CORROSION TESTING NEEDS AND CONSIDERATIONS FOR ADDITIVELY MANUFACTURED MATERIALS IN NUCLEAR REACTORS

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Metal additive manufacturing (MAM) holds significant promise as an enabling technology for the 21st century nuclear energy industry. Metal additive manufacturing can allow the fabrication of novel materials and innovative component designs that are not achievable through conventional manufacturing. Metal additive manufacturing has been deployed successfully in the aerospace and defense industries [1] and even by the United States Navy for the fabrication of reactor doors [2].

Due to the very different fabrication methods, as-fabricated MAM components are characteristically different from conventionally manufactured components both in terms of microstructure and as-fabricated surface finish [3]. The corrosion behavior of MAM components can vary significantly from that of conventionally formed components [4, 5] as a result of these differences. The Advanced Materials and Manufacturing Technologies program within the Department of Nuclear Energy in the United States Department of Energy is assessing the unique concerns of MAM structural component corrosion and testing methodologies in advanced nuclear reactor environments as part of its program. Very little work has been published regarding the corrosion of MAM components for nuclear applications to date and the focus has been on water environments [6, 7, 8, 9].

Generally, corrosion in the context of structural alloys is the degradation of the metallic material by chemical or electrochemical reactions with the other species of the service environment. This is frequently an oxidation reaction with, e.g., air or water. Corrosion leads to the conversion of the metal into another species such as an oxide compound or salt. This corrosion product may remain tightly adhered to the surface of the component being corroded; may occur within the bulk of the component; or may be removed from the surface of the component by, e.g., spalling. Corrosion becomes a concern when the engineering properties of the material are degraded or the geometry of the component are changed beyond acceptable engineering tolerances.

Many forms of corrosion exist. Uniform or generalized corrosion occurs when the attack is uniform across the surface of the material, while localized corrosion occurs when a small region is more susceptible to corrosion than its surroundings. Localized corrosion can include pitting, crevice, and intergranular corrosion morphologies, and frequently involves the galvanic corrosion mechanism. Galvanic corrosion refers to the creation of a galvanic cell, in which two dissimilar metals are connected by an electrolyte medium. This creates an electrical circuit and results in the preferential corrosion of one material (the anode) and the protection of the other material (the cathode). Selective leaching of a species (due to differences in solubility into the coolant or electrolyte) can be considered corrosion on its own, but also leads to the development of a galvanic cell. Flow-accelerated or flow-assisted corrosion results from the continuous removal of a normally adherent corrosion layer by fast-

flowing fluid, resulting in ongoing corrosion processes. The poorly soluble corrosion product is dissolved due to high flow rates of unsaturated fluid, allowing dissolution and exposure of the metal beneath. Flow-assisted corrosion is not the same as erosion (which results from mechanical means such as particulate or bubble impingement against the surface), though the result is generally similar.

Pitting corrosion typically results when a passive film on a surface is damaged or disrupted, allowing the creation of a galvanic cell. As the pit forms, the local environment within the pit will generally become even more conducive to continued corrosion, accelerating pit formation. Pitting corrosion is of particular engineering concern because it is frequently hard to detect, e.g., a small (microns to millimeter) pinhole on the surface of the metal can hide a large hole within the material. Crevice corrosion is closely related to pitting corrosion, in that it is localized corrosion that occurs within a region with trapped and stagnant electrolyte, such as narrow gaps between mating surfaces of components and cracks within components. Crevice corrosion usually occurs in gaps on the scale of microns and involves a similar mechanism of electrolyte composition change as pitting corrosion.

Intergranular corrosion is another form of localized corrosion that results from the preferential attack of grain boundaries. Intergranular corrosion frequently results from the localized loss of elements that form passivating films at grain boundaries. These elements may migrate away from the grain boundary into the bulk of the grain due to radiation-induced segregation, be selectively leached into the electrolyte, or become locally bound in an insoluble, non-film-forming precipitate. As a result, a localized galvanic couple forms, with the grain boundary being anodic and the surrounding passivated grains being cathodic, causing preferential corrosion of the grain boundary.

