A Review of High-temperature Oxidation Behaviour of Thermally Sprayed Boiler Tube Materials in Advanced Coal-fired Thermal Power Plants

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Abstract

Coal-fired thermal power plants are the prime source of electricity worldwide. The higher operating temperature and pressure of these power plants cause high-temperature oxidation and corrosion of the boiler materials used in these power plants. Various advanced materials have been developed to resist these degradations, but individual advanced materials were found insufficient to resist such degradations for longer. It is accomplished by providing an additional protective coating of the oxidation-resistant material over the surface of the metallic component having desired mechanical properties. Researchers have investigated the high-temperature performances of various base materials and coatings combinations. Different coating techniques have been used to deposit the coatings, including electroplating, thermal spray coating, physical vapor deposition, chemical vapor deposition, etc. Among all these methods, the thermal spray technique is reported to be a cost-effective method to deposit coatings with good mechanical and microstructural properties. In this paper, a brief review of the literature on the high-temperature oxidation performance of thermally sprayed boiler tube materials has been presented and discussed.

Keywords
High-temperature oxidation, Degradations, Thermal spray coating

Introduction

Coal is the primary source of electricity generation [1]. Although the world is focusing on renewable energy resources for electricity generation, coal-fired thermal power plants share the major electricity production. Hence, it is essential to address the problems associated with material failures in existing coal-fired thermal power plants. Many coal-based power plants are modified into advanced, supercritical, and ultra-supercritical coal-fired thermal power plants to overcome the low thermal efficiency and high pollutant emission from burning fossil fuels [2]. Advanced coal-fired thermal power plants are categorized, in table 1, based on their temperature and pressure range [3-5].

The higher operating temperature of modern power plants causes high-temperature oxidation of the boiler materials [6, 7]. Figure 1 shows the high-temperature oxidation mechanism of boiler tube steels. The outward diffusion of metal ions (M²⁺) and the inward surface adsorption of oxide ions occur at higher operating temperatures in advanced power plants. The oxide ions then react with the metal ions to produce metal oxides at the surface of the boiler material. With the increase of oxide thickness, porosity and micro-cracks develop over time, causing spallation or delamination of these oxide scales. The high-temperature oxidation decreases the life of metallic components, which is mainly responsible for early repair or replacement of the boiler tube materials, thus increasing the plant’s maintenance costs [8].
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Various methods have been used to reduce the high-temperature oxidation of boiler materials in advanced coal-fired power plants [9]. Among these, the development of oxidation-resistant coatings over the surface of the boiler material is widespread [10]. There are various techniques to deposit the coatings over the material surfaces, among which thermal spraying finds a broad scope as it provides a coating with good mechanical and microstructural properties [11]. This work presents a comprehensive review of studies on the oxidation behaviour of thermal spray coatings over different boiler materials at high temperatures, which may help select the suitable material or coating technique in preventing materials against harsh industrial environments.

Materials and Methods

Steel is the most common material used in advanced thermal power plants to make water walls, superheaters and reheater tubes, turbine blades, etc. [12, 13]. Different materials have been developed over the last few decades, supporting the installation of advanced supercritical and ultra-supercritical power plants globally [4, 5]. Some important boiler materials, oxidation-resistant coatings and various thermal spray coating deposition techniques are discussed here.

Boiler tube steels

Materials used in advanced coal-fired thermal power plants should have high creep strength and oxidation resistance to withstand the high temperature and pressure conditions of power plants [14]. Various elements (Cr, Ni, W, V, Nb, Mo, etc.) are added to boiler steels to enhance their properties like creep strength, oxidation resistance, corrosion resistance, etc. [15, 16]. The chemical compositions of some of the widely used boiler steels of the advanced thermal power plants are presented in table 2.

Table 1: Temperature and pressure range of different power plants [3-5].

<table>
<thead>
<tr>
<th>Type of power plant</th>
<th>Main steam pressure, MPa</th>
<th>Main steam temperature, °C</th>
<th>Average efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subcritical</td>
<td>&lt;22</td>
<td>&lt;565</td>
<td>35 - 40</td>
</tr>
<tr>
<td>Supercritical</td>
<td>22 - 25</td>
<td>540 - 580</td>
<td>40 - 45</td>
</tr>
<tr>
<td>Ultra-Supercritical</td>
<td>25 - 30</td>
<td>580 - 620</td>
<td>45 - 50</td>
</tr>
<tr>
<td>Advance Ultra-Supercritical</td>
<td>30 - 35</td>
<td>620 - 700</td>
<td>&gt;50</td>
</tr>
</tbody>
</table>

Table 2: Some commonly used boiler steels in modern power plants [3-5].

