

High-Temperature Oxidation of XM19 Stainless Steel in Air and Steam-Air: Grain Size Effect and Comparison with SS304H Stainless Steel

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1. Introduction

XM19 (Nitronic 50, UNS S20910) is a nitrogen-strengthened austenitic stainless steel with high strength, corrosion resistance, and toughness [1,2]. Compared with Type 304 stainless steel, XM-19 contains higher Cr, Mn, and N contents, together with Mo, Nb, and V [3], providing enhanced strength and austenite stability [1,4]. Owing to these properties, XM-19 has been applied to highly stressed components in nuclear systems, including BWR core-shroud repair assemblies and SMR reactor components. However, its favorable aqueous corrosion resistance does not necessarily ensure superior oxidation resistance under severe high-temperature steam-containing environments. Steam-air atmospheres can develop during off-normal nuclear events involving water evaporation, continuous steam generation, and air ingress. Previous studies have shown that water vapor can accelerate Cr depletion and promote the transition from protective Cr-rich scales to rapidly growing Fe-rich oxides. The relatively high Cr and Mn contents of XM-19 may improve scale stability through enhanced Cr supply and the formation of Cr-Mn spinel oxides. Initial grain size may also affect oxidation behavior by controlling the short-circuit diffusion of Cr and Mn toward the oxidizing surface.

Nevertheless, the combined effects of alloy chemistry and grain size on XM-19 oxidation in high-temperature steam-air environments remain insufficiently understood. Therefore, this study investigates the oxide-scale formation, elemental distribution, and scale stability of XM-19 with grain sizes of approximately 65–225 μm at 1000 and 1100 $^{\circ}\text{C}$ in air and steam-air, with comparison to SS304H.

2. Experimental

XM19 and SS304H specimens with dimensions of 20 mm $\times$ 8 mm $\times$ 3.5 mm were prepared for high temperature oxidation experiments. Each specimen was provided with a 1.5 mm hole near its upper edge, allowing it to be suspended from the microbalance for continuous mass-change measurements. The chemical composition of the alloy is summarized in Table 1. For SS304H, the additional trace elements not included in Table 1 were 0.027 wt.% Cu, 0.0018 wt.% Ti, and 0.022 wt.% Co.

Table 1. Composition of Xm19 and SS304H

Material	C	Cr	Ni	Mn	Mo	Si	V	Nb	N	P	S	Fe
SS304H	0.054	18.25	8.06	1.07	0.004	0.43	–	0.003	–	0.016	0.002	Bal.
XM19-FG	0.032	21.51	12.04	4.94	2.03	0.39	0.12	0.18	0.338	0.028	<0.0005	Bal.
XM19-MG	0.011	21.19	13.07	4.98	2.10	0.39	0.14	0.14	0.340	0.023	<0.0003	Bal.
XM19-CG	0.050	21.89	12.26	5.33	1.69	0.20	0.24	0.28	0.340	0.019	0.007	Bal.

Representative micrographs and grain-boundary traces used for grain-size analysis are shown in Fig. 1. Grain sizes were measured from optical micrographs using Image J and expressed as equivalent-circle diameters (ECDs), excluding annealing-twin boundaries and grains intersecting the image borders. The mean grain sizes were $39.41 \pm 19.36 \mu\text{m}$ for SS304H(1,897 grains), $65.20 \pm 39.78 \mu\text{m}$ for XM19-FG(1,183 grains), $117.09 \pm 70.81 \mu\text{m}$ for XM19-MG(206 grains), and $225.27 \pm 136.96 \mu\text{m}$ for XM19-CG(93 grains).

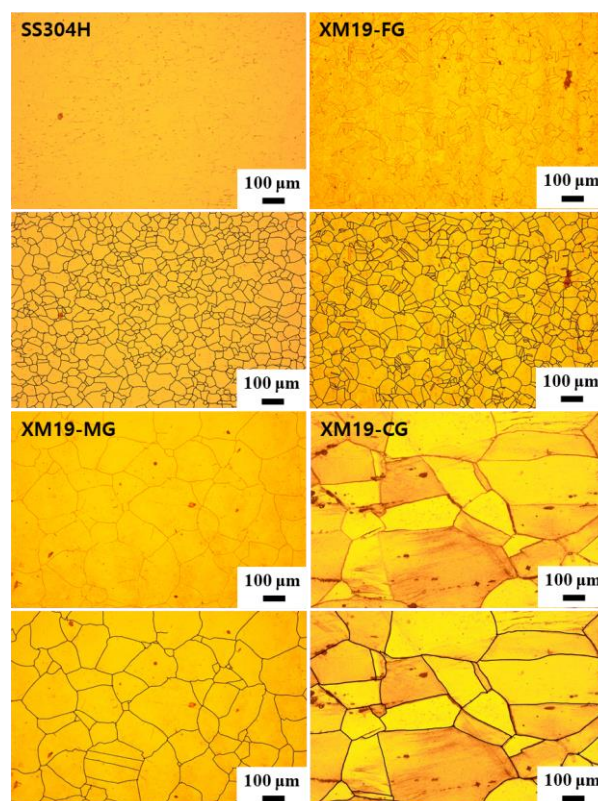


Fig. 1 Optical micrographs (top) and corresponding manually traced grain boundaries (bottom) of SS304H, XM19-FG, XM19-MG, and XM19-CG.