Other forms of corrosion or corrosion-mediated phenomena include environmentally assisted cracking, including corrosion fatigue, stress corrosion cracking, and hydrogen embrittlement; and liquid metal corrosion, which can include dissolution, mass transfer, carburization/decarburization, and liquid metal embrittlement; and corrosion by gasses (e.g., entrained water vapor in helium gas coolant).

Corrosion in reactors is a vast topic that depends on the specific reactor type and the exact material system within the reactor: it can occur in fuel systems and structural materials. Each reactor has its own corrosion concerns. Molten salt reactors generally operate in the range of 500-1000°C and the coolant consists of highly corrosive fluoride or chloride salts. In the case of fueled salts, the coolant is also mixed with actinides and other fission products. Liquid metal fast reactors use sodium, lead, or lead-bismuth eutectic as the coolant. Sodium fast reactors operate in the range of 500-650°C, and although sodium is generally considered compatible with structural metals, dissolution and mass transfer, as well as impurities in the sodium such as C, O, and N are a concern. Lead- or lead-bismuth-cooled fast reactors operate in the range of 500-800°C. Lead-based coolants are corrosive to structural metals and can lead liquid metal embrittlement. High-temperature gas-cooled reactors operate at >700°C and the major corrosion concern relates to impurities in the coolant gas, such as H_2, CH_4, N_2, O_2, H_2O, CO_2/CO. Water-based advanced reactors include water-cooled reactors operating with coolant temperatures <330°C and subjected to similar corrosion concerns as in the existing water-cooled commercial reactor fleet.

The as-built material is structurally and chemically heterogeneous in MAM materials, which may affect their corrosion behavior versus a conventionally wrought material of the same

type (e.g., 316 stainless steel) [5]. One benefit of MAM processing is building net or near-net shape components; without post-build surface machining, surface roughness created by the MAM process is a macroscopic concern. MAM surfaces typically have roughness on the order of the feed powder or metal wire used during the build. This roughness may be sufficient to promote localized crevice corrosion. Build porosity is also a concern, with pore volume fractions of 5% or more possible depending on processing parameters [10], although full density is typically targeted. Porosity intersecting the surface (or just under the surface, to be revealed after some amount of uniform corrosion) is another source of possible crevice corrosion initiation. Additionally, other phases may be present in MAM material that are not present in conventional material of the same composition. Oxide phases or atypical inclusions may be present in MAM material due to feedstock oxidation or other contamination, while previously unreported phases may occur as a result of the rapid cooling and repeated thermal cycling in MAM build processes. The microstructure of MAM materials is generally complex. The details depend on the material and process, but melt pool boundaries are generally visible at the macroscale in fusion-based methods and individual grains (defined by high angle grain boundaries) are generally elongated along the thermal gradient present during the build process. Within each grain, a cellular dislocation structure generally occurs during MAM builds of stainless steels and other metals [11], similar to the dislocation cell structure that occurs during plastic deformation and may also have solute segregation to the cell walls. Finally, residual stresses from the build process can be significant enough to cause visible warping of as-built components upon release from a build plate.

Thus, several features of MAM material can impact corrosion behavior: for example, the surface roughness and porosity may contribute to promoting crevice corrosion; dislocation cell structure, chemical segregation, and atypical phases and inclusions could promote galvanic corrosion (including pitting) or leaching; lamellar or columnar grain structures and melt pool boundaries could lead to exfoliation; and residual stresses could change the pitting potential.

Given the features of MAM materials (surface roughness, solute segregation, complex microstructure, and residual stresses), some amount of post-build processing generally occurs. The surface may be machined, as previously discussed. Post-build annealing is also common for stress relief, solution annealing, or microstructure homogenization [3]. However, post-build processing incurs additional time and cost, and it generally will not resolve the presence of additional oxide phases, atypical inclusions, and build porosity, and may or may not remove the original build microstructure. Furthermore, a material may be processed to optimize its structure for one property, e.g., creep strength, which may impact its corrosion behavior. As a result, the corrosion behavior should be assessed for each instantiation of the MAM-built and postprocessed material. This will reveal how microstructure tuning for a given property and component performance will affect the corrosion behavior.

