The Degradation of SA213-T22 steels Coated with Ni-based Alloy Containing WC-Co in Simulated Molten Salt Atmospheres

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Abstract. This work reveals the high-temperature oxidation resistance of WC-Co coated on SA213-T22 by High-Velocity Oxy-Fuel (HVOF) technique in simulated molten salt atmospheres and compare that with the uncoated Cr-containing steel. The corrosion behaviors of SA213-T22 coated and uncoated with WC-Co alloys were studied by immersion test under simulated molten salt atmospheres at 600 °C for 3 hours and investigated their corrosion current densities by electrochemical test. Scanning electron microscope equipped with EDS technique and X-ray diffraction were used to evaluate the surface morphology and phase constitution. The oxidation rate of the coated and uncoated steels was observed under simulated atmospheres at 750 °C for 120 hours before the immersion test. The mass gain scale increase with increasing the oxidation time and the oxidation rate of scale are limited by the WC-Co alloys coating layer, which acted as a protective layer. The low corrosion current density of the WC-Co self-fluxing coated steel after oxidation was shown 5 – 10 µA/cm\textsuperscript{2} after the corrosion test in molten salt for 3 hours. After the immersion, the scale layer on the uncoated specimen was disappeared, but one-half of the oxidized coating layer on the coated specimen has remained.

1. Introduction
Molten salt is the one excellent heat transfer fluids (HTFs) for solar thermal power plants due to thermal stability at high temperatures. There are high viscosity, low vapor pressure, and high viscosity at high temperature. Molten salt is based on nitrates/nitrites (NaNO\textsubscript{3} 60% and KNO\textsubscript{3} 40%) that would be used for HTFs in the solar thermal power plant. It melts at 223°C, stable liquid phase up to 600°C [1, 2]. The molten nitrate salt contains an oxidizing agent as NO\textsubscript{3}, the corrosion reaction of molten nitrate salt
attacked the parts at high temperature followed by Equation 1-6 [3]. The commercial-grade were also dissolved chloride ion coming from these impurities may be concerned for increased corrosion rate.

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\begin{align*}
\text{NO}_3^- + 2e^- & \leftrightarrow \text{NO}_2^- + \text{O}^{2-} \\
\text{Fe} + \text{O}^{2-} & \leftrightarrow \text{Fe} + 2e^- \\
3\text{FeO} + \text{O}^{2-} & \leftrightarrow \text{Fe}_3\text{O}_4 + 2e^- \\
2\text{Fe}_3\text{O}_4 + \text{O}^{2-} & \leftrightarrow \text{Fe}_3\text{O}_4 + 2e^- \\
2\text{Cr} + 3\text{O}^{2-} & \leftrightarrow \text{Cr}_2\text{O}_3 + 6e^- \\
\text{Fe} + \text{Cr}_2\text{O}_3 + \text{O}^{2-} & \leftrightarrow \text{FeCr}_2\text{O}_4 + 2e^-
\end{align*}
\]

To combat the high-temperature corrosion, the basic grade of the ferrous alloys is carbon steel, which gives iron oxides on the surface at high temperature. Cr can be added up to about 2-9 wt % giving alloys T22, T23, T24, T91, and T92 to increase the use temperature to 550-600 °C [8-4]. The Cr addition can also be higher than 12 wt % giving stainless steels, which can be used up to 675 °C for the boiler application [9, 10]. The effect of the oxide layer on the corrosion resistance of low carbon boiler steels in oxidation atmospheres were investigated by electrochemical test and showed a dense-double layer of FeO and Fe3O4 acts as the protective film[11]. The present study focuses on the application of T22 steel, which is the intermediate grade between the cheaper carbon steel and the more expensive stainless steel. Since the coating can be applied to increase the high-temperature corrosion resistance of the alloy, the T22 intermediate grade will be coated for such a purpose in this study.