High-temperature oxidation tests were conducted using a custom induction-heated apparatus consisting of a quartz reaction tube, induction coil, infrared pyrometer,

electronic microbalance, and steam-generation system shown in Fig. 2. Specimens were suspended within the induction coil using Chromel wire, and mass changes were continuously recorded during oxidation. The specimen temperature was monitored by an infrared pyrometer calibrated against a thermocouple. For steam-containing tests, deionized water was evaporated at approximately 4.2 mL min^{-1} , and the generated steam was supplied upward through the quartz tube. Because no carrier gas was used and the tube was open to the atmosphere, the test condition is referred to as a steam-air environment. Oxidation tests were performed for 2 h at 1000 and 1100 °C in both laboratory air and steam-air environments.

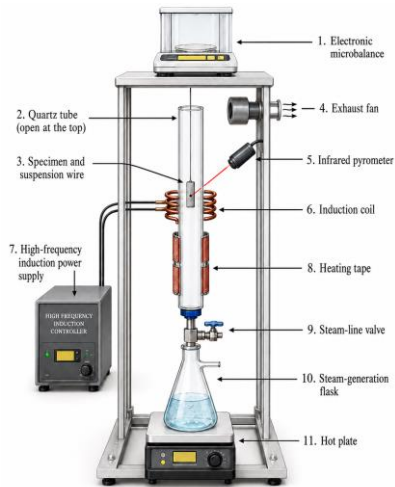


Fig. 2 Schematic diagram of the experiment.

Surface appearance after oxidation was documented to evaluate discoloration, oxide coverage, and scale spallation. Surface morphology and elemental distributions were characterized by SEM-EDS, while oxide phases were identified by XRD using $\text{Cu K}\alpha$ radiation over a 2θ range of $20\text{--}90^\circ$. Cross-sectional specimens were examined using BSE imaging, EDS mapping, and line scans to evaluate oxide-scale morphology, layer structure, and compositional variations across the oxide/alloy interface. Oxide phases were interpreted based on combined XRD and EDS results and were generally classified as corundum-type or spinel-type multicomponent oxides.

3. Results and Discussion

Fig. 3 shows the mass-gain behavior in air at 1000 and 1100 °C. The 2 h mass gain of SS304H increased markedly from 0.47 to 3.61 mg cm^{-2} , while XM19-CG increased from 0.97 to 2.71 mg cm^{-2} . In comparison, XM19-FG and XM19-MG showed only limited temperature dependence, with mass gains remaining below 1 mg cm^{-2} at 1100 °C. Overall, the results indicate that finer-grained XM19 exhibits greater resistance to high-temperature oxidation, particularly at 1100 °C.

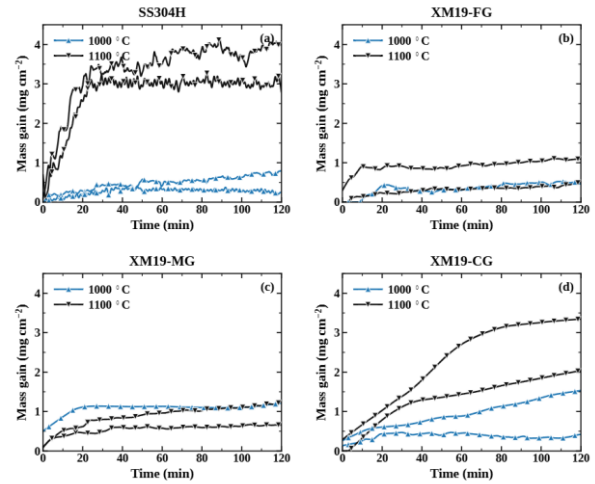


Fig. 3 mass-change curves of SS304H and the three XM-19 conditions during 2 h oxidation in air at 1000 and 1100 °C.

Fig. 4 shows the oxidation behavior in the open steam-fed steam-air environment. SS304H exhibited rapid and sustained oxidation, with the 2 h mass gain increasing from 10.93 mg cm^{-2} at 1000 °C to 16.95 mg cm^{-2} at 1100 °C, accompanied by breakaway-type oxidation at 1100 °C. In contrast, all XM-19 specimens maintained significantly lower mass gains below 2.5 mg cm^{-2} and showed relatively weak temperature dependence. At 1000 °C, the mass gain increased with grain size from FG to MG and CG, whereas this grain-size dependence became less pronounced at 1100 °C. These results demonstrate the superior steam-air oxidation resistance of XM19 compared with SS304H, with the grain-size effect being most evident at 1000 °C.

