

Atomic-scale Understanding of Cu Effect on Mechanical, Antibacterial, and Corrosion Properties of Ultrahigh-strength Maraging Stainless Steel

Boxin Wei^{a,b,c,1}, Mengchao Niu^{d,1*}, Zheng Cai^{b,c}, Jin Xu^{b,c}, Cheng Sun^{b,c}, Tangqing Wu^{e3}

^a School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore, 639798, Republic of Singapore

^b Institute of Metal Research, Chinese Academy of Sciences, Shenyang, 110016, China

^c School of Materials Science and Engineering, University of Science and Technology of China, Shenyang, 110016, China

^d Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon 999077, Hong Kong, China

^e School of Materials Science and Engineering, Xiangtan University, Xiangtan 411105, China

Ultrahigh-strength stainless steels are critical materials in industries demanding both high performance and durability. These steels exhibit excellent mechanical properties, making them suitable for harsh environments such as offshore platforms, downhole equipment, and high-pressure vessels [1-3]. However, these environments present a significant risk of microbiologically influenced corrosion (MIC), which is primarily driven by sulfate-reducing bacteria (SRB) [4-7]. This form of corrosion is a growing concern in the oil field, as SRB have a remarkable ability to colonize metal surfaces, accelerating localized corrosion rates and compromising the structural integrity of critical components. Addressing MIC in ultrahigh-strength stainless steels, therefore, becomes paramount for improving the safety and longevity of these systems.

While conventional stainless steels such as 316L, 2205 duplex, 321 SS, and 304 SS have been developed with superior corrosion resistance, they remain vulnerable to SRB-induced MIC. The ability of SRB to thrive in anaerobic conditions, metabolize sulfates into sulfides, and trigger severe pitting corrosion highlights the limitations of current corrosion mitigation approaches. Recent research has focused on augmenting

³ Corresponding authors: mengchao.niu@polyu.edu.hk, tqwu@xtu.edu.cn

stainless steels with antibacterial properties as a novel strategy to counter MIC. One promising approach involves the incorporation of copper (Cu) into stainless steel alloys. Copper is well known for its strong antimicrobial activity, which is effective against a wide spectrum of bacteria, including those responsible for MIC and biofilm formation. Cu-bearing stainless steels have shown considerable promise in reducing bacterial colonization and biofilm formation, thereby offering an additional line of defense against microbial corrosion [8, 9]. However, Cu alloying could introduce complexities in corrosion resistance, such as promoting pitting corrosion in environments where chloride ions are present [10]. The overall impact of Cu on corrosion behavior depends on the specific alloy composition, the environmental conditions, and the interaction between Cu and other alloying elements like Cr and Ni. In ultrahigh-strength materials like maraging steels, the main challenge lies in balancing the mechanical properties and corrosion resistance. The atomic-scale mechanisms of Cu's effect on both mechanical and corrosion properties are still under investigation.

In this study, we explored the potential of Cu alloying in ultrahigh-strength Fe-Ni-Co-Cr-Ti maraging stainless steels. These maraging steels are notable for their exceptional mechanical properties, with tensile strengths exceeding 1.8 GPa due to the high-density precipitation of (Ni,Ti)-rich nano-precipitates during aging treatment. By introducing Cu into the maraging stainless steel, we aimed to enhance not only its mechanical properties but also its antibacterial performance and corrosion resistance in SRB environments. Our investigation revealed that Cu addition improves both the strength and the corrosion resistance of the maraging stainless steel. The presence of Cu significantly enhanced the stability of the passive oxide layer on the steel surface, which plays a critical role in pitting corrosion resistance. Cu ions (Cu^{2+}), released from the steel, disrupt bacterial cell membranes and interfere with essential cellular processes, effectively reducing SRB colonization and biofilm formation. This antibacterial mechanism, coupled with improved corrosion resistance, suggests that Cu-bearing maraging stainless steels could be highly effective in MIC-prone environments.

To comprehensively understand the role of Cu in these improvements, we employed advanced characterization techniques. Using 3D atom probe tomography (3D-APT), we studied the element segregation and nanoscale precipitation behavior of the alloy. High-resolution transmission electron microscopy (HR-TEM) provided insights into the microstructural evolution of the steel during aging, while X-ray photoelectron spectroscopy (XPS) enabled us to analyze the surface chemistry and the composition of the passive oxide layer. Our results showed that the co-precipitation of Cu with Ni_3Ti nano-precipitates contribute to the alloy's increased strength. Cu addition promoted a more uniform distribution of Cr and Mo, improving the corrosion resistance, reducing the likelihood of pitting corrosion induced by SRB.