The Cr-Ni alloy was applied by electroplating technique for the protective coating layer on T22 steel, which showed a cracking coating layer through the substrate.[12] Thermal spray coating processes are considered for coating the boiler components to increase corrosion and erosion resistance[14, 13]. High-Velocity Oxy-Fuel (HVOF) is commonly used because of its flexibility in a variety of selected materials, good efficiency, and cost-effectiveness. Thermally sprayed coatings were mainly attacked through oxides and voids at splat boundaries[15]. The NiCr alloy is suitable for high-temperature corrosion resistance [17, 16]. Most literature revealed that the addition of WC-Co alloys improve the micro-hardness value of materials, wear and erosion resistance when compared with the other powders [19, 18]. In addition, WC-based coatings usually showed higher wear resistance than Cr2C-based coatings. [22–20] They found that the corrosion potential of WC-Co coating increased after the process of heat treatment [23]. This paper investigated SA213-T22 steel uncoated and coated with WC-Co self-fluxing alloy powder by HVOF spray system at the high-temperature oxidation of the air and water vapor environment at 750 °C, and under the simulated corrosive atmosphere of molten salts at 600 °C.

2. Experimental method

2.1. Test specimens and coating preparation

This study used ferritic steel with 2.25wt%Cr (SA213-T22) in a power plant, and the chemical composition is shown in Table 1. The coating material used was a WC-Co self-fluxing alloy powder with the chemical composition shown in Table 2. The powder particles contained 88WC-12Co particles (Figure 1(a)) and self-fluxing alloy particles (Figure 1(b)) in the ratio of 50:50 by weight. The specimens were machined with dimensions of approximately 10 mm x 15 mm x 5 mm and polished with 600 grit SiC papers, then cleaned with acetone. The specimens for coating were blasted before by alumina grit, and the coating parameters were reported in Table 3 [24], and the coating layer is shown in Figure 1. The SEM-EDS analysis showed the phase rich in W, Co, and C in the white area and the phase rich in Ni, Cr, Fe, and S in the gray area.

| Table 1. Chemical composition of SA213-T22 steel (wt.%). |
|-----------------|---|---|---|---|---|---|---|
| C    | Si | Mn | S  | P  | Cr | Mo | Fe  |
| 0.12 | 0.5| 0.6| 0.025 | 0.025 | 2.25 | 0.54 | Bal. |
Table 2. Chemical composition of WC-Co self-fluxing alloy coating powder (wt%).

| WC  | Co | Ni | Cr | Fe | Si | B | C |
|-----|----|----|----|----|----|---|---|
| 44  | 6  | 36 | 8  | 2  | 2  | 1.7| 0.3|

Table 3. Process parameters for the HVOF spray coating.

| Parameter            |       |
|----------------------|-------|
| Kerosene (gph*)      | 5.2   |
| O₂/fuel ratio (scfh*/gph) | 385   |
| Spray distance (mm)  | 390   |
| Powder feed (g/min)  | 120   |
| Carrier gas (L/min)  | 23    |

*gph =gallon per hour, **scfh =standard cubic feet per hour

2.2. High-temperature oxidation tests
High-temperature oxidation tests were conducted on the uncoated and coated specimens in air (21%O₂-N₂ bal.) and 10%water vapor containing condition in a quartz tube furnace at 750 °C. The water vapor was carried out by 50%O₂ and 40%N₂ (Figure 2.). The exposure times were 24, 48, 72, 96, and 120 hours and cooling to room temperature by argon. The specimens were weighed before and after the exposure by using a five-digit analytical balance, respectively.

2.3. Corrosion in molten salt and electrochemical test
The coated and uncoated specimens were placed in quartz crucibles and heated in a horizontal furnace at 750 °C for 120 hours in the air (21%O₂-N₂ bal.). After the oxide formation, the specimens were tested by a commercial molten salt with a composition of 60%NaNO₃ and 40%KNO₃ at 600 °C for three hours. Every one hour, the specimens were further measured corrosion-resistant properties by the potentiodynamic polarization technique. The electrochemical cell was introduced with the applied potential of 0.167 mVs⁻¹ and 0.5 M of NaCl solution at room temperature, and then the corresponding cables of the potentiostat connected to the electrochemical cell for current intensity measurement.

