Researchers uncover culprits behind pitting corrosion in 3D-printed stainless steel

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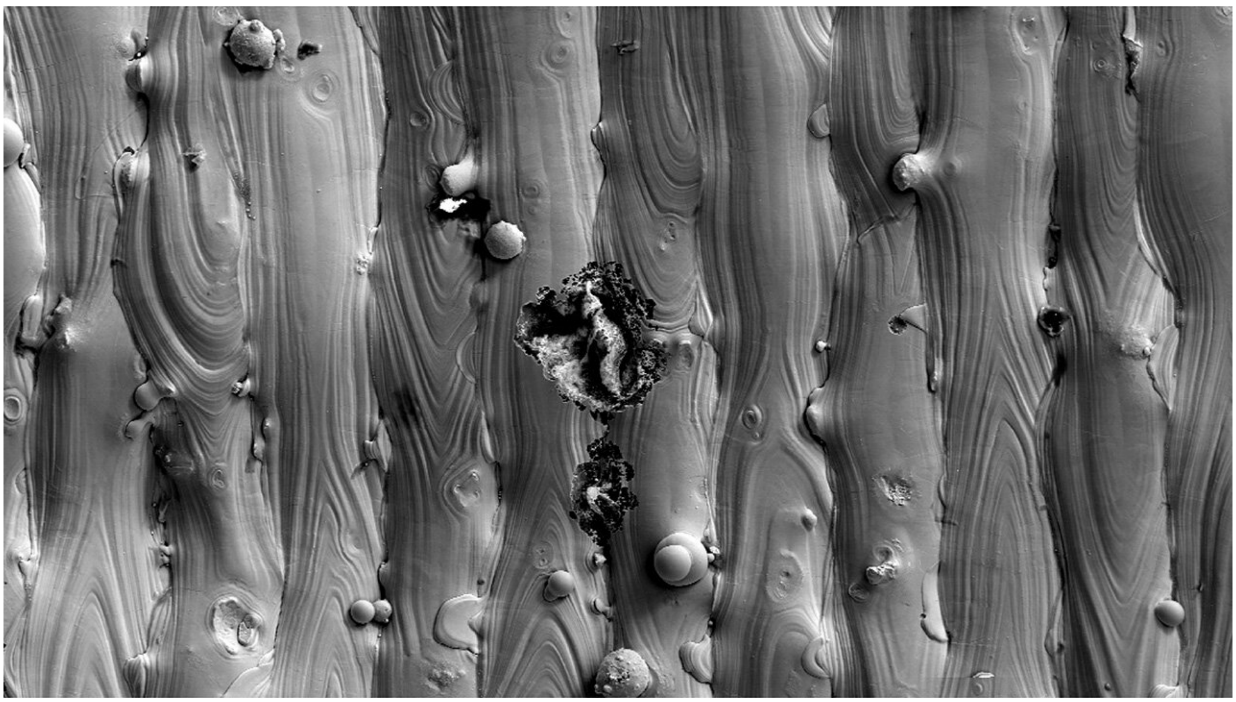

A photo taken by a scanning electron microscope shows a pit at the surface of an additively manufactured (3D-printed) stainless steel part. Credit: Thomas Voisin.

Like a hidden enemy, pitting corrosion attacks metal surfaces, making it difficult to detect and control. This type of corrosion, primarily caused by prolonged contact with seawater in nature, is especially problematic for naval vessels.

In a recent paper published in *Nature Communications*, Lawrence Livermore National Laboratory (LLNL) scientists delved into the mysterious world of pitting corrosion in additively manufactured (3D-printed) stainless steel 316L in seawater.

Stainless steel 316L is a popular choice for marine applications due to its excellent combination of mechanical strength and corrosion resistance. This holds even more true after 3D printing, but even this resilient material isn't immune to the scourge of pitting corrosion.

The LLNL team discovered the key players in this corrosion drama are tiny particles called "slags," which are produced by deoxidizers such as manganese and silicon. In traditional stainless steel 316L manufacturing, these elements are typically added prior to casting to bind with oxygen and form a solid phase in the molten liquid metal that can be easily removed post-manufacturing.

Researchers found these slags also form during laser powder bed fusion (LPBF) 3D printing but remain at the metal's surface and initiate pitting corrosion.

"Pitting corrosion is extremely difficult to understand due to its stochastic nature, but we determined the material characteristics that cause or initiate this type of corrosion," said lead author and LLNL staff scientist Shohini Sen-Britain.

