

Metal Dusting Resistance of N06235 Alloy and its Weld Overlay Under High Pressure Condition

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ABSTRACT

A relatively new N06235 alloy has been developed to offer excellent metal dusting resistance by utilizing the effect of copper on inhibiting carbon deposition and graphite formation, and its weld overlay could provide a cost-efficient alternative for metal dusting and other high temperature corrosion protection. The current paper studied metal dusting resistance of the N06235 alloy and its weld overlays, which were applied by Gas Metal Arc Welding (GMAW) or Hot-Wire Laser process on N06230 alloy plate, along with a wrought N06025 alloy for comparison. The metal dusting test was conducted in a 47CO-47H₂-2H₂O-4CO₂ gas with high carbon activity under 18bar pressure at 620°C. The test coupons were periodically removed from the furnace to measure weight change and check on metal dusting attack. After 790h exposure, the N06235 alloy and its weld overlays showed excellent metal dusting resistance, while metal dusting attack was observed on the wrought alloys, N06025 and N06230, after the first 50h exposure. Metallurgical examination after the metal dusting test was performed to characterize the metal dusting attack on the N06235 weld overlay and the wrought alloys N06025 and N06230. Detailed investigation and discussion on the N06235 weld overlays, including oxide scale, surface pit, and subsurface chemistry change, were presented.

Keywords: Metal Dusting, Ni-Base alloy, Chromia-Former, Copper Addition, Weld Overlay

INTRODUCTION

Many industrial processes contain H₂, CO, CO₂, and H₂O gas mixtures, such as syngas production and processing in hydrogen, ammonia, and methanol plants. These process environments have high carbon activity, *i.e.* $a_c > 1$, and low oxygen partial pressure at their elevated operating temperatures, such as in the temperature range of 400-800 °C (752-1472 °F).¹⁻³ The high carbon activity could result in a catastrophic material degradation, *i.e.* metal dusting. The resulting corrosion products consist of carbon or graphite and metal particles, along with possible carbides and oxides, and cause material disintegration.⁴⁻⁸

High carbon activity causes carbon deposit at the gas-metal interface through the following reactions,



With the presence of water vapor, following reactions are likely to occur:



Reactions (1) and (2) are two main reactions to control metal dusting corrosion, and they are often referred as CO-reduction and Boudouard reaction, respectively.⁹ The carbon activity from Reaction (1) and (2) is calculated in Equation (6) and Equation (7):

$$(a_c)_1 = K_1 \cdot \frac{p_{\text{CO}} \cdot p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \quad (6)$$

$$(a_c)_2 = K_2 \cdot \frac{(p_{\text{CO}})^2}{p_{\text{CO}_2}} \quad (7)$$

where $(a_c)_1/(a_c)_2$ and K_1/K_2 are the carbon activity and equilibrium constant for the corresponding reactions (1) and (2), and p is the partial pressure of the corresponding gas. It is noted that the reaction kinetics are low at the elevated temperatures, so the reactions are slow to reach equilibrium for carbon deposit. However, iron (Fe), nickel (Ni), or cobalt (Co), the major alloying elements in commercial alloys, are known to serve as catalyst for carbon dissolution to establish steady-state a_c , especially through Reaction (1) because of its faster kinetics.¹⁰⁻¹¹ For this reason, commercial Fe-, Ni-, and Co-based alloys are vulnerable to metal dusting attack. Among commercial alloy systems, carbon steel and low alloy steels with the body-centered cubic (BCC) crystal structure are more highly susceptible to carbide formation than those with the face-centered cubic (FCC) structure, which has relatively low carbon diffusivity and high carbon solubility.¹²

To resist metal dusting attack, alloys rely on the formation of a protective oxide scale, such as chromium oxide (chromia, Cr₂O₃), aluminum oxide (alumina, Al₂O₃), or silicon oxide (silica, SiO₂). For most commercial alloys, chromium (Cr) is the major alloying element for high temperature oxidation and corrosion resistance by forming a protective chromia scale. Higher chromium

content in an alloy helps to form more protective chromia scale for better metal dusting resistance.¹³⁻¹⁵ However, the ability to establish a protective chromia scale also relies on other factors. A study by Grabke et al.⁴ showed that an Fe-18Cr-1Al-1Si alloy exhibited no metal dusting attack even though the Cr content was relatively low when compared to the austenitic steels 800 and AC 66 because higher Ni contents in the austenitic steels resulted in lower Cr diffusivity. Both aluminum (Al) and silicon (Si) are effective alloying additions to improve metal dusting resistance by forming a protective alumina or silica scale.¹⁴ The addition of relatively high Al or Si content in order to form an alumina or silica scale presents significant challenges to manufacturing and fabrication of components.¹⁶

Copper (Cu) does not form carbides and is non-catalytic to carbon deposition. The metal dusting behaviors of binary Ni-Cu alloys with 2.5 - 50 wt.% Cu were studied in 68%CO-31%H₂-1%H₂O ($a_c=19$) at 680°C for up to 150h, and the results showed that increasing Cu content decreased the rate of carbon uptake.¹⁷ For the alloys with Cu content above 20% wt.%, the weight gain was negligible and no carbon deposit was observed on the test coupons in the study. By utilizing the benefit of Cu for metal dusting resistance, HAYNES® HR-235® ⁽¹⁾ alloy (UNS⁽²⁾ N06235) has been developed and showed excellent metal dusting resistance.^{16,18} Without high amounts of Al and Si additions, the N06235 alloy also exhibits good fabricability.