Figure 1. SEM images of the cross-sectional morphology of WC-Co self-fluxing coating layer.
3. Results and Discussion
The coated and uncoated specimens were evaluated in the simulated oxidation atmosphere at high temperatures as described in the previous section. The average mass gain of both samples is seemingly plotted as a parabolic curve, as shown in Figure 4. In Figure 5, the uncoated samples in the 10%H₂O-50%O₂-N₂ atmosphere showed intensive oxidation when compared with those exposed in 21%O₂-N₂ atmospheres. They were higher for every oxidation time and around 10 mg/cm² after 120 hours. Moreover, it was significantly higher than that from the previous works at 500 °C.[25] It can be noted that the mass gain of scale increased when increasing the oxidation time, and the percentage of oxygen and water vapor in the atmosphere at the same temperature, following the increase of oxidation kinetics.
After the WC-Co self-fluxing coating, the total mass gain -the accumulation of remain and spalling layers- of the coated specimens was less than that of the uncoated samples in both simulated atmospheres. The total mass gain in the water vapor-containing atmosphere was dramatically decreased at around twenty-two times and about three times for the air atmosphere. The oxide spallation started on the coated specimen after twenty-four hours, but it was slightly decreased after forty-eight hours. According to the past works, the water vapor may be reacted more rapidly with metals than oxygen provided that the formed oxide layer can grow by hydroxyl ion transportation [26–28]. In addition, the oxidation rate constant \( (k_p) \) decreased when compared with that of the uncoated specimens in both simulated atmospheres, as shown in Table 4. The research works which observed the T22 steel in the air at 900 °C [29], and in steam (100%H₂O) at 725 °C showed exceptionally high \( k_p \) because of the effect of high temperature and high amount of water vapor [30]

Besides, the specimens after oxidation were analyzed by XRD. The results of XRD analysis indicated peaks that were identified as scales in the uncoated samples. It was found that hematite \((Fe₂O₃)\) and magnetite \((Fe₃O₄)\) were the main phases on the surface of specimens in both conditions, and there was some wustite \((FeO)\) in the water vapor containing condition (Figure 6(a)). For the coated specimens, NiO, Cr₂C₂, WO₂, and WC were shown in the coating layer before the exposure in both simulated atmospheres, and the Fe₂O₃, Cr₂O₃, and NiCr-spinel occurred after the exposure. However, the high intensity of W₂C peak was observed only in the water vapor containing condition, as shown in Figure 6(b). It can be presumed that NiO, and Cr₂C₂ were oxidized to NiCr-spinel, Cr₂O₃, and some WO₂ during the oxidation test. From a thermodynamics point of view, the standard Gibbs free energy of Cr₂O₃ and WO₂ formations are lower than that of NiO formation. Therefore those former oxides can be stably formed after the oxidation. Furthermore, the Ni and Cr oxides showed excellent formation in the form of NiCr-spinel at high temperature in the coating layer on the steel.

The polarization curves of the uncoated and coated samples oxidized in air at 750 °C for 120 hours after the immersion test for 3 hours were shown in Figure 7. The corrosion potential of the uncoated sample is lower than that of a coated sample, and it can be discussed that the coated samples showed a higher corrosion resistance because of WC-Co self-fluxing coating layer. The corrosion potential decreases when immersion in molten salt for 1, 2, and 3 hours, respectively. In other words, the corrosion current density of the coated and uncoated specimens seemingly increases after immersion at different times, as shown in Figure 8. Moreover, the corrosion current density of the coated samples is lower than that of the uncoated specimens at every time. The uncoated sample had a current density of around 30 µA/cm² before the immersion, but it was decreased after one hour and then rapidly increased to 85 µA/cm² after three hours. The scale layer on the uncoated specimen was disappeared after the test and revealed the strong iron peak on the surface (Figure 9). However, the low corrosion current density was shown in the WC-Co self-fluxing coated steel which is around 5 µA/cm² after immersion for three hours. One-half of the oxidized coating layer on the coated specimen can remain after the test, and the layer was rich in Ni and W. It was deteriorated from 250 µm of thickness at the beginning to 153 µm after the tests. For this reason, it can be related to the low corrosion rate in the molten salt condition and concluded that the WC-Co self-fluxing layer explicitly promotes the high corrosion-resistant coating property. Consequently, the WC-Co self-fluxing layer showed an excellent protective layer.
Figure 4. Mass gain of uncoated SA213-T22 after exposure in simulated atmospheres at 750°C for 120 hours.