<table>
<thead>
<tr>
<th>Composition (%)/ materials grade</th>
<th>AISI 316</th>
<th>AISI 410</th>
<th>T22</th>
<th>T91</th>
<th>T92</th>
<th>Super 304H</th>
<th>IN740</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.08</td>
<td>0.15</td>
<td>0.05 - 0.15</td>
<td>0.07 - 0.14</td>
<td>0.07 - 0.13</td>
<td>0.04 - 0.1</td>
<td>0.03</td>
</tr>
<tr>
<td>Cr</td>
<td>16 - 18</td>
<td>11 - 13</td>
<td>1.9 - 2.6</td>
<td>8.9 - 9.5</td>
<td>8.5 - 9.5</td>
<td>18 - 20</td>
<td>25.0</td>
</tr>
<tr>
<td>Ni</td>
<td>11 - 14</td>
<td>0.75</td>
<td>-</td>
<td>≤0.4</td>
<td>≤0.4</td>
<td>8 - 11</td>
<td>49.5</td>
</tr>
<tr>
<td>Mn</td>
<td>2.0</td>
<td>1.0</td>
<td>0.3 - 0.6</td>
<td>0.3 - 0.6</td>
<td>0.3 - 0.6</td>
<td>2.0</td>
<td>0.3</td>
</tr>
<tr>
<td>P</td>
<td>0.04</td>
<td>0.04</td>
<td>0.025</td>
<td>≤0.02</td>
<td>≤0.02</td>
<td>0.045</td>
<td>0.002</td>
</tr>
<tr>
<td>S</td>
<td>0.03</td>
<td>0.03</td>
<td>0.025</td>
<td>≤0.01</td>
<td>≤0.01</td>
<td>0.03</td>
<td>0.002</td>
</tr>
<tr>
<td>Si</td>
<td>0.75</td>
<td>1.0</td>
<td>≤0.5</td>
<td>0.2 - 0.5</td>
<td>0.2 - 0.5</td>
<td>0.75</td>
<td>0.5</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.001 - 0.006</td>
<td>0.001 - 0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.5 - 3.5</td>
<td>≤0.1</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
<td>≤0.04</td>
<td>0.003 - 0.03</td>
<td>0.9</td>
</tr>
<tr>
<td>Ti</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>≤0.01</td>
<td>-</td>
<td>-</td>
<td>1.8</td>
</tr>
<tr>
<td>W</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.5 - 2.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.18 - 0.25</td>
<td>0.15 - 0.25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mo</td>
<td>2 - 3</td>
<td>-</td>
<td>0.87 - 1.13</td>
<td>0.85 - 1.05</td>
<td>0.3 - 0.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.06 - 0.1</td>
<td>0.04 - 0.09</td>
<td>0.3 - 0.6</td>
<td>2.0</td>
</tr>
</tbody>
</table>
### Oxidation resistant coating materials

Researchers worldwide have investigated various coating combinations [17-21]. According to the literature [22-24], alloying Ni-Cr-based composite coatings with Al, Y, Si, B, etc., increases their resistance to high-temperature oxidation. It has been reported that the formation of the Cr₂O₃ oxide layer is primarily responsible in protecting the material’s surface against high-temperature oxidation [25-27].

Figure 2 presents the effectiveness of the various coating combinations against high-temperature oxidation. Many researchers have conducted cyclic oxidation tests of coating materials.

#### Table 3: Some important literature related to the high-temperature oxidation behavior of thermally sprayed boiler tube materials.