The length scale examined during corrosion testing and the testing methodology should be carefully selected. For example, deployment of a component with as-built surface roughness requires testing rough specimens, rather than the typical convention of testing polished specimens, to obtain representative macroscopic data (e.g., weight change). The assessment of pitting or crevice corrosion in rough specimens may require the use of computed tomography (e.g., X-ray computed tomography) to non-destructively obtain comparative before-and-after data of specimens. Upon identification of areas of interest, these specimens

can then be sectioned to study microstructure and local composition variation with SEM and TEM imaging. Conversely, as-built specimens finished to a smooth surface may be useful to assess underlying corrosion mechanisms and understand the extent to which corrosion is localized to or affected by the rough surface. This is hereafter referred to as the "two-surface test". The corrosion assessment may also include conventionally manufactured (e.g., wrought) smooth specimens of the same composition. This may be of interest if MAM processing is being proposed to replace conventional fabrication of a material currently in service. Similarly, the effect of post-build heat treatments can also be assessed via the two-surface test. The two-surface test strategy is applicable to a variety of tests, such as static corrosion tests, flow tests, and stress corrosion cracking studies.

Process variability impact on MAM material properties is a significant concern and extends to their corrosion behavior. In this context, process variability refers to variations in the as-built microstructure from a single specific machine. Even with the same build parameters in the same MAM machine (e.g., laser power, scan pattern, and speed for laser powder bed fusion), sources of process variability include but are not limited to the laser power and scan speed; feedstock lots; atmospheric storage condition of the feedstock, especially powder feedstock; atmospheric composition during the build, including humidity levels [12]; and heat dissipation during the build as a result of build plate heating, surrounding atmosphere, and build geometry.

Process variability should be addressed with a combination of experiments and data analytics. Variability should be considered at the microscale and the macroscale. At the microscale, the statistical distribution of a corrosion behavior of interest should be understood with respect to key microstructural features. Successful assessment of the impact of process variability on corrosion behavior requires data traceability linking sources of process variability (build parameters, feedstock properties, etc.) and microstructure statistics (grain geometries, dislocation cell characteristics, solute distribution) to the corrosion test results. Conversely, macroscale variability can be tested by taking samples from different locations within a component.

The geometry of the as-built specimen from which corrosion samples are removed should be considered as part of process variability. It is conceivable to take corrosion specimens from short specimens with limited build volume, while the actual component will be larger. Given the impact of build volume on thermal history and resulting microstructure, corrosion specimens sectioned from specimens of representative geometries and volumes of the actual component may also need to be assessed.

The specific corrosion testing strategy employed to assess a MAM material for a reactor environment will depend upon the degree of prior knowledge about the behavior of the material composition in the environment. If prior information exists for, e.g., conventionally manufactured 316H in FLiNaK [13], then the corrosion testing strategy can leverage this prior knowledge to its advantage to rank specific corrosion tests by estimated likelihood of importance for the MAM material. As a result, a mass transfer test in a flowing salt loop would be a high-priority test. If, however, little or no information exists, then a rapid assessment campaign of static coupon tests may be employed to gain a sense of how the material performs and then select additional specific tests.

The testing of un-irradiated specimens outside of a neutron environment is recommended as the first step in testing MAM components for reactor environments. This is due to cost and

time involved with testing irradiated materials or in-situ testing. Ex-situ testing of unirradiated specimens can answer questions regarding the impact of process variability, post-build treatment, surface finish, and corrosion mechanisms. The second stage of corrosion testing for reactor environments can entail ex-situ testing of irradiated MAM material to determine the impact of irradiation-driven microstructural changes on corrosion behavior. Irradiation-driven microstructural changes may be the major driver of irradiation effects on corrosion behavior when the service temperature is elevated sufficiently for rapid defect migration, as in the case of many advanced reactor designs. At lower temperatures, defect production rates may be important. Finally, in-situ testing may be possible (depending on the availability of test capabilities or surveillance specimens in as-built reactors) for fully prototypical testing, which can account for irradiation-induced chemistry changes in the coolant, actual coolant flow rates, etc.

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