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High-Temperature Oxidation Behavior of an Additively Manufactured Alumina-Forming Austenitic Stainless Steel

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Abstract

High-temperature oxidation behavior of an alumina-forming austenitic stainless steel (AFA25) produced by additive manufacturing (AM) has been studied at 850 °C in air and compared to the conventional wrought alloy. The mass gain measurements during high-temperature oxidation tests were performed to understand the rate of oxidation, oxidation characteristics, and morphology of oxides that form in these alloys. X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy were used to characterize the microstructure and oxide scale formation during high-temperature exposure. A similar alumina scale was observed on both wrought and AM alloys. The continuous alumina layer that forms in these alloys provides superior oxidation resistance. This paper shows that a variation in AM build parameters influences the oxidation properties, where one AM alloy with a lower laser power to hatch ratio depicts much better oxidation properties compared to conventional wrought AFA alloys.

Keywords: AFA25 alloy; high-temperature oxidation; additive manufacturing; microstructure characterization



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1. Introduction

AFA25 is a newly developed alumina-forming austenitic (AFA) stainless steel designed for high-temperature applications. This alloy has an attractive combination of elevated-temperature mechanical properties, such as creep resistance, weldability, ductility, and high-temperature oxidation resistance (in the temperature range of 600–900 °C) at relatively low alloy cost [1–3]. The AFA25 alloy shows excellent high-temperature oxidation resistance (HTO) by forming an external, protective, and stable alumina-rich scale on the surface upon exposure to high temperatures. This scale offers superior oxidation resistance to the chromia scale formed on conventional stainless steels and Ni-based alloys [2–5]. The growth of Al₂O₃ is ~1 to 2 orders of magnitude slower than that of Cr₂O₃, which contributes to its fundamentally superior HTO resistance [2,6]. Thus, there has been a focus on the development of AFA alloys as a replacement for far more expensive Ni-base alloys or austenitic steels in various environments containing water vapor, carbon, and sulfur species, where the chromia scale protection can be severely compromised [1,7]. AFA alloys typically contain 2.5 to 4 wt.% Al and less than 15 wt.% Cr to stabilize an austenitic matrix for maintaining high-temperature strength at a relatively low amount of Ni (20–25 wt.%) [1,3].

Building on this foundation, numerous studies have systematically examined the oxidation resistance and mechanical performance of AFA alloys under various high-temperature environments [1–37]. Brady et al. [2,7,9–11] demonstrated that a minimum Al content of ~2.5 at. % enables the formation of a continuous α -Al₂O₃ scale, even in humid air with 10% water vapor at 800 °C. Their long-term oxidation tests—spanning over 1000 h—revealed minimal spallation and parabolic mass gains, which are indicative of slow-growing oxide kinetics. Pint and co-workers [12,13] showed that steam exposure and cyclic oxidation conditions further underscore the importance of scale adherence and precipitate stability in real-world scenarios. Yamamoto et al. [1,5,12,13,17,18] further investigated the influence of microalloying additions, such as Nb, Cr, and Ni, which stabilize β -NiAl and Laves phase precipitates, contributing not only to oxidation resistance but also to high-temperature strength. The beneficial role of reactive elements—particularly Hf, Y, and Zr—has been established in enhancing oxide scale adhesion by suppressing void formation at the scale–metal interface and improving grain boundary cohesion [7,13,17–19]. Hu et al. [14] and Gao et al. [15] linked the precipitation of Laves phases and NiAl to sustained creep resistance at temperatures exceeding 900 °C. Taken together, these studies highlight how AFA alloys, through a combination of optimized Al content, reactive element additions, and precipitation hardening, maintain superior oxidation behavior and mechanical reliability across a broad range of harsh service conditions. This unique combination positions AFA steels as viable candidates for advanced energy systems, including ultra-supercritical steam plants and next-generation nuclear reactors [1,12,18,38].

The design of complex geometries and more sustainable use of metal and alloy powders as raw materials in engineering applications have attracted additive manufacturing (AM) as a candidate for equipment development and manufacturing customized parts [21,22]. Compared to conventional manufacturing, Selective Laser Melting (SLM)-based AM facilitates the fabrication of near-net-shaped structures with good feature resolution and minimal waste generation [22,23,38,39]. However, complex melt and thermal history generate non-conventional microstructures and properties in these alloys. The microstructure and properties of the alloys produced by SLM depend on processing parameters, such as laser power, laser speed, hatch spacing, and printing direction [22,39]. Therefore, investigating the microstructure and properties of the alloys produced by AM before translating them into practical applications is of great importance.

While several investigations have been carried out on the oxidation behavior of AFA alloys [1,2,5,7–22], to the best of the author’s knowledge, no work has been performed on the effect of the AM process on the HTO behavior of the alumina-forming austenitic stainless steel (AFA25). Understanding the oxidation behavior of additively manufactured parts and their comparison to those manufactured by a conventional method (wrought alloy in our case) is needed to lay the foundation for AM in engineering applications. A previous study by Hyer et al. [34] on LPBF (Laser Powder Bed Fusion) of AFA alloys demonstrated that only the alumina oxide scale forms on the surface of the AM-based alloys after oxidation at 900 °C for 100 h. To the author’s knowledge, this was the first reported work of AM of AFA alloys; however, the mechanistic understanding of oxide formation during the HTO of the AM alloys still requires further research to design these classes of AFA steels using AM. In this study, the HTO of AFA25 fabricated by Selective Laser Melting (SLM)-based additive manufacturing has been investigated and compared to conventional wrought alloys. Additionally, a thorough investigation was performed using microscopy to understand the mechanism of oxide layer formation and its stability under HTO in AFA25.

