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Cyclic Oxidation Behavior of HVOF Thermally Sprayed WC Cermet Based on AISI 1045 Steel

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ABSTRACTS

Thermal spray coating technology by High-Velocity Oxygen Fuel (HVOF) has become a solution for metal protection and part reconditions that work in critical environments such as oxidative, erosive, and corrosive. Thermal spray coating (TSC) application has been carried out to improve the oxidation resistance of the Induced Draft Fan (IDF) as a part of a coal-fired steam power plant unit. Cermet WC10Co4Cr and WC17Co were intended to sustain the AISI 1045 steel substrate against the oxidative environment. In this work, cyclic oxidation at a temperature of 500ºC was conducted to reveal the oxidation resistance behavior of the coatings. Several mechanical tests were also presented, including surface roughness of the coatings, coatings microhardness, and coatings adhesion. The coatings morphology was also characterized using an SEM microscope, as well as X-ray diffraction (XRD) for phase analysis after the oxidation test. However, spalling occurred on WC10Co4Cr coatings in the 4th cycle. It is noted that the WC17Co has better characteristics compared to WC16Co4Cr coatings, as evidence: a more stable oxidation rate and lower accumulation of oxide thickness, as well as no spalling at the interface on substrate and coating.

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INTRODUCTION

The AISI 1045 steel is structural carbon steel, which contains 0.420 – 0.50 % of carbon. This kind of steel exhibit a high quality of mechanical strength, sufficient ductility, and toughness. This steel has been widely used in automotive parts, i.e., crankshafts, torsion bars, axles, connecting rods, pins, and other war resistance parts. In this regard, the AISI 1045 was selected to substitute the original material for the Induced Draft Fan (IDF) of the coal-fired power plant.

In a coal-fired power plant system (PLTU), many components or parts are interconnected as an electric generating system, one of which is a combustion chamber. In a combustion process, residual coal ash particles will always be considered a detrimental factor for metal parts. For this reason, a coal ash decomposer is needed [1]. Induced Draft Fan (IDF) is a fan specifically designed to emit the air from the boiler out of the chimney; along the process, it generates negative pressure in the boiler to compensate for combustion air suction. IDF has fan blades mounted on a Rotor Fan Wheel [2]. Potential damage to the IDF may come from the exposure of the turbine impeller to coal particles resulting from the combustion process that is not filtered by the Electrostatic Precipitator (ESP). Surface degradation of the metal surface can be caused by particle impact at a speed of 2000 RPM. However, AISI 1045 is susceptible to the oxidative environment, and the cyclic oxidation of cermet coatings on AISI 1045 was not fully explored in previous works. The application of cermet coatings is expected to increase oxidation resistance at elevated temperatures. On the other hand, advances in cermet coatings application of cermet coating through Thermal Spray Coating (TSC) technology have made significant progress and are considered the best way to meet industrial demands. In this study, cyclic oxidation resistance of the cermet coatings WC10Co4Cr and WC17Co were the primary focus of this research.

HVOF Thermal spraying is a deposition of the metallic or non-metallic coating resulting from melted or semi-melted conditions that are propelled by a combination of several factors, including feedstock, kinetic energy, and thermal energy generated from the combustion of fuel and oxygen. Characteristics of the TSC coatings with ceramic metal provide a dense layer with specific hardness with high corrosion, oxidation, and wear resistance. This coating process is considered a good solution to reduce maintenance repair costs. Oxidation is an interaction of the metal with an oxygen molecule that comes from the air or gas and forms an oxide; occurring at elevated temperature, it is referred to as hot corrosion. The rate of oxidation of metal or alloy depends on its composition, original surface area as opposed to the geometric area, temperature, gas composition, and the nature of the oxidation cycle [3,4]. In the present study, the influence of WC10Co4Cr and WC17Co cermet coatings on the oxidation resistance of AISI 1045 steel specimen using the HVOF thermal spray process was investigated. Microstructure, failure mechanism, and evolution of oxide phases of both cermet coated specimens were studied based on experimental observations. The failure mode of the specimens was analyzed using scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis to reveal the crystalline phases of the coating.

METHODS

Materials and coatings

Two types of cermet coating materials were used, WC10Co4Cr and WC12Co, both manufactured by Praxair Surface Technology. In this work, the deposition of cermet coatings used HVOF thermally sprayed coating on substrate AISI 1045 steel. The substrate was sandblasted with alumina (#16 grit) prior to coating deposition. The chemical compositions of both cermet types are shown in **Table 1**. The TSC process was done with the help of HVOF HIPOJET 2700, supplied with propane (C_3H_8) and oxygen as fuel.