<table>
<thead>
<tr>
<th>Author</th>
<th>Substrate material</th>
<th>Coating material</th>
<th>Coating techniques</th>
<th>Results</th>
<th>Phases identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bala et al. [18, 21]</td>
<td>T22 boiler tube steel</td>
<td>Ni-20Cr, Ni-50Cr</td>
<td>Cold spray</td>
<td>After conducting the thermal cycling test for 50 cycles at 900 °C, the authors concluded that the cold-sprayed specimens provide better oxidation resistance.</td>
<td>The formation of chromium and nickel oxides are mainly responsible for the better oxidation resistance of the coated specimens.</td>
</tr>
<tr>
<td>Abu-Warda et al. [37]</td>
<td>T24 boiler steel</td>
<td>Ni20Cr</td>
<td>HVOF</td>
<td>The coated sample shows better resistance to oxidation at elevated temperatures.</td>
<td>Better resistance to oxidation at elevated temperatures was due to the protective oxide layers of Cr₂O₃ and NiCr₂O₄.</td>
</tr>
<tr>
<td>Kumar et al. [28]</td>
<td>T22 boiler steel</td>
<td>WC-12Co, Ni-20Cr</td>
<td>Detonation Gun spray</td>
<td>After 50 hours of the test at 900 °C, it was found that the Ni-20Cr coated samples are superior against high-temperature oxidation among all the samples.</td>
<td>According to XRD analysis Cr₂O₃ and NiCr₂O₄ protective oxide layers are responsible for the protection of the coated specimens.</td>
</tr>
<tr>
<td>Kumar et al. [29, 38] and Sharma et al. [30]</td>
<td>T22, T91, and SA516 boiler steel</td>
<td>Ni20Cr, NiCrTi, Ni5Al</td>
<td>Wire arc spray</td>
<td>After conducting the thermal cycling test for 50 cycles at 900 °C, it was concluded that among all the coatings, Ni20Cr coated SA516 samples and NiCrTi coated T91 samples show the maximum oxidation resistance. In contrast, Ni5Al coated T22 samples show the least oxidation resistance.</td>
<td>Ni, Cr, and Al Oxides were mainly responsible for the protection of the coated boiler steels. In NiCrTi coatings, Ti peaks were also revealed by XRD analysis.</td>
</tr>
<tr>
<td>Kumar et al. [39] and Singh et al. [19]</td>
<td>SA516 and T22 boiler tube steels</td>
<td>Ni20Cr, NiCrAlY-B,C</td>
<td>Cold spray and HVOF spray</td>
<td>After conducting the thermal cycling test for 50 cycles at 900 °C, it was concluded that the nanocomposite coatings are more effective against high-temperature oxidation than micro composite coatings.</td>
<td>NiO, Cr₂O₃, Al₂O₃, NiCr₂O₇, Ni3Al2O6, and A1B,C phases were found in XRD analysis which was responsible for the protection of coated specimens.</td>
</tr>
<tr>
<td>Kaushal et al. [40]</td>
<td>T22 boiler steel</td>
<td>Ni20Cr, Ni20Cr1Zr</td>
<td>HVOF</td>
<td>After 50 hours of the test at 900 °C, it was found that the Ni-20Cr1Zr deposited specimen was superior among all the samples.</td>
<td>NiO, Fe₂O₃, and NiCr₂O₇ phases were detected in XRD analysis.</td>
</tr>
<tr>
<td>Mittal et al. [41]</td>
<td>T91 boiler tube steel</td>
<td>Ni-Cr, Stellite-21</td>
<td>Detonation Gun spray</td>
<td>After 100 hours of the test at 900 °C, it was found that stellite-21 coated T91 boiler tube steel shows the maximum oxidation resistance among all the samples.</td>
<td>EDS analysis revealed the formation of Cr₂O₃, SiO₂, and Fe₂O₃ scales over coated specimens.</td>
</tr>
<tr>
<td>Singh et al. [20, 24]</td>
<td>T91 boiler tube steel</td>
<td>NiCrAlY, NiCrAlY-20SiC</td>
<td>HVOF</td>
<td>After 50 hours of testing at 900 °C, it was found that uncoated specimens show the least oxidation resistance due to the spallation of Fe₂O₃ oxide layers. NiCrAlY-20SiC coated specimens show better oxidation resistance among all the coatings.</td>
<td>XRD and EDS analysis revealed that the protective oxides of Ni, Cr, and Al are responsible for the coated samples’ better oxidation resistance.</td>
</tr>
<tr>
<td>Sidhu and Prakash [42-44]</td>
<td>GrAl, T11, and T22 boiler tube steel</td>
<td>NiCrAlY, Ni20Cr, Ni3Al, Stellite-6</td>
<td>Plasma spray</td>
<td>After 50 hours of tests at 900 °C, it was found that plasma sprayed GrAl steel shows the maximum oxidation resistance compared to other coated steels. Stellite-6 coatings are superior among all the coatings, followed by NiAl coatings.</td>
<td>Oxides of Ni, Cr, Al, and Fe were detected by XRD analysis which was responsible for the protection of the coated steels.</td>
</tr>
</tbody>
</table>
Materials over T22 and T91 boiler tubes steels at 900 °C for 50 cycles [18-20, 28-31]. Authors have experimentally analyzed different coating combinations to compare the weight gain of the coated material against the uncoated material. High-temperature oxidation causes weight gain of the material, so the coating combination having the lowest weight gain is the most effective. Figure 2a indicates that the NiCrAlY20B coating provides the maximum resistance to high-temperature oxidation, while WC-20Co coatings provide the least resistance to oxidation. Similarly, from figure 2b, it can be concluded that the NiCr2AlYNiCr coating has the maximum resistance, while NiAl coating has the least resistance to high-temperature oxidation.