2. Materials and Methods

2.1. Materials

Wrought alumina-forming stainless steel alloy (W-AFA25) was obtained from the sponsor of this project as a benchmark alloy, and two additively manufactured AFA25 alloys processed by SLM were used as experimental materials in this work. The alloy powders were purchased from Carpenter, headquartered in Richmond, Virginia, US. The AM alloys are named AM-AFA25-1 and AM-AFA25-16, and their printing parameters are presented in Table 1. The density of the AFA25 alloy is 7.89 g/cc. The nominal chemical composition of AFA25 is Fe-25Ni-14Cr-3.5Al-2.5Nb-2Mn-2Mo-1W-0.5Cu-0.2Si-0.1C-0.05V-0.05Ti (wt.%) [2,3]. The AM parameters were developed based on thorough AM parameter development approaches, but this cannot be expressed in detail in the work owing to restrictions due to Intellectual Property (IP) rights. The SLM parameters are distinguished between the two alloys in terms of laser power and hatch spacing; thus, there is a variation in VED between the builds. Before the high-temperature oxidation test, the entire surface of the alloys was abraded with SiC paper of up to 600-grade and ultrasonically cleaned in ethanol.

Table 1. SLM printing parameters and obtained density for AM-AFA25 alloys.

Scheme	Speed [mm/s]	Power [W]	Hatch [μm]	Density [g/cc]	% from Target
AM-AFA25-1	1000	175	100	7.73	98.03
AM-AFA25-16	1000	250	150	7.74	98.10

2.2. Methods

2.2.1. High-Temperature Oxidation Test

The oxidation test was conducted at 850 °C for 600 h in dry air. Samples were placed in pre-annealed alumina crucibles. Mass measurements of the specimens were performed at every 100 h interval using a Sartorius Quintix semi-microbalance. The cyclic oxidation tests were conducted in a Carbolite muffle furnace in dry air at 850 °C for 600 h; the alloys were placed inside the furnace, and the temperature increased at a constant rate of 88 °C/min. After reaching 850 °C, AFA25 alloys were left at this temperature for a total of 100 h of oxidation time (excluding ramp-up and cool-down steps), followed by cooling inside the furnace. The alloys were taken out of the furnace for mass measurements and were returned to the furnace for the next 100 h of oxidation. Six cycles of high-temperature oxidation tests, equivalent to a total exposure time of 600 h at 850 °C, were performed, as shown in Figure 1. Mass measurements of the specimens were performed using a Sartorius Quintix semi-microbalance with a readability of 10^{-5} g. The repeatability and reproducibility of the instrument were verified with the Gage R&R (ANOVA) test [40,41].

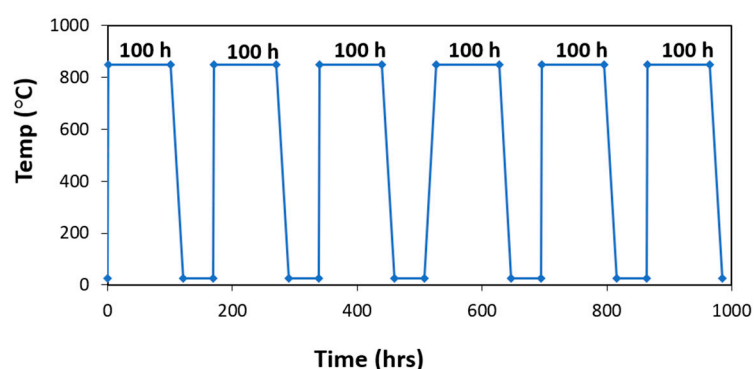


Figure 1. Schematic of oxidation cycles in this research.

The mass change Δm , in mg/cm^2 , for all alloys was calculated using Equation (1):

$$\Delta m = \frac{w_1 - w_0}{A_0} \quad (1)$$

where w_1 and w_0 are the measured mass after and prior to oxidation, respectively, and A_0 is the original sample surface area.

2.2.2. Microstructural Characterization

X-ray diffraction analysis, using Rigaku Smartlab[®] diffractometer manufactured at Tokyo, Japan was performed to investigate the phase composition and the oxide structure formed on the wrought and AM-AFA25 alloys before and after oxidation using Cu K-alpha radiation (wavelength = 0.1541 nm). The scan rate was 2°/minute, and the step size was 0.02° [40,41].

Specimen preparation for SEM involved grinding up to 1200-grit SiC sandpaper, followed by wet polishing with diamond suspension up to 1 μm . Specimens were subsequently ultrasonically cleaned in ethanol for ~5 min, dried with air, and stored in a desiccator. Scanning electron microscopy (SEM), coupled with energy-dispersive X-ray spectrometry (EDS), was performed to investigate the surface morphology of the alloys prior to oxidation and to examine the oxide scale surface and cross-sectional morphologies after the oxidation tests. SEM was performed in backscatter electron (BSE) mode at an accelerating voltage of 20 kV in a Tescan Lyra 3 FIB-FESEM instrument manufactured in the Czech Republic. For the top surface, the oxidized specimens were sputter-coated with a thin Pt layer [6]. For the cross-sectional oxide scale analysis, the Pt-coated oxidized specimens were electroplated in CuSO_4 , mounted in an epoxy resin, ground with SiC sandpaper from 400- to 1200-mesh, and polished to a 1 μm surface finish [3,6,40,41].

The software PANDAT[™] version 2016.1 was used to calculate the phase present at equilibrium as a function of temperature.

3. Results and Discussion

3.1. Pre-HTO Characterization

The microstructure of three alloys (AM-AFA25-1, W-AFA25, and AM-AFA25-16) is shown in Figure 2. Columnar dendrites are observed in the AM-AFA25 alloys, and the grains are elongated along the build direction (Z) (Figure 2a,c). The layer-by-layer deposition and complex cooling cycle in the AM process lead to a columnar dendritic morphology, similar to what has been observed by previous authors [21–23,38,39,42,43]. EDX analysis demonstrates that the bright inter-dendritic regions are Nb-rich second-phase precipitates. The dendritic morphology is different between the two AM-AFA25 alloys, which are expected to result from different SLM processing parameters for each alloy, leading to a different solidification rate and thermal gradient. The high-magnification SEM images of AM-AFA25 are selected to highlight the columnar dendritic structure in AM alloys. Additionally, several microstructural features of laser-based powder processing, including a lack of fusion pores (which is a common defect in SLM processes of alloys [43]), are observed in AM-AFA25 alloys. On the other hand, the microstructure of W-AFA25 alloy (Figure 2b) consisted of Fe and an Ni-rich matrix (γ phase) with a dispersion of bright spherical Nb particles. EDX analysis indicates that the bright particle is Nb-rich precipitation like NbC phases, which is consistent with previous studies [1,5,7,34,44].

