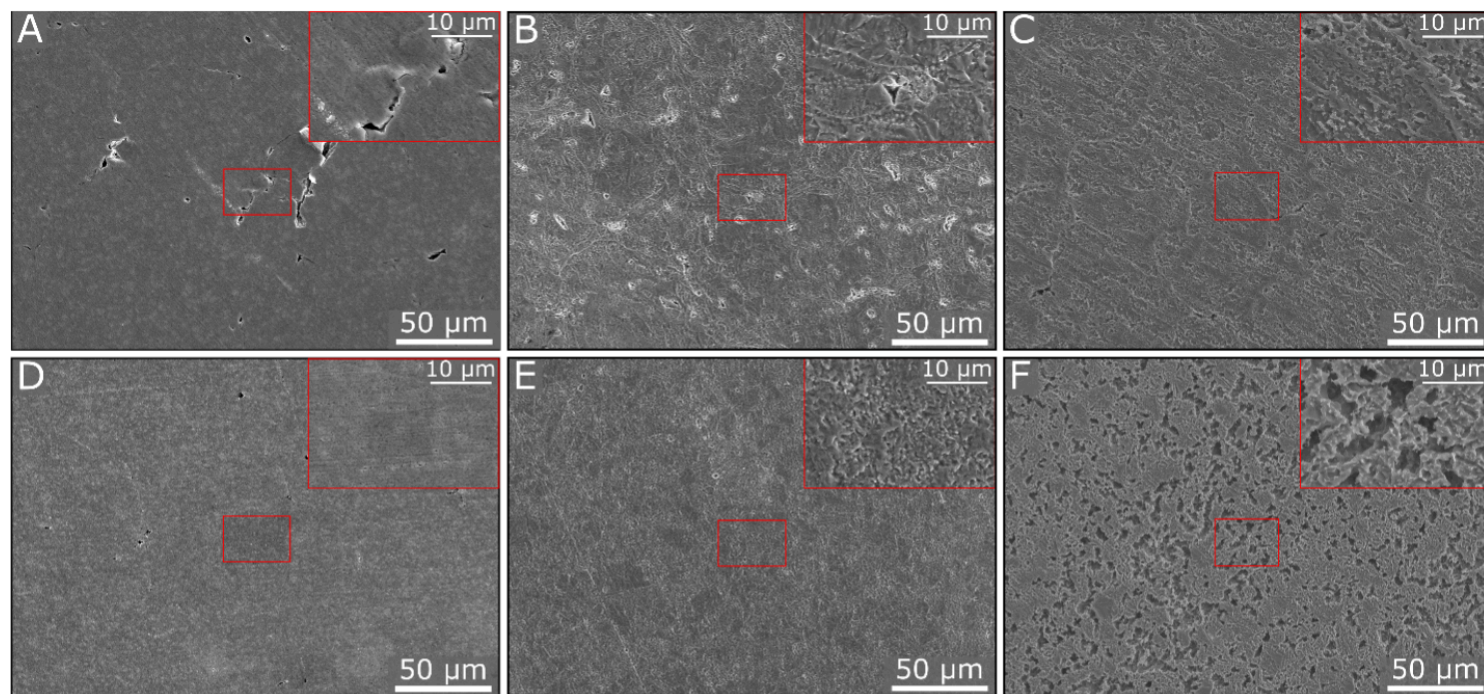


Figure 2

SEM images of cold-sprayed and electrodeposited copper after 72 h immersion in deaerated: A) 0.1 M HNO_3 + 4 mM HCl (cold-spray); B) 0.1 M HNO_3 + 4 mM HCl + 1 mM Cu_2O (cold-spray); C) 0.1 M HNO_3 + 4 mM HCl + 1 mM $\text{Cu}(\text{NO}_3)_2$ (cold-spray); D) 0.1 M HNO_3 + 4 mM HCl (electrodeposited); E) 0.1 M HNO_3 + 4 mM HCl + 1 mM Cu_2O (electrodeposited); F) 0.1 M HNO_3 + 4 mM HCl + 1 mM $\text{Cu}(\text{NO}_3)_2$ (electrodeposited). Red boxes mark the locations of the inset magnified images.

