Study on microstructure and cyclic oxidation behavior of WC-CoCr cermet based Plasma sprayed coatings on austenite steel

Md Sarfaraz Alam (✉ mda.phd19.me@nitp.ac.in)
National Institute of Technology Patna

Anil Kumar Das
National Institute of Technology Patna

Research Article

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Abstract

This article studies the cyclic oxidation behavior of WC-10Co-4Cr powder coatings obtained by plasma spraying on AISI316L austenitic stainless steel in an ambient air at 850°C for 50 cycles. Weight change observations of coated samples have been used to establish the oxidation kinetics, and the outcomes for the uncoated and coated specimens were compared. Utilizing scanning electron microscopy (SEM) and X-ray diffraction (XRD) the coating's microstructure has been identified before and after oxidation. XRD, SEM and energy dispersive spectroscopy (EDS) were utilized to analyse the scales surface-morphology of coated austenite steel samples following the oxidation cycle. The uncoated AISI 316L Steel had severe spalling, peeling-off, and sputtering from its oxide scale. Additionally, the scale is rich in $\text{Fe}_2\text{O}_3$, which contributed to the large weight gain. The findings showed that coatings outperform uncoated materials in terms of oxidation resistance. The coating lowered the weight gain of austenite 316 steel by 84.34%. It was discovered that the protective $\text{WO}_3$ and $\text{Cr}_2\text{O}_3$ phase generated on the oxide scale provided higher oxidation resistance.

1. Introduction

The most frequent issues with component surfaces in industries working at higher temperatures are wear, corrosion and high temperature oxidation, which reduce the performance of the substrate being utilised. Austenitic stainless steels are employed for industrial, domestic, architectural and transport products not only due to its superior resistance against corrosion but also for their strength, their formability and their sustainability at extreme temperatures [1]. Austenitic stainless steels are among the most significant alloy systems employed as structural parts in existing and upcoming nuclear reactor systems [2]. It is utilised to build massive plasma and nuclear reactors as well as vacuum systems. As a result, it is frequently exposed to a variety of unusually harsh circumstances. Due to the fact that stainless steel is an alloy, several distinct oxides may develop on its surface, altering the material's chemical, mechanical and physical characteristics. Due primarily to its outstanding corrosion resistance in many settings, austenitic stainless steel, and particularly AISI316L, has received considerable attention and is utilised extensively in many industrial applications. When they are, however, exposed to the simultaneous action of chemical treatment and mechanical wear, their low hardness and poor wear performance impose substantial constraints in many circumstances [3–5].

Thermal spray coatings are created by molten individual particles being solidified by a series of impingements and inter-bonding materials. The deposits formed by the spray method have a variety of microstructures and characteristics depending on the processing parameters used [6]. To provide the high resistance against wear and hardness, WC-Co/Ni/Cr cermet coatings are extensively applied by thermal spray processes. Because of their dense microstructure, which is composed mostly of WC particles, and their adherence with substrate, the coatings have demonstrated greater resistance to abrasion and sliding wear [7–9]. Coatings applied via atmospheric plasma spraying (APS) exhibit good resistance to sliding, adhesive and abrasive wear. The restoration and repair of worn-out surfaces may frequently be accomplished with APS, which also creates thermally conductive or resistant surfaces. The oxidation that
occurs when processing thermally sprayed metal coatings is crucial due to the fact that thermally sprayed coated materials' oxidation can considerably affect the microstructure's characteristics, composition of phase, and sprayed coating's performance. It is well known that, in comparison to bulk material, the coating's oxides alter the deposit material's characteristics [10]. Certain qualities, like as wear resistance or strength under compressive stress, are thought to be improved by these metal oxides in some situations [11, 12]

It has not yet been reported how thermal sprayed coatings on AISI 316L steel substrates react to high-temperature oxidation. To evaluate the effectiveness of the coatings, the cyclic behaviour of AISI316L steel was also examined. The cyclic circumstances were chosen with the knowledge that the majority of industrial components really operate in cyclical environments. In the present work, WC-10Co-4Cr powder was used to fabricate coatings on AISI 316L substrate by atmospheric plasma spraying and characterized with X-ray diffraction, scanning electron microscopy & energy dispersive spectroscopic analysis. The aim of this study is to identify phase changes for WC-CoCr coatings and analyse the coating's microstructure both before and after the oxidation cycle.