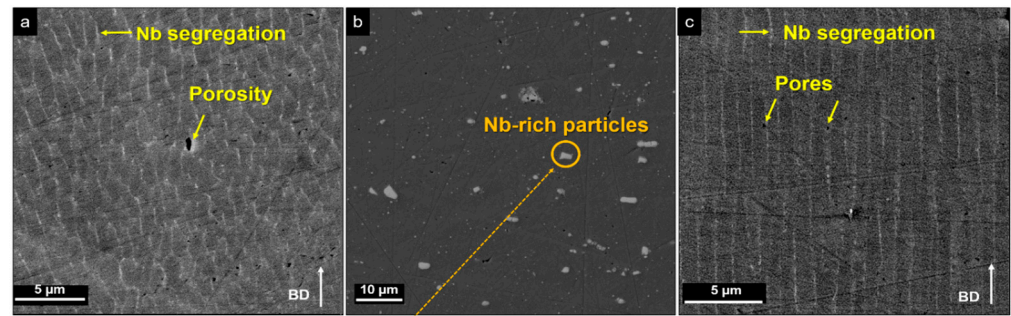


Figure 2. Backscattered electron images of as-received (a) AM-AFA25-1, (b) W-AFA25, and (c) AM-AFA25-16.

Nb and C have a high affinity for each other, thus forming stable and fine-sized NbC. Studies by Du et al. [35] and Zhao et al. [44] show that its formation is essential for enhanced high-temperature strength and hardness for AFA steels. The morphology of Nb-rich phases varies in AM alloys and conventional alloys, where complex heat cycles in AM result in the precipitation of Nb-rich phases or their segregation along the grain boundaries.

3.2. HTO Test and Oxidation Kinetics

Figure 3 shows the mass gain per unit area as a function of oxidation time at 850 °C in dry air for two AM-AFA25 and wrought alloys. The mass gain plots of AM-AFA25 alloys with different printing parameters fall at the top and bottom of the dashed yellow region for the mass gain plots of the AM-AFA25-1 and AM-AFA25-16 alloys (Figure 3).

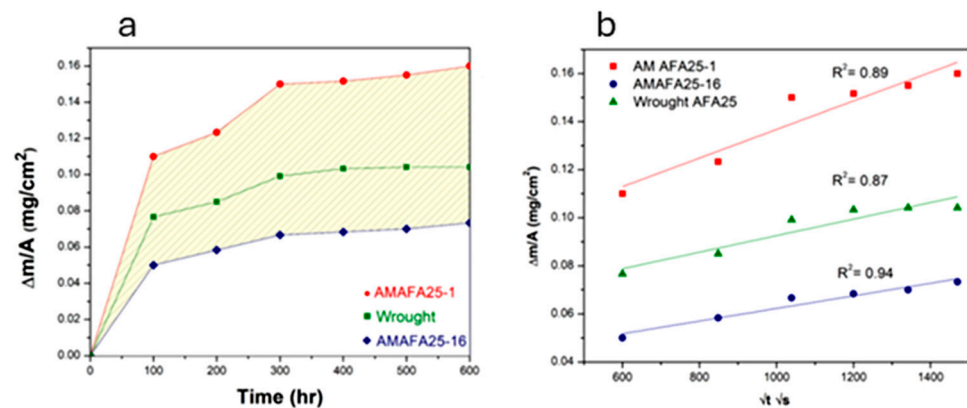


Figure 3. (a) Mass gain per unit area at 850 °C for AM and W-AFA25 alloys. (b) Oxidation kinetics graphs for wrought and AM-AFA25 alloys.

The mass gain data of W-AFA25 are roughly in the middle of the shaded region and were used as the baseline for this study. The mass gain for the AM-AFA25-16 alloy, shown in navy-blue color, shows the highest oxidation resistance in comparison to the other alloys. On the other hand, the red plot shows the relatively poor resistance of AMAFA25-1. The growth rates of the oxide scales for the three alloys follow the parabolic kinetics rate calculated according to Equation (2), which is expressed as [6,45]:

$$\frac{\Delta m}{A} = \sqrt{k_p \times t} \quad (2)$$

where $\Delta m/A$ is the mass change per unit area, k_p is the parabolic oxidation rate constant, and t is the oxidation time.

Mass gain per unit area was plotted according to Equation (2), which indicates parabolic oxidation kinetics. The parabolic oxidation rate constants are presented in

Table 2 and show that the oxidation rate of AMAFA25-1 alloys is higher (almost two times) compared to that of AMAFA25-16. The differences in mass gain per unit area between the AM-AFA25 alloys are attributed to defects such as micro-cracks and pores, which are typically formed during the layer-by-layer manufacturing process and variation in build parameters during the laser additive process, which results in inherent variation in the microstructure. However, the AM-based AFA25-16 alloy shows a lower rate constant and better oxidation behavior than the other AM alloy, indicating that lower volume energy density may have promoted better oxidation resistance.

Table 2. Parabolic rate constant (k_p) calculated for AM and W-AFA25 alloys.

Sample	k_p ($\text{mg}/\text{cm}^{-2}\text{s}^{-1/2}$)
AM-AFA25-1—850 °C	5.94×10^{-5}
W-AFA25—850 °C	3.45×10^{-5}
AM-AFA25-16—850 °C	2.62×10^{-5}

3.3. Post-HTO Characterization

3.3.1. Surface Morphology

The surface morphologies of oxide scales formed on AM-AFA25 and W-AFA25 alloys after HTO testing at 850 °C for 600 h are shown in Figure 4. The initial grinding traces are visible even after high-temperature oxidation, and numerous fine nodules formed on and around the grinding traces during the HTO. This indicates that the oxide layers formed on the surfaces of oxidized alloys are not thick and have wrinkled morphologies. EDX point analysis revealed the presence of Al_2O_3 traces as nodules in the AM alloys, similar to those reported by Hyer et al. [34] in their work on AM of AFAs and Nb-rich oxides in the wrought alloy. To investigate the oxides further, EDX area maps were generated.