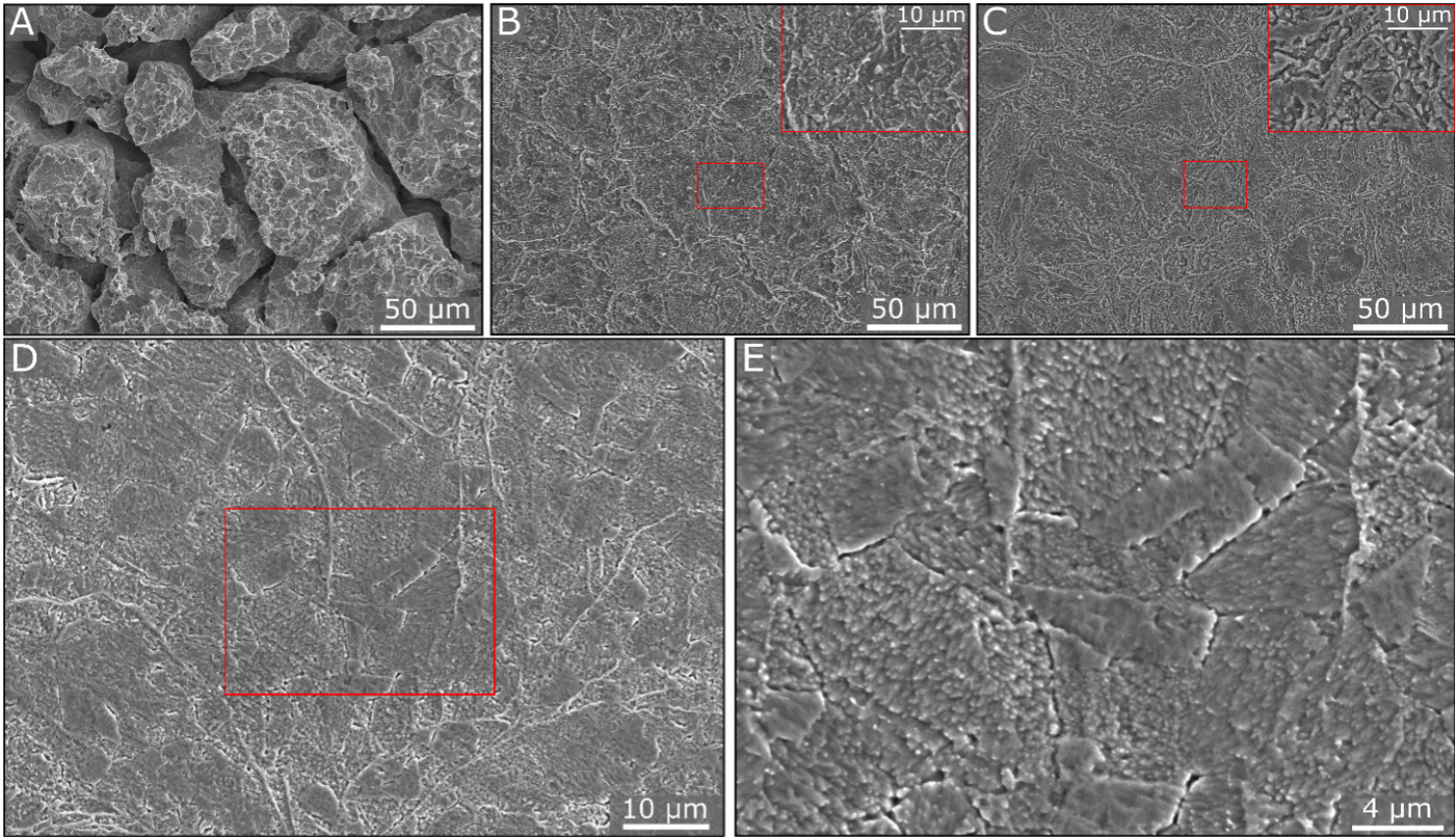


Figure 3

SEM images of cold-sprayed copper after 24 h immersion under aerated conditions in: A) 0.1 mM HNO_3 , B) 0.1 M HNO_3 + 4 mM HCl, C) 0.1 M HNO_3 + 4 mM HCl + 1 mM NaNO_2 , and D/E) 0.05 mM H_2SO_4 . Red boxes in panels B and C mark the locations of the inset magnified images. The red box in panel D indicates the location of the image in panel E.