Figure 5. Mass gain of coated SA213-T22 with WC-Co self-fluxing after exposure in simulated atmospheres at 750°C for 120 hours.
Figure 6 XRD spectrum of (a) uncoated and (b) coated SA213-T22 before and after exposure in simulated atmospheres at 750°C for 120 hours
Table 4. Calculated values of the parabolic rate constant ($k_p$) at 750 °C.

| Descriptions                                      | $k_p$ ($10^{-5}$ mg$^2$ cm$^{-4}$ s$^{-1}$) |
|--------------------------------------------------|--------------------------------------------|
| Uncoated in Air                                   | 12.60                                      |
| Uncoated in 10%H$_2$O containing                  | 1,487.14                                   |
| Coated in Air                                     | 1.48                                       |
| Coated in 10%H$_2$O containing                    | 3.13                                       |
| Uncoated T22 at 900 °C [29]                       | 71,830*                                    |
| Coated in 100%H$_2$O containing at 725 °C [30]    | 6.67                                       |
| Uncoated T22 in molten salt at 900 °C [31]        | 125,621.8                                  |

- $*k_p$ of uncoated T22 at 900 °C was $71,830 \times 10^{-5}$ mg$^2$ cm$^{-4}$ s$^{-1}$ after exposure 24 hours.

**Figure 7.** The polarization curves of uncoated and coated SA213-T22 exposed to 60%NaNO$_3$-40%KNO$_3$ after the immersion test for 3 hours (a) and at different immersion times (b).

**Figure 8.** Current time series and cross-section of uncoated and coated SA213-T22 exposed to 60%NaNO$_3$-40%KNO$_3$ at 600 °C for 0 to 3 hours.
Figure 9. SEM/EDS of uncoated and coated SA213-T22 exposed to 60%NaNO₃-40%KNO₃ at 600 °C for 3 hours.
5. Conclusions
The WC-Co self-fluxing coating by using HVOF thermal spray method can be one optional method for protecting the oxidation of SA213-T22 steel at high temperature in thermal processing in molten salts for biomass power plants. The degradation behavior of SA213-T22 coated and uncoated with WC-Co alloys can be summarized as follows.

- The oxidation rate of SA213-T22 steel at 750 °C in water vapor containing condition (10% H2O-50% O2- N2) was much higher than that found in air (21% O2- N2) because of the high percentage of oxygen and the inward transport of OH- from water vapor, which promoting rapid scale cracking and accelerating oxidation.
- The total mass gain of WC-Co self-fluxing coated specimen was lower than that of the uncoated one by around 3 times in the air and 22 times in the water vapor containing condition.
- The spallation of the coating layer started at the beginning of the oxide formation mechanism before the NiCr-spinel formation.
- The formation of FeO and Fe3O4 prohibited on the WC-Co self-fluxing coated T22 steel at high temperature in simulated atmospheres, but a small content of Fe2O3 existed.
- The WC-Co self-fluxing coating was an excellent protective layer for exposure in air and water vapor conditions. It showed a good corrosion resistance in a simulated molten salt (60%NaNO3-40%KNO3) at high temperature due to the ability of NiCr-spinel, Cr2O3, WC, and W2C on the high-temperature corrosion resistance and molten salt atmospheres.
- The NiCr-spinel was able to form Ni and Cr oxides after exposure at high temperature. Nonetheless, some of the coating layers started to deteriorate after oxidation for 24 hours and then decreased around 1.6 times after immersion in molten salts for 3 hours.

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