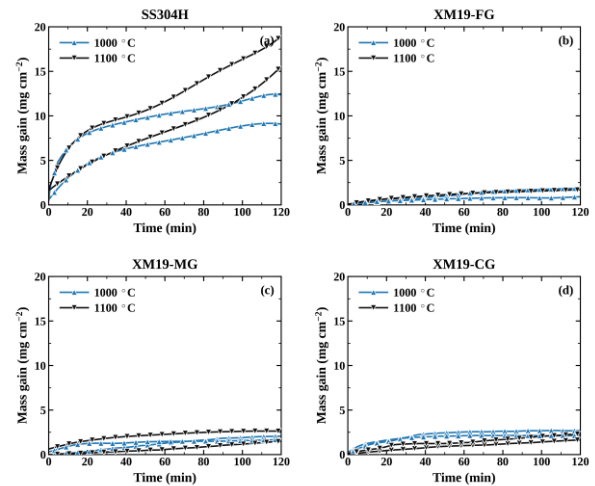


Fig. 4 normalized mass-change curves of SS304H and the three XM-19 conditions during 2 h oxidation in the open steam-fed steam-air environment at 1000 and 1100 °C.

Fig. 5 highlights the distinct environmental sensitivity of SS304H and XM19. Steam-air markedly accelerated the oxidation of SS304H at both temperatures, whereas

XM-19 showed only a limited increase compared with air. The largest difference occurred at 1100 °C in steam–air, where the mass gain of SS304H was nearly an order of magnitude higher than that of the XM-19 specimens. Significant post-exposure scale spallation was observed for SS304H, while XM-19 showed no comparable large-scale detachment. Within XM-19, the influence of grain size depended on the oxidation condition and became relatively weak in steam–air at 1100 °C.

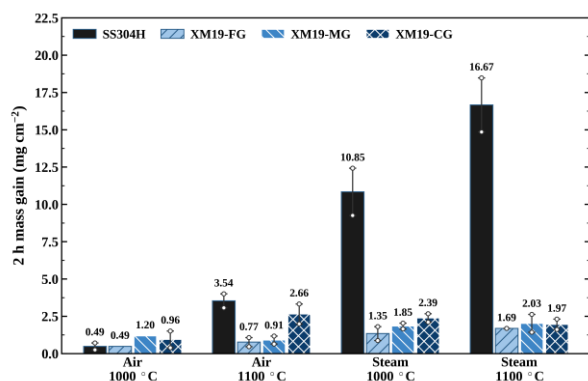


Fig. 5 mass changes of SS304H and the three XM-19 conditions after 2 h oxidation in air and steam–air at 1000 and 1100 °C.

Fig. 6 compares the macroscopic appearance of SS304H and the three XM19 materials after 2 h oxidation. SS304H developed increasingly heterogeneous oxide coverage at the higher temperature and under steam–air exposure, with pronounced surface mottling and extensive scale loss after the steam–air tests. The SS304H specimens shown after steam–air exposure at 1000 and 1100 °C represent the residual specimen surfaces after scale detachment during cooling. In contrast, the XM19 specimens generally retained more continuous oxide coverage, with no comparable extensive scale detachment. Among the XM-19 materials, XM19-CG generally exhibited a more heterogeneous and mottled surface appearance than FG and MG, whereas XM19-FG tended to retain a finer and more uniform surface morphology.

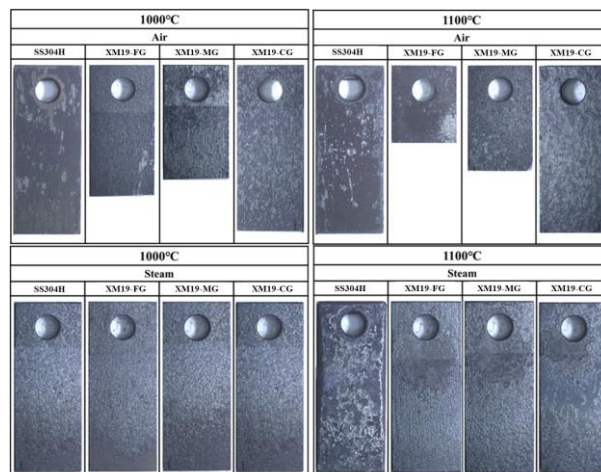


Fig. 6 Surface appearance of SS304H and XM-19 specimens with different grain sizes (FG, MG and CG) after oxidation at 1000 °C~1100 °C in air and steam–air.