Table 1. Chemical composition (wt.%) of WC-based coatings

Specification	Coatings	
	WC10Co4Cr	WC17Co
Chem. composition	86% WC- 10%Co- 4%Cr	88% WC- 12%Co

HVOF is the most recommended technology process to deposit the thermal spray coating, which can improve corrosion and oxidation resistance of the surface with low porosity and good adhesion strength. **Table 2** shows the parameter used in the HVOF thermal spraying process.

Table 2. Parameters used in the HVOF thermal spraying process

Parameter	**Rate**
O_2 Flow	75 (kg/cm^2)
Propane Flow	75 (kg/cm^2)
Air Flow	150 (kg/cm^2)
Spray distance	300 mm

Characterization of the coatings

Microstructural analysis was carried out to study: porosity, grain morphology, and oxide inclusions. The samples were prepared as follows: the cross-section of the coating sprayed on the carbon steel substrate was cut and resin mounted; after that, the sample was sanded with silica paper gradually using 80-320-800-1200 mesh. The sample was also polished with 6 m diamond particles. The microstructure at high magnification was evaluated using a scanning electron microscope (SEM) Zeiss Evo 10 with energy dispersion spectroscopy (EDS) Oxford X-act to evaluate the oxidation result.

The surface roughness index for each cermet coating was measured by the Kosaka Lab AS-1700α stylus model profilometer. The microhardness was measured on a polished cross-section coatings surface using a Metkon Duroline M microhardness tester with a load selection of 300 gf, and a dwelling time of 10 seconds. Three data points were acquired across the coatings. Each data was collected and averaged.

Adhesion strength was performed using Hung Ta tensile tester type HT-8503 capacity 2 ton and standard jig in accordance with standard ASTM C633. Adhesive Cytec FM1000 was inserted between the cylindrical test of the coated and grit-blasted face, while a customized block fixture was used to hold the specimen pairs to be heated at 250°C degrees for 1 hour in the electric furnace. The heating temperature was established in order to have better specimen adhesion.

RESULTS AND DISCUSSION

Research Results

The TSC process showed similar results. The difference was that WC10Co4Cr components were smaller than those produced by WC17Co (see **Figure 1**). It was due to the influence of Cr controlling the coating grain size. The thickness of the coatings measured 259.7 µm and 286.4 µm, respectively.

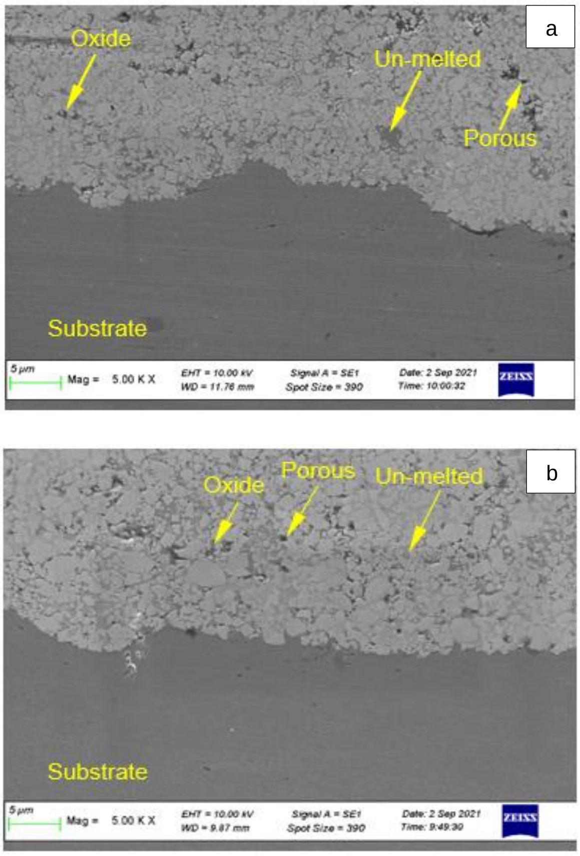

Figure 1. SEM Micrograph of cross-section TSC result on AISI 1045 Steel 5000X magnification. (a) WC10Co4Cr, (b) WC17Co.

The average microhardness obtained from WC10Co4Cr was 1011.25 HVN, and the average hardness from WC17Co was 971.55 HVN. The hardness difference between both cermet coatings was quite significant; this was caused by the addition of 4% Cr in WC10Co4Cr, which was done to increase the hardness value of the coatings. WC17Co showed a lower hardness value than the WC10Co4Cr. This was because the stability of the β phase in the WC-17Co phase was increased due to the greater Co element content and the decreased WC phase. This also correlated with the WC10Co4Cr coating material, the 10%wt Co in WC10Co4Cr content was lower than the WC17Co. Hence, the hardness value was increased [5,6].