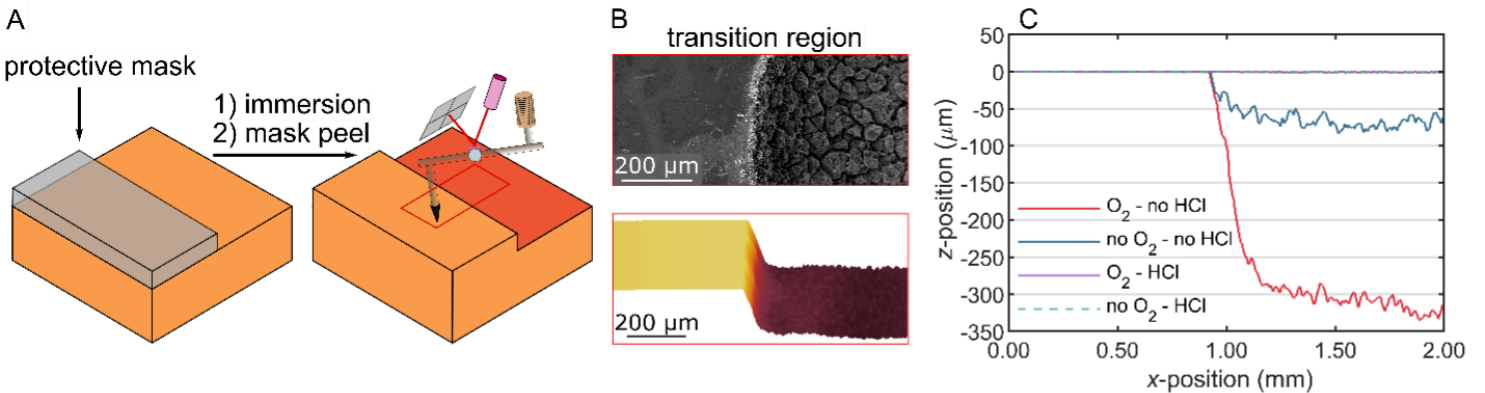


Figure 4

A) Scheme showing the methodology for evaluating corrosion damage to high-oxygen cold-sprayed copper. A mask prevents corrosion in a reference area used for topography measurements. B) SEM (top) and topography images (bottom) show the transition from uncorroded to corroded regions in A). C) Topography line profiles across this transition for high-oxygen cold-sprayed copper in 0.1 M HNO_3 with/without aeration and 4 mM HCl: aerated, no HCl, 24 h immersion (red); deaerated, no HCl, 72 h (blue); aerated, 4 mM HCl, 24 h (purple); and deaerated, 4 mM HCl, 72 h (green).

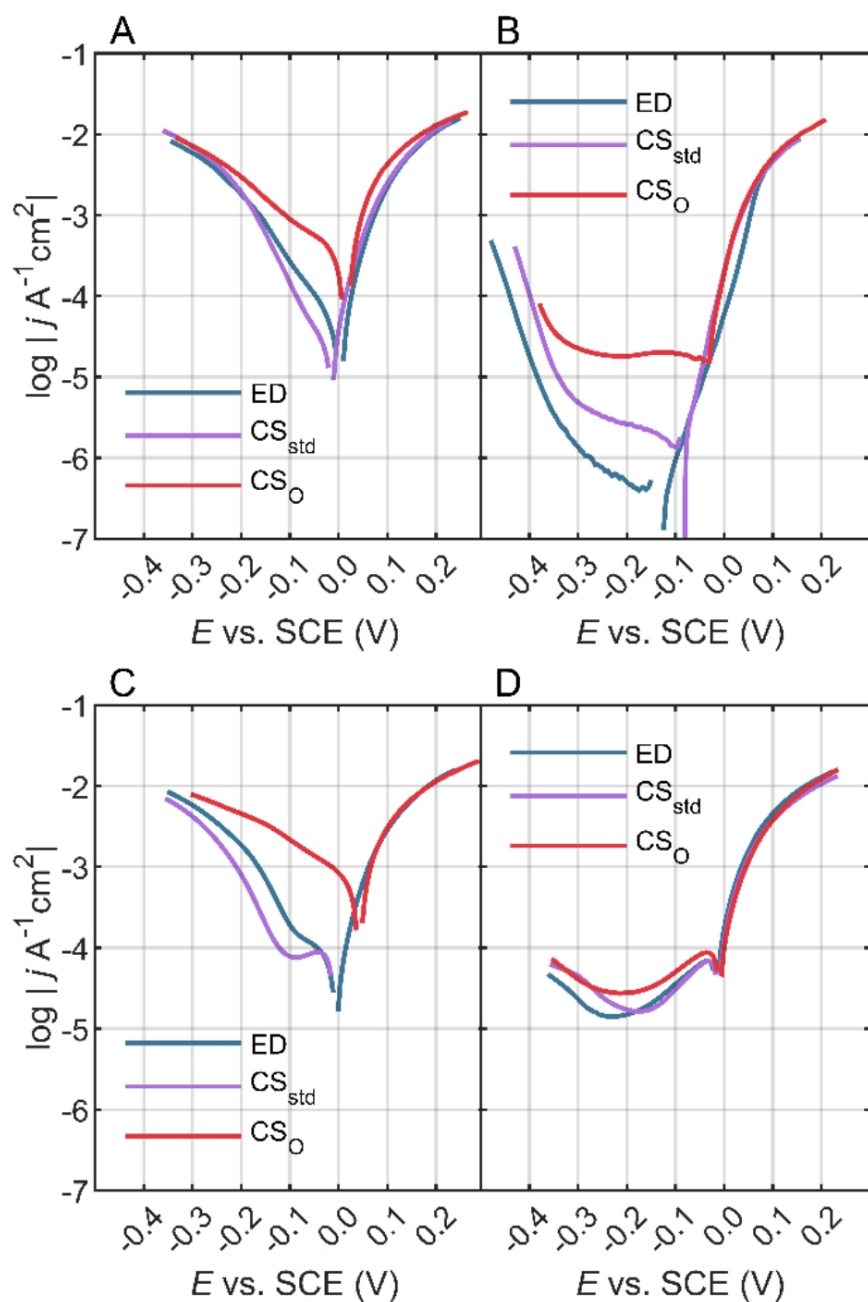


Figure 5

Potentiodynamic polarization curves of electrodeposited (ED, blue lines), standard cold-sprayed copper (CS_{std} , purple lines), and high-oxygen cold-sprayed copper (CS_O , red lines). The scan rate was 2 mV/s, and scans started at E_{corr} . Conditions: A) deaerated 0.1 M HNO_3 ; B) deaerated 0.1 M HNO_3 + 4 mM HCl; C) aerated 0.1 M HNO_3 ; D) aerated 0.1 M HNO_3 + 4 mM HCl.

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