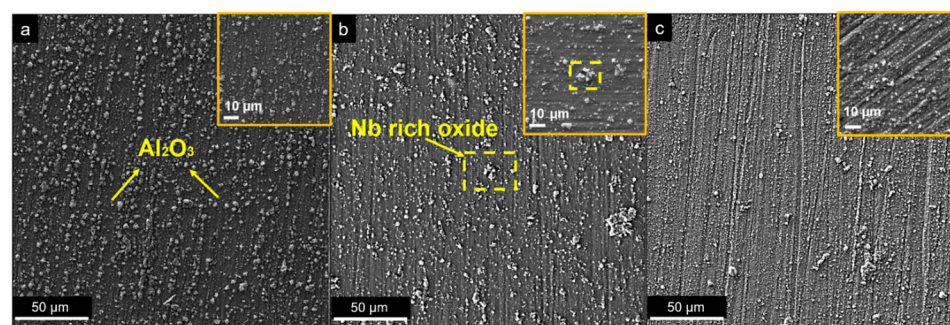


Figure 4. Surface morphology (SE images) of (a) AM-AFA25-1, (b) W-AFA25, and (c) AM-AFA25-16 oxidized at 850 °C for 600 h in the air.

Figures 5 and 6 show the EDX area maps for the top surfaces of AM-AFA25 and W-AFA25 alloys. The EDX results revealed a similar composition of oxide scales on AM and wrought alloys. The EDX results for AM-AFA25-1 only are shown here. The spherical nodular oxide products mainly consist of Al and O elements, which could be due to the formation of Al_2O_3 . The EDX area maps (Figures 5 and 6) also reveal the presence of Mn-rich oxide nodules on top of the oxide surface. The role of Mn in the alloy is to substitute Ni with the low-cost and low-density element (Mn) while stabilizing the austenite matrix [19,46] and to provide creep resistance at temperatures above 650 °C [19–23,38–47]. A previous study reported that high Mn content increases the scale growth rate in former chromia alloys [45], and it degrades the high-temperature oxidation resistance of former alumina alloys [48]. No clear mechanism has been found for this detrimental effect of Mn, except for the formation of a less protective Mn-rich oxide.

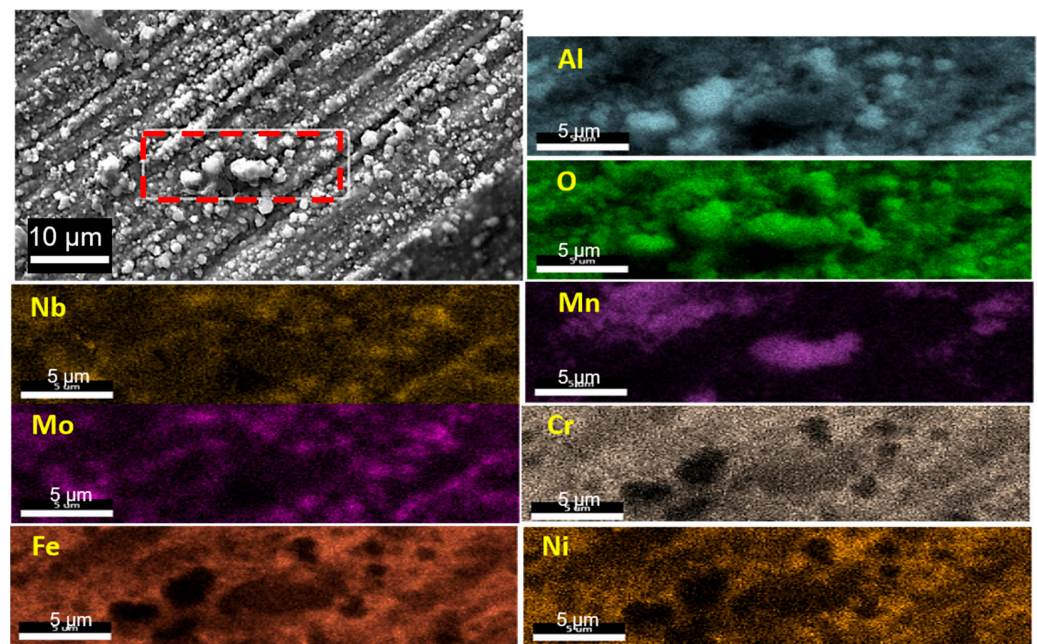


Figure 5. EDX map analysis for the top surface of AM-AFA25-1 oxidized at 850 °C for 600 h in the air. EDS spectra have been depicted for the region shown in the red box in the SEM image.

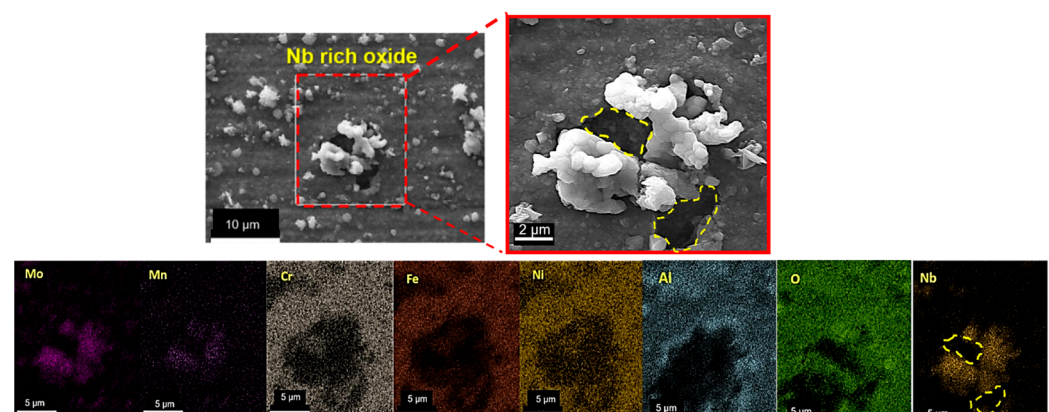


Figure 6. EDX map analysis for the top surface of W-AFA25 oxidized at 850 °C for 600 h in the air.