In summary, the novel Fe-Ni-Co-Cr-Ti maraging stainless steel alloyed with Cu demonstrates a unique combination of ultrahigh strength, enhanced antibacterial properties, and superior resistance to MIC. This study bridges the gap between mechanical performance and corrosion resistance in maraging stainless steels, highlighting the atomistic mechanisms responsible for these enhanced properties. The findings pave the way for the development of next-generation materials for critical applications in the oil and gas industry, where microbial corrosion poses a significant threat to structural integrity and operational safety. This research provides an atomic-scale understanding of how Cu influences the mechanical, antibacterial, and corrosion properties of maraging stainless steel. The insights gained from this study can guide future alloy design and open up new avenues for combating MIC in demanding industrial environments.

Reference

- [1] G. Roscioli, M. Repka, S. Pedrazzini, C.C. Tasan, Chemo-mechanical effects on the cutting-induced mixed-mode II-III fracture of martensitic stainless steels: An in-situ investigation, *Acta Materialia* 231 (2022) 117803.
- [2] F. Niessen, A.A. Gazder, J. Hald, M.A.J. Somers, Multiscale in-situ studies of strain-induced martensite formation in inter-critically annealed extra-low-carbon martensitic stainless steel, *Acta Materialia* 220 (2021) 117339.
- [3] Y.H. Fan, B. Zhang, H.L. Yi, G.S. Hao, Y.Y. Sun, J.Q. Wang, E.H. Han, W. Ke, The role of reversed austenite in hydrogen embrittlement fracture of S41500 martensitic stainless steel, *Acta Materialia* 139 (2017) 188-195.
- [4] Y. Jin, E. Zhou, T. Ueki, D. Zhang, Y. Fan, D. Xu, F. Wang, D.R. Lovley, Accelerated Microbial Corrosion by Magnetite and Electrically Conductive Pili through Direct Fe₀-to-Microbe Electron Transfer, *Angewandte Chemie International Edition* 62(38) (2023) e202309005.
- [5] Z. Li, M. Sun, Q. Xia, Z. Yu, M. Zhao, W. Li, D. Zhang, Y. Fan, D. Xu, F. Wang, Accelerated microbial corrosion of 316L SS in extreme acidic environment by a typical bioleaching strain *Acidithiobacillus ferrooxidans*, *Corrosion Science* (2024) 112353.
- [6] Y. Hu, L. Huang, Y. Lou, W. Chang, H. Qian, D. Zhang, Microbiologically influenced corrosion of stainless steels by *Bacillus subtilis* via bidirectional extracellular electron transfer, *Corrosion Science* 207 (2022) 110608.
- [7] L. Zhao, H. Qian, W. Chang, D. Guo, C.T. Kwok, L.M. Tam, D. Zhang, Effect of aging heat treatment on microbiologically influenced corrosion of 17-4PH stainless steel by *Pseudomonas aeruginosa*, *Corrosion Science* 227 (2024) 111739.
- [8] J. Jiang, D. Xu, T. Xi, M.B. Shahzad, M.S. Khan, J. Zhao, X. Fan, C. Yang, T. Gu, K. Yang, Effects of aging time on intergranular and pitting corrosion behavior of Cu-bearing 304L stainless steel in comparison with 304L stainless steel, *Corrosion Science* 113 (2016) 46-56.
- [9] J.-L. Zhao, D. Sun, M. Arroussi, T.-Y. Lian, X.-R. Zhang, C.-G. Yang, K. Yang, Effect of anodic polarization treatment on microbiologically influenced corrosion resistance of Cu-bearing stainless steel against marine *Pseudomonas aeruginosa*, *Corrosion Science* 207 (2022) 110592.
- [10] H. Liu, D. Xu, K. Yang, H. Liu, Y.F. Cheng, Corrosion of antibacterial Cu-

bearing 316L stainless steels in the presence of sulfate reducing bacteria, Corrosion Science 132 (2018) 46-55.