"While our slags looked different than what had been observed in conventionally manufactured materials, we hypothesized that they could be a cause of pitting corrosion in 316L. We confirmed this by taking advantage of the impressive materials characterization suite and modeling capabilities we have at LLNL, where we were able to prove without a doubt that slags were the cause. This was extremely rewarding."

While slags can also form during traditional stainless steel manufacturing, they're typically removed with chipping hammers, grinders, or other tools. Those post-processing options would defeat the purpose of additive manufacturing (AM) the metal, said the researchers, who added that prior to their study, there was almost no information on how slags are formed and deposited during AM.

To help address these unanswered questions, the team used a combination of advanced techniques, including plasma-focused ion beam milling, transmission electron microscopy, and X-ray photoelectron spectroscopy on AM stainless steel components.

They were able to zoom in on the slags and uncover their role in the corrosion process in a simulated ocean environment, finding they created discontinuities and allowed the chloride-rich water to penetrate the steel and wreak havoc. Additionally, the slags contain metal inclusions that dissolve when exposed to the seawater-like environment, further contributing to the corrosion process.

"We wanted to do a deep-dive microscopy study to figure out what could potentially be responsible for corrosion when it does happen in these materials, and if that's the case, then there may be additional ways of improving them by avoiding that particular agent," said principal investigator Brandon Wood.

"There is a secondary phase that's formed that contains manganese—these slags—that appeared to be what was most responsible. Our team did some additional detailed microscopy looking at the neighborhood of those slags, and sure enough, we were able to show that in that neighborhood, you have enhancement—a secondary indicator that this is probably the dominant agent."

Using transmission electron microscopy, the researchers selectively lifted small samples of 3D-printed stainless steel from the surface—about a few microns—to visualize the slags through the microscope and analyze their chemistry and structure at atomic resolution, according to lead investigator Thomas Voisin.

The characterization techniques helped shed light on the complex interplay of factors that lead to pitting corrosion and enabled the team to analyze slags in ways never done before in AM.

"During the process, you locally melt the material with the laser, and then it solidifies very rapidly," Voisin said. "The rapid cooling freezes the material in a non-equilibrium state; you're basically keeping the atoms in a configuration that is not supposed to be, and you're changing the mechanical and corrosion properties of the material."

"Corrosion is very important for stainless steel because it is used a lot in marine applications. You could have the best material with the best mechanical properties, but if it cannot be in contact with seawater, this is going to restrict the applications significantly."

Researchers said the study marks a significant step forward in the ongoing battle against corrosion, not only deepening scientific understanding of corrosion processes but also paving the way for developing improved materials and manufacturing techniques.

By unraveling the mechanisms behind the slags and their relationship to pitting corrosion, engineers and manufacturers can strive to create stainless steel components that are not only strong and durable but also highly resistant to the corrosive forces of seawater, with implications extending beyond the realm of marine applications and into other industries and kinds of harsh environments.

"When we 3D print the material, it's better for mechanical properties, and from our research, we also understand that it's better for corrosion as well," Voisin said.

"The surface oxide that forms during the process is developing at high temperatures, and that also gives it many different properties. What's exciting is understanding the reason why the material corrodes, why it's better than other techniques, and the science behind it. It is confirming, again and again, that we can use laser powder bed fusion AM to improve our material properties way beyond anything we can do with other techniques."

Now that the team understands the causes behind pitting, Sen-Britain and Voisin said the next steps to enhancing the performance and longevity of 3D-printed stainless steel 316L would be altering the formulation of the powder feedstock to remove manganese and silicon to limit or eliminate slag formation.

Researchers also could analyze detailed simulations of the laser's melt track and melting behavior to optimize the laser's processing parameters and potentially prevent the slags from reaching the surface, Voisin added.

"I think there's a real pathway to actually co-designing these alloy compositions and the way they are processed to make them even more corrosion resistant," Wood said.

"The long-term vision is to go back to a prediction-validation feedback cycle. We have an idea that the slags are problematic; can we next leverage our composition models and process models to then figure out how to change our base formulations, such that what we get is basically an inverse design problem. We know what we want, now we just have to figure out how to get there."

More information: Shohini Sen-Britain et al, Critical role of slags in pitting corrosion of additively manufactured stainless steel in simulated seawater, *Nature Communications* (2024). DOI: 10.1038/s41467-024-45120-6

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