During the early stages of high-temperature oxidation of AFA stainless steel alloys, a Fe-oxide scale typically grows rapidly, which is followed by the formation of a continuous Cr_2O_3 layer below the Fe-oxide scale. An unstable Al-oxide is the next layer to form, which eventually turns into $\alpha\text{-Al}_2\text{O}_3$ after exposure to the external environment [46,49]. This transition to the steady-state condition is illustrated schematically in Figure 7. Considering the concentration of the alloying elements and their affinity to oxygen, the composition of the oxide layer can significantly change with an increase in oxidation time [24,25]. Once a continuous Al_2O_3 scale forms, it acts as a barrier to further diffusion of the oxidation species, hence decreasing the oxidation rate [46].

Cracking the underlying alumina on the Ni-rich oxide was observed in a few regions of W-AFA25, as shown in the red rectangle in Figure 6, although a similar phenomenon was not seen in AM-AFA25 alloys. The fast-growing Nb-rich oxide nodules, together with some amount of Mn, were detected on the surface of the W-AFA25 alloy. This observation corroborates previous studies [15,26]. The formation of Nb-rich oxides could be related to the oxidation of primary NbC phases [15,26,34]. NbC formed in the AM alloys along the grain boundary actively reacts with oxygen, forming NbO. The PBRs of NbC and NbO are

nearly equal and twice that of Al_2O_3 . This results in cracks, allowing oxygen to diffuse and react with the underlying aluminum in the steel. The variation in Nb concentrations along the grain boundary results in a higher oxidation rate in AFA AM 25-1 steels than in the AFA AM 25-16 steel type. Furthermore, additional defects in AFA AM 25-1 steel result in a higher oxidation rate.

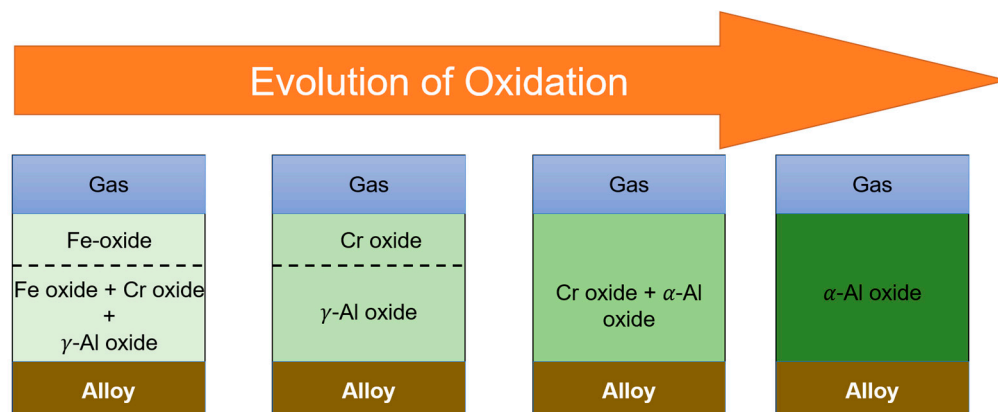


Figure 7. Schematic depiction of high-temperature oxidation progression in alumina-forming austenitic steels [25,27].

The process of $\alpha\text{-Al}_2\text{O}_3$ scale formation and the later cracking during cooling in alumina-forming alloys is illustrated schematically in Figure 8. All the alloying elements oxidize to form a thin oxide scale at very early stages of oxidation, and the partial pressure of oxygen is reduced at the scale/alloy interface. The oxidation kinetics are mainly controlled by the inward diffusion of oxygen through the outer oxide layer formed at initial oxidation [29,31]. Alloys with enough Al can make an external Al_2O_3 scale due to the lowest dissociation of oxygen partial pressure for alumina. During the cyclic oxidation process, the constraint from the bulk alloy limits the expansion of the oxide scale and causes compression in the oxide scale. Eventually, the thermal expansion mismatch between the base alloy and the oxide scale facilitates cracking or exfoliation of the alumina scale during the cyclic oxidation [27]. One method of understanding stress growth in the oxide scale is the Pilling Bedworth Ratio (PBR) [28,29]. The PBR refers to the ratio of the molar volume of oxide to metal [28,29]. The PBR of Nb_2O_5 is more than twice that of the Al_2O_3 [28].

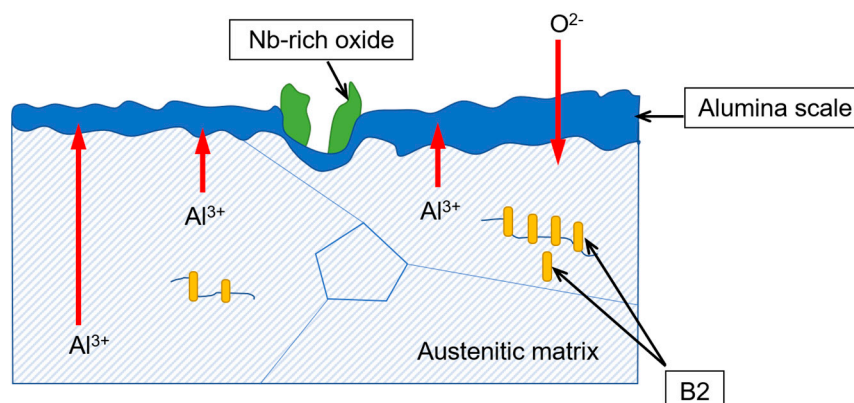


Figure 8. Schematic diagram presenting oxidation of W-AFA25 at 850 °C after 600 h exposure [31,32].