Weld overlays have been used as a cost-efficient alternative for high temperature corrosion resistance. However, there are significant differences in the metallurgical aspects between a wrought alloy and its weld overlay format. The weld overlay has dendritic structure, alloying element segregation, and a certain level of alloying element dilution due to the mixture of filler metal and base metal during overlay welding process, which could result in lower concentration of alloying elements, such as Cr, in the weld overlay. In the current study, GMAW and Laser N06235 weld overlays were deposited on wrought HAYNES® 230® alloy (UNS N06230) plate, and the metal dusting test under high pressure condition was performed on the N06235 alloy and its weld overlays, along with a wrought alloy, 602CA (UNS N06025), for comparison. This paper characterizes the weld overlay microstructure and chemistry, and analyzes the metal dusting behaviors of the weld overlays and the wrought alloys N06230 and N06025.

EXPERIMENTAL

The nominal chemical compositions of the alloys studied are listed in Table 1. The three alloys are Ni-based with high Cr contents to form a chromia scale for high temperature corrosion protection, in which the N06235 alloy has the highest Cr content (31 wt.%), followed by 25 wt.% Cr in N06025, and N06230 contains the least Cr content (22 wt.%). 3.8 wt.% Cu is added to N06235 for metal dusting resistance. N06025 contains 2.1 wt.% Al to help its high temperature oxidation and corrosion resistance, while Al contents in the other alloys are less than 0.5 wt.%.

⁽¹⁾ HAYNES, HR-235, and 230 are registered trademarks of Haynes International Inc.

⁽²⁾ UNS Unified Numbering System for Metals and Alloys (UNS). UNS numbers are listed in Metals & Alloys in this Unified Number System, 10th ed. (Warrendale, PA: SAE International and West Conshohocken, PA: ASTM International, 2004)

Because of the beneficial effects of reactive elements on high temperature oxidation resistance, N06230 and N06025 alloys contain La, Y, and/or Zr additions.

Table 1
Nominal chemical composition of the alloys studied (wt.%)

Alloy	Ni	Co	Cr	Al	Si	Ti	Fe	Mo	W	C	others
N06235	Bal.	-	31	0.4 ^a	0.6 ^a	0.5 ^a	1.5 ^a	5.6	-	0.06 ^a	3.8Cu
N06230	Bal.	5	22	0.3	0.4	0.1 ^a	3	2	14	0.1	0.02La
N06025	Bal.	-	25	2.1	0.5 ^a	0.2	10	-	-	0.2	0.1Y 0.1Zr

^a maximum value

N06235 welding wire 0.045" (1.14mm) in diameter was used to generate weld overlay samples for the metal dusting test. The N06235 GMAW and Laser weld overlays were applied on ~6" x 6" x 0.472"-thick (150mm x 150mm x 12mm) and 6" x 6" x 0.1875"-thick (150mm x 150mm x 4.8mm) N06230 plates by using Pulsed GMAW (GMAW-P) and Hot-Wire Laser processes, respectively. The thickness of the N06235 and N06025 plates to be tested was 0.125" (3.175mm). The weld overlay and wrought alloy plates were cut to an approximate size of 0.5"-1.0" (13-25mm) x 0.3"-0.4" (8-10mm) x thickness for the metal dusting test. The weld overlay surface was kept in its as-welded condition for the metal dusting test, and the other cut sides of the weld overlay and the surfaces of the wrought alloy coupons were polished to P1200-grit finishing using silicon carbide paper. The test coupons were then cleaned with alcohol and acetone, and weighed before they were inserted into the furnace for the metal dusting test.