The TSC application was propelled at high temperatures and solidified while it formed the lamellar structure and decomposition of WC [7]. Each WC10Co4Cr and WC17Co coatings formed hard carbide phases WC and W_2C as written in Equation 1, but the concentration of W_2C was higher than the WC phase [8]. This was attributed to the decomposition of WC at elevated temperatures to form a semicarbide phase W_2C according to Equation 1 [9], the high temperature referred to HVOF thermal spraying process, as indicated in Equation 2, the decomposition is continued to form free carbon, and further reaction C and O were combined to form CO gas as written in Equation 3 [10].

$$2WC \rightarrow W_2C \tag{1}$$

$$W_2C + \tfrac{1}{2}\,O_2 \rightarrow W_2\,(C, O) \tag{2}$$

$$W_2\,(C, O) \rightarrow 2W + CO \tag{3}$$

Based on surface roughness measurement. It was also noted that the coating roughness (*Ra*) of WC10Co4Cr and WC17Co were 11.910 µm and 8.607 µm, respectively. The WC10Co4Cr cermet coating had a greater coating roughness index compared to WC17Co.

Greater coating surface roughness value also affected the oxide deposition process, where the rougher the surface, the greater the potential for oxide deposition to occur. This will affect the lifetime of a coating. Oxidation testing shows the relationship between weight change and the testing cycle at a certain temperature. The longer the material is exposed, the higher the possibility of a reaction to oxidation at high temperatures, which greatly affects the thickness of an oxide layer. The oxide layer can behave as protective or non-protective properties; a non-protective oxide layer is easily affected by corrosion driving force factors that can accelerate the degradation of the material due to pitting phenomena [11,12, 13].

To determine the adhesiveness of the HVOF thermally sprayed coatings, an adhesion strength test was carried out referring to the standard ASTM C-633 Thermal Spray Adhesion Testing. The adhesion strength of WC10Co4Cr and WC12Co coating was 22.19 MPa and 25 MPa. The entire basic quality characterization of HVOF thermal spray coating of WC Cermet-based feedstock on AISI 1045 Steel is tabulated in **Table 3**.

Figure 2 shows that WC17Co coatings had better oxidation resistance and integrity when compared to WC10Co4Cr. These are shown in the graph that there was no significant weight change ΔW during the oxidation test from 1st cyclic (0,0026 g) to 25th cyclic (0.0064 g). Unlike WC17Co coatings, WC10Co4Cr experienced triple weight gain at 9th cyclic (0.0365 g) from its initial 1st cycle condition (0.0012 g). However, further oxidation test shows that WC10Co4Cr had weight loss and fell to -0.1788 g, followed by coating disintegration (spalling). Both WC10Co4Cr and WC17Co coatings experienced a linear increase in oxide thickness during the oxidation test; it can be seen from the graph that WC17Co had a smaller oxide thickness compared to WC10Co4Cr. The oxide thickness of both coatings from the 1st cycle condition to the 9th cycle was significantly different, while in the 16th to 25th cycle, the oxide thickness for both coatings was quite similar. The maximum thickness of oxide coatings obtained at the 25th cycle condition for WC10Co4Cr was 31.99 μm, while for WC17Co was 31.62 μm.

Table 3. Summary of quality characteristics data of HVOF thermal spray coating.

Coating specification		**Thickness (μm)**	**Microhardness (HVN)**	**Roughness index, *Ra* (μm)**	**Adhesion (Psi)**
Coating systems	**Chemical composition of the feedstock**				
WC10Co4Cr	86%WC-10%Co-4%Cr	295.7	1011.25	11.910	3219.83
WC17Co	83%WC-17%Co	286.4	971.55	8.607	3625.94

The predominancy of WC17Co was strongly influenced by the addition of 17% Co to increase the oxidation resistance at elevated temperatures, and this also resulted in stabilization of the WC phase.