The shedding of Nb- and Mn-oxides causes the underlying Al_2O_3 scale to crack because of the expansion of the holes and defects that cause the thinning of the oxide scale. Figure 8 schematically shows the presence of Nb-oxide in the scale. Since the PBR of Nb-oxide is about 2.6, which is much higher than that of Al_2O_3 (1.28), it generates higher

stress in the scale [27,28]. This suggests another explanation for the cracking of the alumina scale due to stress generation in the W-AFA25 alloy, where the Nb-oxide appeared in the top surface image in Figure 6.

3.3.2. Identification of Oxide Phases

Figure 9 shows X-ray diffraction patterns for the AM and wrought AFA25 alloys following HTO tests for 600 h. The XRD data revealed diffraction peaks corresponding to the austenite matrix (γ -Fe) and ferrite (α -Fe) phase in all three alloys. A single austenite matrix, in the presence of ferrite promoter (Al), can become a dual-phase matrix [34], thus explaining both α and γ phases in XRD peaks. In alumina-forming austenitic (AFA) stainless steels, the ferrite phase (α -ferrite) plays a crucial role in influencing both hot cracking susceptibility and the formation of embrittling phases during high-temperature service. While a small amount of ferrite can help prevent solidification cracking during welding, excessive ferrite can lead to the precipitation of brittle phases like sigma (σ) phase, reducing creep resistance and overall mechanical properties [36,37]. All our alloys show lower and nearly equal ferrite volume fractions. According to XRD, the alumina phase intensity was very low in AM-AFA25-1 and W-AFA25 alloys, and no diffraction peak of alumina was observed in the AM-AFA25-16 sample. This may be due to the thin thickness of the alumina scale (about 0.6 μm) in this AMAFA25-16 alloy. In addition to γ -Fe, precipitate peaks for β -NiAl were detected, which will be further confirmed in the cross-sectional SEM results in the next section.

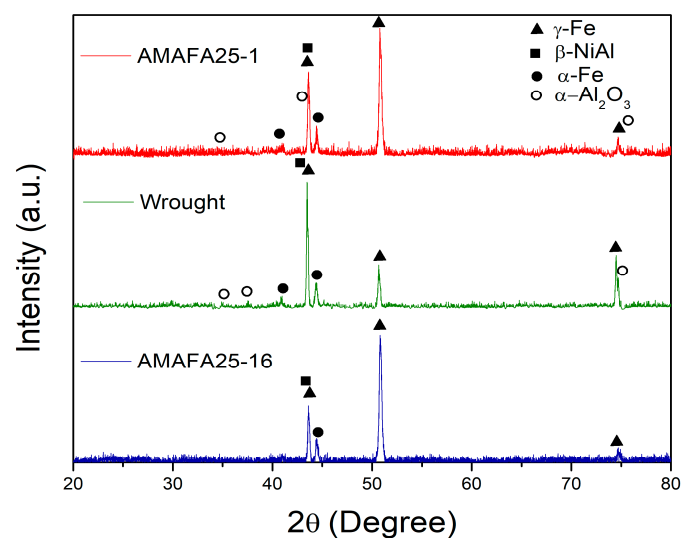


Figure 9. XRD patterns of wrought and AM-AFA25 alloys following oxidation at 850 °C for 600 h.

3.3.3. Cross-Sectional Microstructure Study

Figure 10 shows the backscattered cross-sectional SEM images of the oxidized AM-AFA25 alloys and W-AFA25 after 600 h of oxidation in the air. Cross-sectional images show a dense, continuous, and extensive alumina scale in all three alloys. A denuded zone of β -NiAl is observed underneath the aluminum oxide scales. The main difference in the cross-sectional microstructure between AM and wrought alloys is the orientation and morphology of Nb and aluminide precipitates. In contrast to the conventional W-AFA25, the precipitates in AM-AFA25 alloys seem to be formed and oriented along the build direction (Z), and they appear to be finer in size. Oxide scale thickness and β -NiAl zone depth were measured for AM and wrought alloys (Table 3) and showed that AMAFA25-16 has a thinner oxide scale and thinner β -NiAl denuded zone (~0.6 and ~4.5 μm , respectively) compared to AMAFA25-1 (~1.5 and

~9.4 μm , respectively) and W-AFA25 (~1.0 and ~10.4 μm , respectively) alloys. The EDX area maps of AM-AFA25 alloys (Figure 11) demonstrate the β -NiAl denuded zone in both AM alloys and occasionally Mn-rich oxide nodules only in AMAFA25-1, even though the Al_2O_3 scale remained continuous in these regions. The cross-sectional EDX mapping result for W-AFA25 was discussed in our previous work [3], and the presence of Mn-oxide was also observed in oxidized W-AFA25. β -NiAl precipitates are expected to play a critical role in the continuous formation of the oxide scale in the subsequent oxidation since aluminum diffuses from the NiAl to the interface, forming a continuous oxide layer, as confirmed through microscopy studies. The XRD data showing the β -NiAl peaks are thus confirmed in this section.

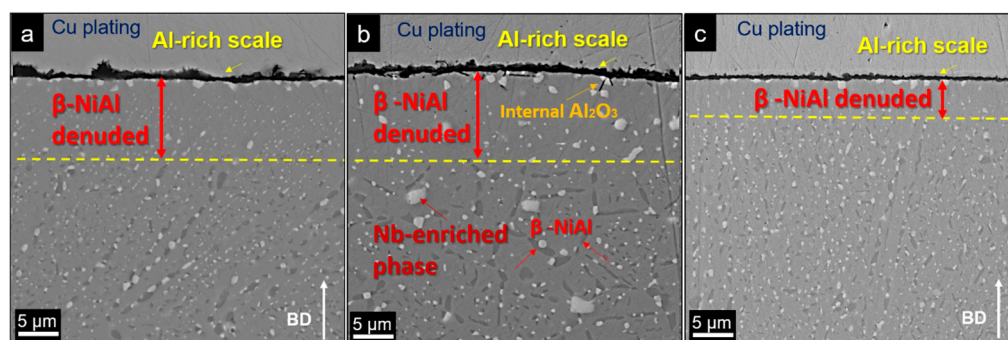


Figure 10. Backscattered electron images showing cross-sections of (a) AMAFA25-1, (b) W-AFA25, and (c) AMAFA25-16 following oxidation at 850 °C for 600 h in the air.