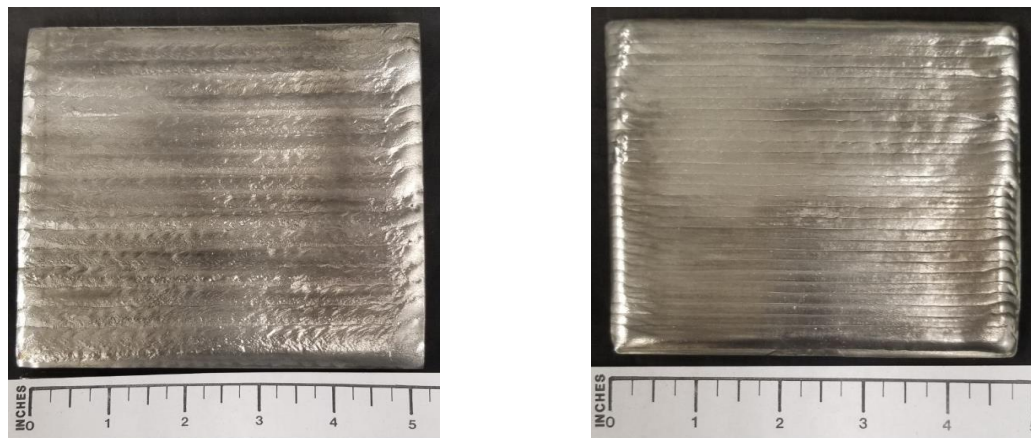
The metal dusting test was performed in a pressurized tube furnace in a lab flowing gas environment. The testing temperature and pressure were 1148 °F (620 °C) and 261 psi (18 bar), respectively. The test gas composition was 47%CO-47%H₂-2%H₂O-4%CO₂, and its carbon activity (a_c) was calculated to be 601 based on the CO reduction reaction (Reaction (1) and Equation (6)). The test coupon was placed in an alumina crucible for the metal dusting test. To reduce the cross contamination of coke deposit, each crucible only contained one coupon. The test coupons were periodically removed from the furnace for visual examination and weight measurement. After the test coupons were removed from the furnace, the coupon surface was brushed to remove carbon deposit, and then the coupons were ultrasonically cleaned in alcohol prior to weight measurements. The total test period was 790 hours, and the time to observe the first pit, *i.e.* the sign of metal dusting attack, was recorded. After the metal dusting test, all coupons were cleaned and weighed, followed by surface and cross-sectional examination. Because the wrought N06235 coupon did not show any sign of metal dusting attack after 790h test, it was still kept for further metal dusting testing to evaluate its long-term performance. Hence, this paper does not include the cross-sectional examination of the wrought N06235 coupon.

Optical metallographic and Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM/EDS) techniques were used for examination and analysis. The weld overlays and wrought alloys were characterized in the aspects of weld overlay microstructure, oxide scale formation, compounds in metal dusting pit, internal carbide precipitation, and composition profiles in the weld overlay, etc.

EXPERIMENTAL RESULTS

After the overlay deposition, the edges of the weld overlay samples were cut to have weld overlay only on the top of the sample. Figure 1 showed the overlay samples in the as-welded

condition. The GMAW and Laser weld overlays exhibit excellent finishing with consistent surface profiles, and no weld defects were observed. Laser weld overlay exhibited smaller and smoother weld beads, while more weld ripples appeared on GMAW weld overlay.

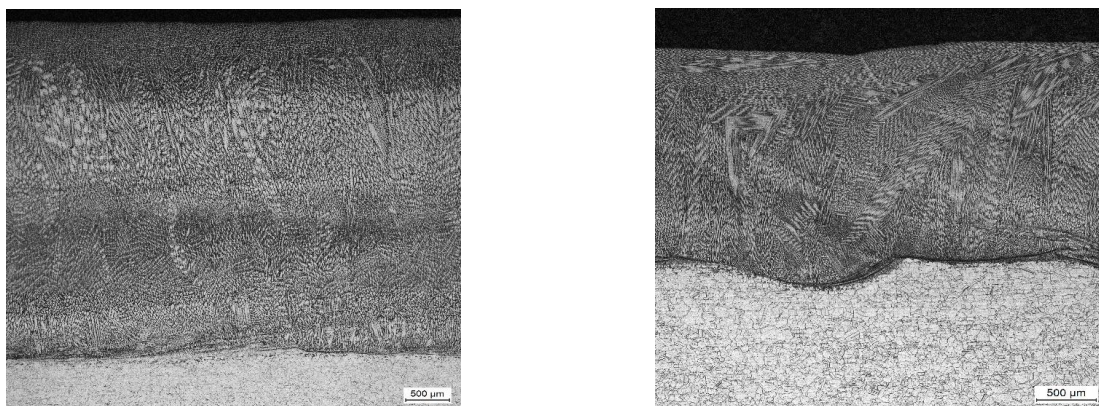


(a) GMAW weld overlay

(b) Laser weld overlay

Figure 1: As-Welded N06235 GMAW and Laser weld overlays

The etched transverse cross-sections of two N06235 weld overlays were examined under optical microscope (Figure 2). The weld overlays showed excellent integrity, and the welding fusion line did not show porosity or lack of fusion, which are two major defects often occurring in weld overlay. The thickness of the GMAW and Laser weld overlays were measured to be about 0.2" (5 mm) and 0.08" (2 mm), respectively, responding to the different welding processes. A typical dendritic microstructure of weldment was observed in both weld overlay coupons.



(a) GMAW weld overlay

(b) Laser weld overlay

Figure 2: Cross-sectional images of N06235 GMAW and Laser weld overlays

The chemical composition from the N06235 overlay surface to the base N06230 alloy was measured using EDS techniques, as shown in Figure 3. GMAW and Laser weld overlays showed consistent Cr and Cu profiles across the weld overlay thickness, which is important to be able to provide consistent high temperature corrosion resistance through the weld overlay thickness. The average Cr contents were 28.5 and 28.3 wt.% in the GMAW and Laser weld overlays, respectively. The similar Cr contents indicate similar welding dilution levels of the two welding processes.