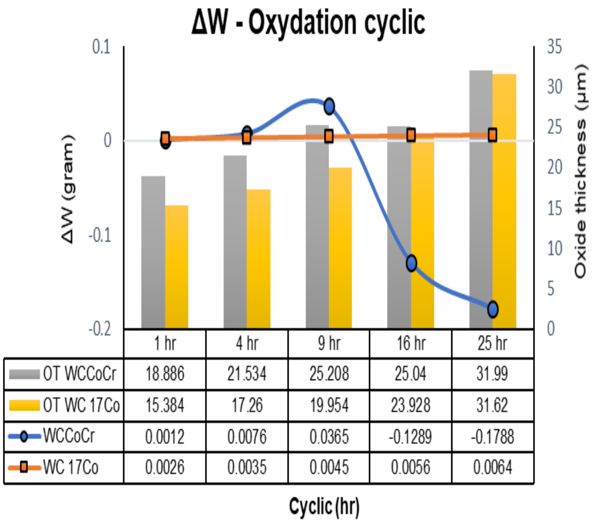

Figure 2. Oxidation rate and oxide thickness change of cermet coatings WC10Co4Cr and WC17Co.

The addition of 4% Cr in the WC10Co4Cr system was expected to increase the resistance of the oxide formation at elevated temperatures. It is known that the Cr element has oxidation resistance at elevated temperatures. **Figure 3** shows the anomalies that began at the 16th cycle, where the coating surface began to degrade and continued until the spalling phenomenon occurred. Spalling is caused by the disintegration of coatings due to the weakening of the interlocking bond between the coating and the substrate resulted by the influence of the continuous oxidation cycle. The disintegration of WC10Co4Cr coatings can also be caused by differences in the thermal expansion where the expansion of the substrate is greater than the coatings, causing the coating bond to weaken and eventually causing spalling [14].

The diffractogram depicted in **Figure 4** describes the oxide formation to the spalled coating of WC10Co4Cr after the 4th cyclic. While cyclic oxidation of WC-based coatings was continuing, Co and W were combined to form Co_2O_3, CoO, WO_3, and CO_2. The chemical reaction is expressed in the following Equation 4 [14].

$$4Co + WC + 5O_2 \rightarrow Co_2O_3 + 2CoO + WO_3 + CO_2 \quad (4)$$

Equation 4 represents the oxidation of the elements Co, W, and C included in the feeedstock resulting in CoO and WO_3, and CO_2. Further, the oxidation reaction of the WC element is continued to form WO_3 with the following reaction as specified in Equation 5

$$WC + 5/2O_2 \rightarrow WO_3 + CO_2 \quad (5)$$

The weight loss was identified at the 16th to 25th cycle and signified by the oxidation of Cr as expressed in Equation 6.

$$2Cr + 3/2O_2 \rightarrow Cr_2O_3 \quad (6)$$

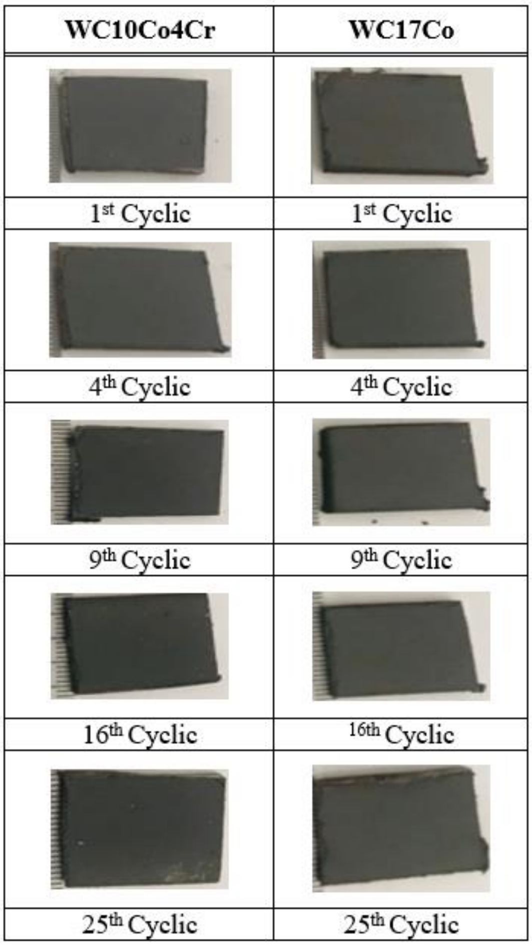

Figure 3. Macro photographs of coatings taken after the 1st to 25th oxidation cyclic of the cermet coatings WC10Co4Cr and WC17Co

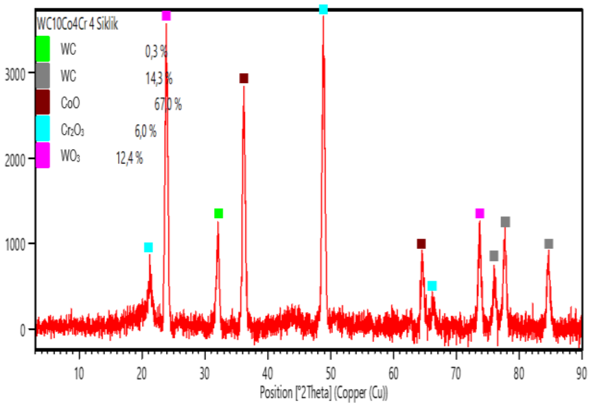

Figure 4. X-ray diffraction pattern of WC10Co4Cr after 4th cycle in temperature 500°C.