Table 3. Oxide scale thickness and denuded β -NiAl depth for AFA25 alloys measured by ImageJ V1.5 software.

Sample	Oxide Thickness (μm)	Denuded β -NiAl (μm)
AM-AFA25-1—850 °C	1.5 ± 0.5	9.4 ± 0.1
W-AFA25—850 °C	1 ± 0.2	10.4 ± 0.3
AM-AFA25-16—850 °C	0.6 ± 0.09	4.5 ± 0.2

Figure 12 schematically presents the formation of the β -NiAl denuded zone and Al_2O_3 at the interface of the alloy/oxide scale. When the alloy is continuously oxidized at a high temperature (850 °C), oxygen tends to diffuse inwards through the oxide scale, and eventually, Al_2O_3 forms at the alloy/scale interface. As the oxidation proceeds, the thickness of the β -NiAl precipitate zone increases, and the neighboring β -NiAl precipitates dissolve to supply Al to the oxidation front. β -NiAl precipitates act as an Al reservoir to maintain the Al_2O_3 surface scale [7,31]. The β -NiAl denuded zone detected below the oxide scales of Figure 10 supports the conclusion that β -NiAl near the oxidized alloys decomposes as Al diffuses outwards (towards the surface) and reacts with oxygen to form the oxide scale. Also, the relative Cr content in the austenite matrix increases as the aluminide forms in the matrix of the alloy due to the depletion of Al and Ni [9,46]. The increase in Cr content leads to the formation of an alumina layer that acts as a protective scale. This is the result of a so-called third-element effect. This phenomenon implies that the addition of Cr reduces the key content of Al to form an external oxide layer. The reason is that the oxygen affinity of Cr is between that of Al and Fe [32]. Therefore, Cr behaves as the “getter” of oxygen during the initial stage of oxidation. It also hinders the inward diffusion of oxygen to the alloy, and as a result, it minimizes the internal oxidation [9,33,46]. Aluminum has a high affinity for oxygen. Additionally, the AM alloys have NbC-rich phases along grain boundaries, which promote reaction with oxygen and form Nb-oxide.

Since Nb-oxides have a high PBR, they crack and allow oxygen to diffuse and react with the underlying aluminum in the steels.

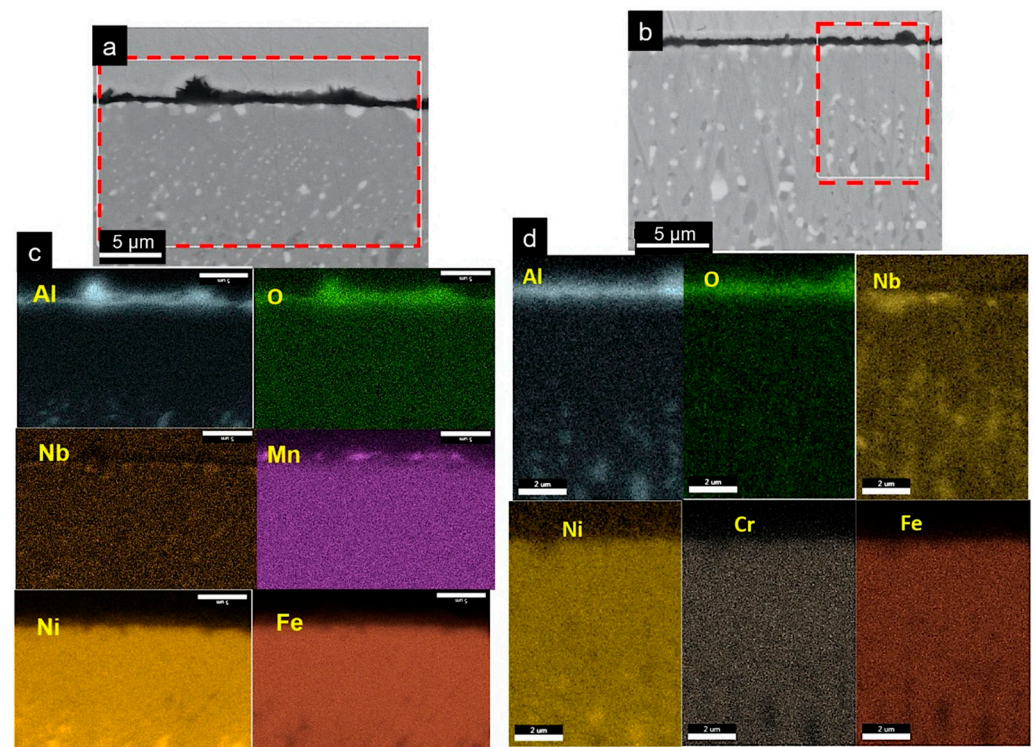


Figure 11. Backscattered electron images showing cross-sections of (a) AMAFA25-1 and (b) W-AFA25 following oxidation at 850 °C for 600 h in the air. EDX area maps of the regions in the red box for (c) AMAFA25-1 and (d) W-AFA25.