2. Experimental Details

2.1 Substrate materials

The substrate material was taken from Kanak Steel Overseas, (An ISO 9001: 2015 Certified Company) which is located at Mumbai, India. Stainless steel AISI316L has been selected as the substrate. Composition of steel verified by the AUM Metal Lab (An ISO 9001: 2015 Certified Company), recognised by the govt. department classifications societies, located at Carpenter Street, Mumbai, India. The composition by weight of AISI 316L steel is illustrated in Table 1. The dimensions of all samples for experimentations were kept 15mm×15mm×8mm approximately.

<table>
<thead>
<tr>
<th>Chemical (wt%) composition of the AISI316L austenite steel.</th>
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<tbody>
<tr>
<td>C%</td>
</tr>
<tr>
<td>0.0191</td>
</tr>
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</table>

2.2 Feedstock material

The available commercially WC-10Co-4Cr weight percentage crushed, spray dried and sintered powder used as the feedstock powder was purchased from Metallizing Equipment Pvt. Ltd. (An ISO 9001: 2015 & NABL Accreditation Certified Company), Jodhpur, India. The powder is composed of WC 86%, Co10%, Cr4%, and the mean particle size is 10-45 μm. A spherical shape of WC 10Co 4Cr powder is demonstrated in SEM image (Figure. 1). The image clearly shows that the WC-CoCr particles are as small as 10-45 μm, as stated by the manufacturer of powder.
The elemental distribution was represented by XRD analysis. XRD pattern of WC-10Co4Cr powder, Figure. 2 depicts the WC as a dominant phase beside a minor cobalt peak. In addition, W2C and ternary phases are absent from the powder. The feedstock powder material contains W, C, Co, and Cr in significant amounts.

2.3 Deposition technique and equipment

The AISI 316L steel substrate was cleaned with acetone and then grit blasted with aluminum oxide 200–300 µm to create a surface roughness of Ra 5–10 µm before the coating was deposited. At a blasting pressure of 5 bar. Blasting was done at a distance of 150 mm and an angle of 90°. For the plasma spraying method of coating deposition, the substrate size was 15 mm 15 mm 8 mm. In order to apply the WC-10Co-4Cr coatings, an MPS-50M plasma spray gun was used. coating thickness is of 400–500 µm. the coating deposition was completed using the stable spraying conditions stated in Table 2. at Metallizing Equipment Pvt. Ltd. in Jodhpur, India.

<table>
<thead>
<tr>
<th>Process Name (Actual)</th>
<th>Parameters</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gun</td>
<td>SPRAY GUN MPS 50M</td>
<td>-</td>
</tr>
<tr>
<td>Coating Powder</td>
<td>WC-10Co-4Cr</td>
<td>-</td>
</tr>
<tr>
<td>Primary gas (Argon)</td>
<td>Pressure</td>
<td>10.0 kg/cm²</td>
</tr>
<tr>
<td></td>
<td>Flow rate</td>
<td>38 slpm</td>
</tr>
<tr>
<td>Secondary gas (Hydrogen)</td>
<td>Pressure</td>
<td>7.0 kg/cm²</td>
</tr>
<tr>
<td></td>
<td>Flow rate</td>
<td>8 slpm</td>
</tr>
<tr>
<td>Spray distance</td>
<td>-</td>
<td>100 mm</td>
</tr>
<tr>
<td>Powder feed rate</td>
<td>-</td>
<td>35 gm/min</td>
</tr>
<tr>
<td>Voltage</td>
<td>-</td>
<td>65V</td>
</tr>
<tr>
<td>Current</td>
<td>-</td>
<td>500A</td>
</tr>
</tbody>
</table>

2.4 Coating Characterization

SEM examination using a SIGMA 500 FEG-SEM (Carl Zeiss Sigma, Germany) was used to characterize the microstructure of powders and coatings before and after an oxidation cycle, and XRD analysis with a Smart Lab SE diffractometer (Japan) was used to identify the phases present in the samples. To determine the composition of the coatings, we used energy dispersive spectroscopy (EDS) on a Carl Zeiss Sigma 500 FEG-SEM equipped with EDS and ESBD (Germany). EDS examination of the cross section of
coated samples demonstrates the presence of W, C, Co & Cr. The oxidation studies were conducted in the air for 50 cycles and at 850 °C. The test cycle includes heating the ceramic alumina boat specimen for one hour in the Muffle furnace (Ikon Instruments, India), then twenty minutes of cooling it at ambient temperature in air (Schematic diagram of Muffle furnace is shown in Fig. 3.). PID temperature control accuracy ± 2°C in muffle furnace in throughout oxidation study. Weight gain during oxidation studies has been measured by precision balance (Panasonic Ind. Japan).