**High-temperature Oxidation Behaviour of Thermally Sprayed Boiler Tube Materials**

A single material cannot fulfill all the requirements of advanced thermal power plants. Material properties can be improved by adding an extra protective layer on the surface of the base material [36]. Some vital research works on the oxidation behaviour of thermally sprayed boiler tube materials are presented and discussed in table 3.

**Discussion**

Various thermally sprayed coatings such as Ni2Cr, NiCrAlY, WC-Co, NiCrTi, NiCrAlY-B, etc. have been investigated by the researchers to resist the high-temperature oxidation of the boiler tube materials. Different thermal spray coatings methods, such as high-velocity oxy-fuel, wire arc spray, plasma spray, detonation gun spray, etc., have been used to enhance the microstructural and mechanical properties of the boiler tube materials. Isothermal and cyclic oxidation studies show that the thermally sprayed coatings protected the boiler tube materials from high-temperature oxidation. The researchers have used various material characterization methods to analyze the high-temperature oxidation behaviour of the coated and un-coated materials. Therefore, it is essential to select the most effective coating combination for advanced thermal power plants.
coated specimens. Microstructural examinations conducted by various researchers showed the presence of non-protective $\text{Fe}_2\text{O}_3$ oxide over the surface of uncoated materials, which is responsible for the loss of the material through delamination and spallation of the oxide layer. On the other hand, various protective oxide phases such as $\text{Cr}_2\text{O}_3$, $\text{NiO}$, $\text{Al}_2\text{O}_3$, $\text{SiO}_2$, $\text{TiO}_2$, $\text{Cr}_{27}$, $\text{Cr}_{31}$, $\text{Cr}_{32}$, $\text{NiCr}_2\text{O}_4$, $\text{NiAl}_2\text{O}_4$, etc., were detected on the coated specimens, which were responsible for the protection of the boiler tube materials form high-temperature oxidation.

**Conclusion**

After a comprehensive study of different research conducted, it can be concluded that the thermally spray coatings are very effective for protecting boiler tube materials against the high-temperature oxidation environment of advanced coal-fired thermal power plants. According to literature reviews, the most commonly used oxidation-resistant coating materials are $\text{Ni}-\text{Cr}$, $\text{NiCrTi}$, $\text{Ni-Al}$, $\text{NiCrAlY}$, $\text{NiCrAlY-B-C}$, $\text{NiCrAlY-SiC}$, $\text{Cr}_{27}-\text{NiCr}$, $\text{Al}_2\text{O}_3$, $\text{SiC}$, $\text{Al}_2\text{O}_3$, $\text{TiO}_2$, $\text{WC-Co}$, etc. According to many works of literature, SEM, EDS, and XRD analysis revealed that the formation of protective oxides of various elements ($\text{NiO}$, $\text{Cr}_2\text{O}_3$, $\text{Cr}_{27}$, $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, etc.) at higher temperatures is mainly responsible for protection against high-temperature oxidation.

**Acknowledgements**

None.

**Conflict of Interest**

There is no conflict of interest.

**Credit Author Statement**

All the authors contributed equally. All the authors read and approved the manuscript.

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