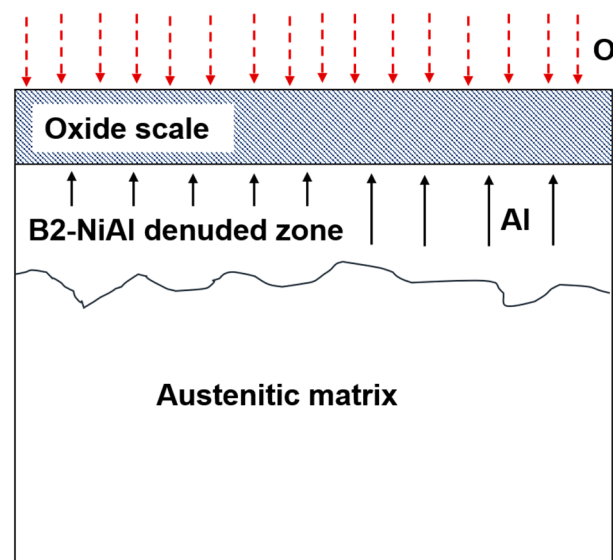


Figure 12. Schematic diagram representing high-temperature oxidation of the AFA alloy [7,35].

Thermodynamic calculations of the weight fraction of precipitate phases as a function of temperature for the AFA25 alloy, along with its chemical composition, are shown in Figure 13. This thermodynamic assessment of AFA25 revealed a tendency towards the formation of a brittle σ phase below ~ 750 °C, MC, Laves phase, and β -NiAl phases at 850 °C, and the austenite phase (dominant phase), which confirms the experimental results in this study. The presence of Laves phases in AFA steels generally enhances oxidation

resistance by stabilizing alumina formation and improving scale adhesion, but only when properly controlled. Excessive precipitation or improper distribution can lead to aluminum depletion and reduced protective scale formation [5]. Note that the Laves phase was not observed in this study for both the conventional wrought and AM alloys using SEM or XRD. This thermodynamic calculation also confirms our hypothesis that NiAl acts as an aluminum reservoir since its volume fraction falls with increasing temperature, allowing the formation of aluminide at the interface.

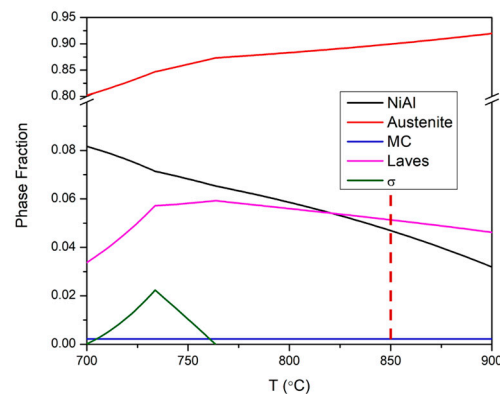


Figure 13. Temperature dependency of phase composition of the AFA25 alloy by PANDAT™ V2016 software.

Internal oxidation, in the form of intergranular oxidation of Al, was observed in W-AFA25 (Figure 10b). Intergranular oxidation can degrade the mechanical properties of the material after very long exposure [23]. This type of internal oxide was also observed in AMAFA25 alloys (Figure 10a,c), along with some internal cracks. Discrete oxide particles were observed inside the substrate of AMAFA25-1 and AMAFA25-16 alloys, as shown in Figure 14. Other defects, like oxide particles and inclusions, were also observed (Figure 14). The formation of the oxides could be attributed to the high oxygen content of the feedstock or the build environment [43].

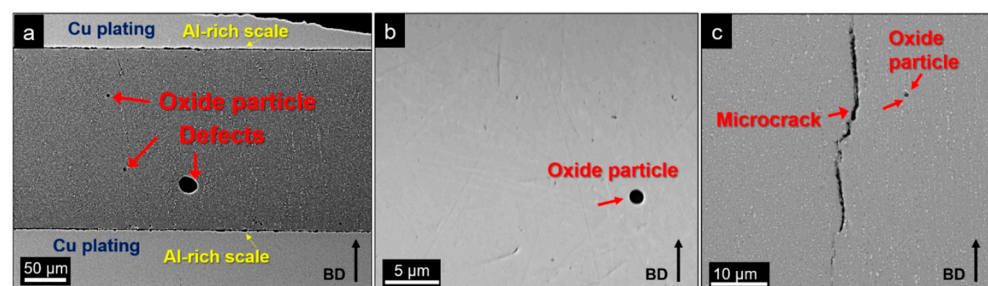


Figure 14. Backscattered electron images of (a,b) AM-AFA25-1 and (c) AM-AFA25-16 following oxidation at 850 °C for 600 h.

4. Conclusions

The high-temperature oxidation (HTO) behavior of alumina-forming austenitic (AFA25) stainless steel processed by AM at 850 °C in dry air was investigated and compared to that of the wrought alloy. The following are the main conclusions:

- The oxide scale formed on the AM and wrought AFA25 alloys is similar in nature and is composed of Al_2O_3 . The continuous external Al_2O_3 scale acts as a barrier for oxygen diffusion from the oxide surface towards the matrix of the alloy and provides a superior high-temperature oxidation resistance.

- An Al-denuded zone of β -NiAl phase was observed in the region underneath the oxide scale in the AM and wrought alloys. The depth of β -NiAl in AMAFA25-16 was much lower compared to the wrought and AMAFA25-1 alloys after 600 h of oxidation. Moreover, a dense and protective oxide scale formed on the surface of AMAFA25-16. This shows that AMAFA25-16 possesses not only good oxidation resistance after 600 h of exposure but also has enough Al reservoir due to lower depletion of the β -NiAl precipitate. Since the layer height and scan velocity were the same for both alloys, it appears that a variation in VED has a significant impact on the oxidation properties. The VED is expected to be higher for the AMAFA25-1 alloy, which shows inferior oxidation properties.
- Internal oxide was observed in both wrought and AM-AFA25 alloys. Wrought alloys showed the presence of intergranular alumina, whereas oxide particles were observed inside the AM-AFA25 alloy.
- Further research is required to understand how variation in each AM parameter can influence the underlying microstructures and their effect on high-temperature oxidation of AFA steels. Additionally, oxidation at each temperature interval needs to be investigated to better understand the oxidation mechanism of AM-based AFA alloys. The effect of the ferrite volume fraction in the AFA steels on oxidation behavior has not been investigated in this work and can be the focus of future research.

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