3. Results And Discussion

3.1 Cyclic oxidation behaviour at high temperature uncoated vs WC-CoCr coated samples

Following fifty cycles of cyclic oxidation in ambient air at 850°C, the uncoated samples and the WC CoCr coated AISI 316L steel substrate are demonstrated in macrograph images in Figure. 4(a) & 4(b), respectively. In case of uncoated steel, severe spalling was seen. During oxidation experiments, the uncoated steel substrate's oxide scale was continually removed after every cycle. The mechanism behind the formation of surface cracks in the sample, accompanied by the removal of microscopic scale flakes. Along with the spalled regions, thick oxide-scale with an uneven structure was obtained from the uncoated sample, as illustrated in Figure. 4(a). The comparable AISI 316L coated steel macrograph picture is displayed in Figure. 4(b). In comparison to the uncoated substrate, relatively little oxide scale is removed from the coated specimen, giving it greater oxidation resistance. It is clear that the WC-CoCr plasma sprayed coating made the AISI 316L steel more oxidation resistant. The coating increases oxidation resistance by acting as a diffusion barrier for the oxidising species.

Figure 5 (a) illustrates the weight change plot for WC-CoCr cermet coated and uncoated AISI 316L steel under cyclic-oxidation in ambient air for fifty cycles at 850°C. Maximum Weight gain of WC-CoCr coated steel (0.302202011 mg/cm²), is much lower compared to the uncoated steel substrate (1.929513894 mg/cm²). Figure 5 (b) indicates the cumulative weight gain per unit surface area for the WC-CoCr plasma sprayed coated AISI 316L steel and uncoated AISI 316L steel substrate up to fifty cycles. Uncoated AISI 316L steel substrate reveals a greater rate of oxidation than specimen, as is seen in the plot with a cumulative weight gain (43.79746881 mg/cm²) of uncoated that of coated steel with a cumulative weight gain (13.54698668 mg/cm²) almost 3.25 times.

3.2 XRD analysis on WC-10Co-4Cr coatings before and after oxidation cycle

The WC-10Co4Cr plasma spray coating's XRD spectrum is shown in Fig. 6. It demonstrates the existence of W₂C, WC, Co & Co₃W₃C Phase.

The coating exhibits sharp and identifiable peaks of WC and W₂C. The spraying process causes the Co binder phase to melt, and it has been found that this leads to considerable dissolution of tungsten...
carbide into binder phase of Cobalt. The WC grains are dissolved in molten Co, increasing the carbon and tungsten content of the matrix and decreasing the relative size of the carbides. Dissolved carbon in the liquid first diffuses across the medium and then reacts with ambient oxygen to release carbon. When a Co-rich liquid is cooled, its supersaturation leads to the development of $W_2C$ and W-rich phases. The higher peaks of the WC and $W_2C$ phases demonstrate how much of the WC phase has been dissolved and decarburized. Due to the WC-CoCr powder's high surface area to volume ratio, the tungsten carbide grains could easily interact with the spray temperature, that is the primary reason for decarburization in coatings[13]

Figure 7. depicts XRD pattern after completion of oxidation cycle test in ambient air for fifty cycles at 850°C of cermet coating's on AISI 316L steel substrates. The principal phases found in the coated sample according to the X-ray diffraction patterns are $WO_3$, $CoWO_4$, $Cr_2O_3$, and there are also a few traces of $Fe_2O_3$ phase. The formation of tungsten oxide phase occurs as per equation.

$$WC(s) + 2O_2(g) = WO_3 + CO(g) \text{ Eq. (1)}$$

Some of the produced $WO_3$ underwent further CoO reactions to produce the more stable $CoWO_4$ spinel [13]. When AISI 316L uncoated steel was analysed, $Fe_2O_3$ was shown to be the predominant phase [14].

### 3.3 Surface morphology of WC-10Co-4Cr cermet coatings before and after oxidation cycle with SEM/EDS analysis

The surface morphologies of cermet coatings were evaluated using scanning electron microscopy. As-sprayed cermet coating's SEM micrograph is displayed in Fig. 8. The microstructure is composed of interlocked particles grains with uneven morphology. The micro-structure reveals the existence of porosity, flaws and partly fused grains in cobalt matrix, as seen in Figure.8.