Figure 7 compares the XRD patterns after oxidation in air and steam–air at 1000 and 1100 °C. For XM-19, the oxide scales were mainly composed of corundum-type M_2O_3 and spinel-type M_3O_4 phases, together with reflections from the underlying γ -austenitic substrate. Because Fe, Cr, and Mn can form multicomponent oxides, the oxide products were classified primarily by crystal structure rather than by specific stoichiometric composition. In contrast, SS304H showed metallic substrate reflections after air oxidation, whereas these reflections disappeared after steam–air exposure, consistent with its more extensive oxidation. The persistent γ -austenite peaks of XM-19 under all conditions indicate comparatively limited oxide-scale growth.

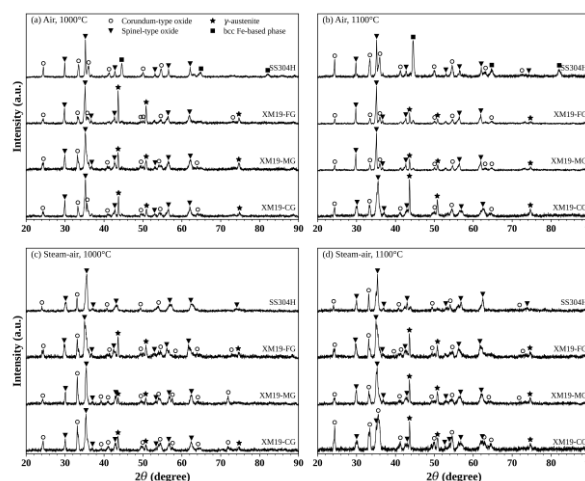


Fig. 7 XRD patterns of SS304H and the three XM-19 conditions after 2 h oxidation

Fig. 8 shows the cross-sectional oxide structures. At 1100 °C, the oxide scales became thicker and more heterogeneous, with interfacial gaps and cracks indicating the formation of a less compact and less adherent protective layer. In contrast to SS304H, XM19

exhibited substantially less oxide development under all exposure conditions, particularly in steam–air. Among the XM19 specimens, XM19-FG showed the least extensive oxide formation compared with the coarser-grained MG and CG conditions.

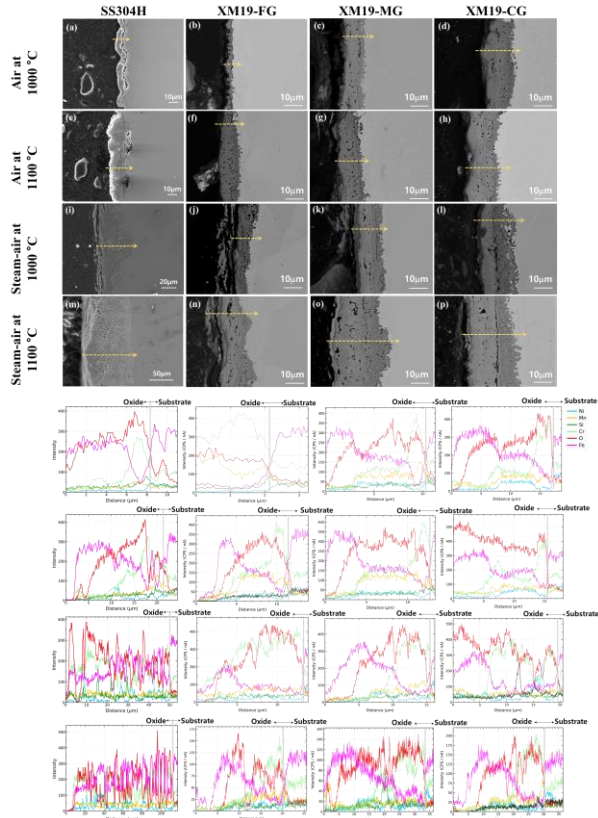


Fig. 8 Cross-sectional images and EDS Lines profiles of SS304H and XM19 oxidized in air and steam-air.

4. Conclusion

XM-19 exhibited significantly better oxidation resistance than SS304H at 1000 and 1100 °C, particularly under steam–air conditions. While SS304H underwent extensive Fe-rich oxidation and severe scale degradation, XM-19 maintained comparatively protective Cr–Mn-enriched inner oxide regions. The improved resistance of XM-19 is attributed primarily to sufficient Cr availability and replenishment, with Mn-containing oxides likely contributing to the stabilization of the Cr-rich scale under steam–air exposure. Grain-size effects were most evident in air at 1100 °C and steam–air at 1000 °C, where finer-grained XM19-FG showed lower mass gain and more effective Cr/Mn-containing oxide development. These results suggest that grain-boundary-assisted transport of protective elements influences oxidation kinetics and oxide chemistry, even when the overall mass-gain differences become small at higher temperature.

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