The surface found rich in the WC, Co and $W_2C$ phases, with traces of $Co_3W_3C$, according to the XRD examination. A thick coating with a few pores is seen in the SEM image in Figure. In plasma sprayed cermet coating, pores are frequently visible. According to the microstructure that was found, the top layer of the coating is where the pores are mostly located. The microstructure of coated samples further demonstrates that WC crystallised into needle- and dendritic-shaped structures contained in CoCr matrix, according to Fig. 8.

The SEM analysis and EDS analysis of the WC-CoCr coated AISI 316L steel subjected to fifty cycles of cyclic oxidation in the ambient air at 850 °C are displayed in Figure 9.

It demonstrates the development of a fairly dense scale adhere on the substrate. It denotes the existence of cracks on the oxide scale's surface. the elements Fe and oxygen are present throughout the scale's composition, $Fe_2O_3$ may form. The formation of globule-like oxide scales is also shown in the SEM image. The scales have larger concentrations of W and O, and it's probable that protective $WO_3$ has developed on their surface, further inhibiting oxidation [14, 15]. The growth of $Cr_2O_3$ on the scale is
indicated by the presence of Cr and O. To increase the alloy's resistance to oxidation and corrosion, the chromium concentration is crucial, it forms a protective, adherent, and slowly growing $\text{Cr}_2\text{O}_3$ (chromia) oxide layer [16–20]. As transport mechanisms across this scale are typically slow, this oxide prevents the inward-diffusion of gaseous impurities and the outward-diffusion of other alloy components due to its slow growth [21, 22].

4. Conclusion

The following are conclusions drawn from the research.

- On AISI 316L Steel, WC-CoCr coatings successfully be created using the plasma spray technique. It was observed that WC-Co Cr cermet plasma sprayed coatings showed oxidation resistance at elevated temperature during cyclic conditions.

- In the cyclic oxidation study at 850°C in ambient air, the uncoated AISI 316L Steel had severe spalling, peeling-off, and sputtering from its oxide scale. Additionally, the scale is rich in $\text{Fe}_2\text{O}_3$, which contributed to the large weight gain, this can be overcome by WC-CoCr coating.

- The WC-CoCr cermet coating was found to successfully lower the AISI 316L steel's oxidation rate, and iron (Fe) diffusion from AISI 316L steel base to the plasma spray coating has also noted.

- The weight gain of AISI 316L steel was decreased by 84.34% due to the WC-CoCr coating, which was shown to be better.

- The coating may have exhibited greater oxidation resistance due to the protective $\text{WO}_3$ phase that is produced in the oxide scale.

Declarations

Acknowledgment

I am grateful to Thapar Institute of Engineering & Technology Patiala, India to provide facility for SEM/XRD/EDS analysis. We are also grateful to MECPL, Jodhpur, India, that offers coating powder and coatings on substrates and last but not the least, Kanak Steel Overseas, an ISO 9001: 2015 Certified Company based out of Mumbai, supplied the raw substrate material.

Funding declaration

There is no funding to report for the current work.

Conflict of Interest

There are no conflicts of interest to record for any of the authors.

Authors’ Contributions
Md Sarfaraz Alam.: designed the experiment, processed the experimental data, performed the oxidation kinetics calculation, analysed the data, wrote the manuscript, and made the figures.

Anil Kumar Das.: participated in the design and oversight of the research, helped interpret the findings, and worked on the article.

References


**Figures**
Figure 1

SEM images of WC-10Co-4Cr powder

Figure 2

XRD pattern of feedstock powder
Figure 3

Schematic diagram of Muffle furnace

Figure 4

(a). macrograph of uncoated AISI 316L steel sample (b). macrograph of WC-CoCr coated AISI 316L steel sample after oxidation cycles
Figure 5

(a). Weight gain/surface area against oxidation cycles graph  (b). Cumulative Weight gain/surface area plot
Figure 6

XRD pattern of WC-10Co4Cr coating on AISI 316L before cyclic oxidation

Figure 7

XRD pattern of WC-10Co4Cr coating on AISI 316L after cyclic oxidation
Figure 8

SEM image of WC CoCr coated sample before oxidation
Figure 9

SEM with EDS image at after oxidation