The spalling occurred due to a large PBR (Pilling Bedworth Ratio) value, and a mismatch was formed between the oxide lattice and the metal, causing a weak interfacial bond between the metal and the oxide. The property of Cr_2O_3 was no longer an opportunity for a protective layer, yet the effect had become detrimental to coatings integrity. Cr_2O_3 was easily impacted by oxygen at the elevated temperature and accelerated the coating degradation [15].

Pilling Bedworth Ratio (PBR) is the ratio between the volume of oxide and the volume of the substrate. Zeng et al. in 2014 stated that the perfection or density of the oxide layer could be characterized by PBR [16]. The scale of oxide with a value of <1 is a very thin oxide layer and also prone to damage, an oxide layer of value >2 is an oxide layer that is non-protective, and a value of 1<PBR<2 is a passive oxide layer that provides a protective effect against further oxidation. **Table 4** summarizes each PBR value for CoO and Cr_2O_3.

Table 4. PBR value for CoO and Cr_2O_3 [15].

Oxides	PBR
CoO	1,86
Cr_2O_3	2,07

Figure 5. a reveals the micrograph of WC10Co4Cr coating degradation due to oxidation. The degradation begins in the 4th cycle, and it was signified by an increase in weight gain until the 9th cycle; as shown in **Figure 2**, the oxidation continued and resulted in weight loss as, lowering the coating integrity. This is associated with the spalling, which was visible at the interface.

Figure 5. b reveals the micrograph of WC17Co coating degradation after the 4th cycle. Physically the comparison from the micrograph of both coatings showed a similar pattern where the crater was formed as a result of oxidation at the elevated temperature. However, the integrity of the microstructure WC17Co coatings was better than the WC10Co4Cr since no spalling was identified after the oxidation test.

As the oxidation reaction of WC17Co coatings, the cyclic oxidation of WC17Co only takes place from Equation 1 to Equation 5, and this is clear because there is no Cr in the WC17Co feedstock. The diffractogram of the WC17Co 4th cycle is depicted in **Figure 6**.

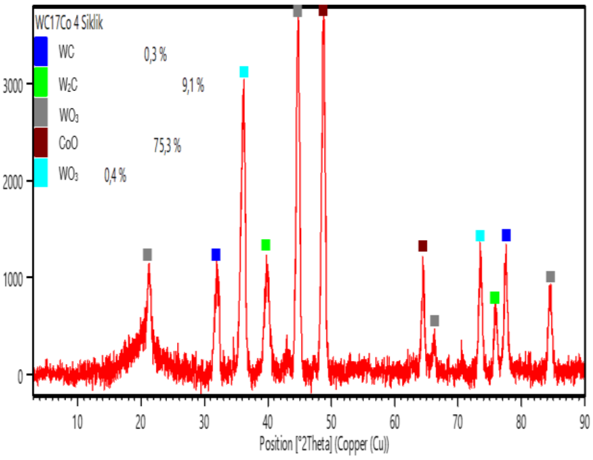

Figure 6. X-ray diffraction pattern of WC17Co after the 4th cycle in temperature of 500°C.

Discussions

Metals and alloys are thermodynamically unstable. The effect of oxidation occurs at elevated temperatures indicating a series of chemical reactions that change the integrity of the coatings. Physically the microstructure of the coating generally experiences degradation, such as spalling on WC16Co4Cr coatings and reduction of density on WC17Co coatings. A series of characterization processes carried out in this work showed that WC17Co was better than WC16Co4Cr coatings with the following evidence: a more stable oxidation rate and lower accumulation of oxide thickness, as well as no spalling found at the interface on substrate and coating.

Recommendations can be given to improve the integrity of WC16Co4Cr coating by application of bond coat before spraying top coat layer [17], post-spray heat treatment to improve coatings quality [18], and sealing [19]. The purpose of those recommendations is to improve the coating adhesiveness, improve cohesion bonds of the interface, reduce the hot corrosion risk in the oxidative environment at elevated temperature, reduce the level of porosity, and reinforce carbide precipitate.

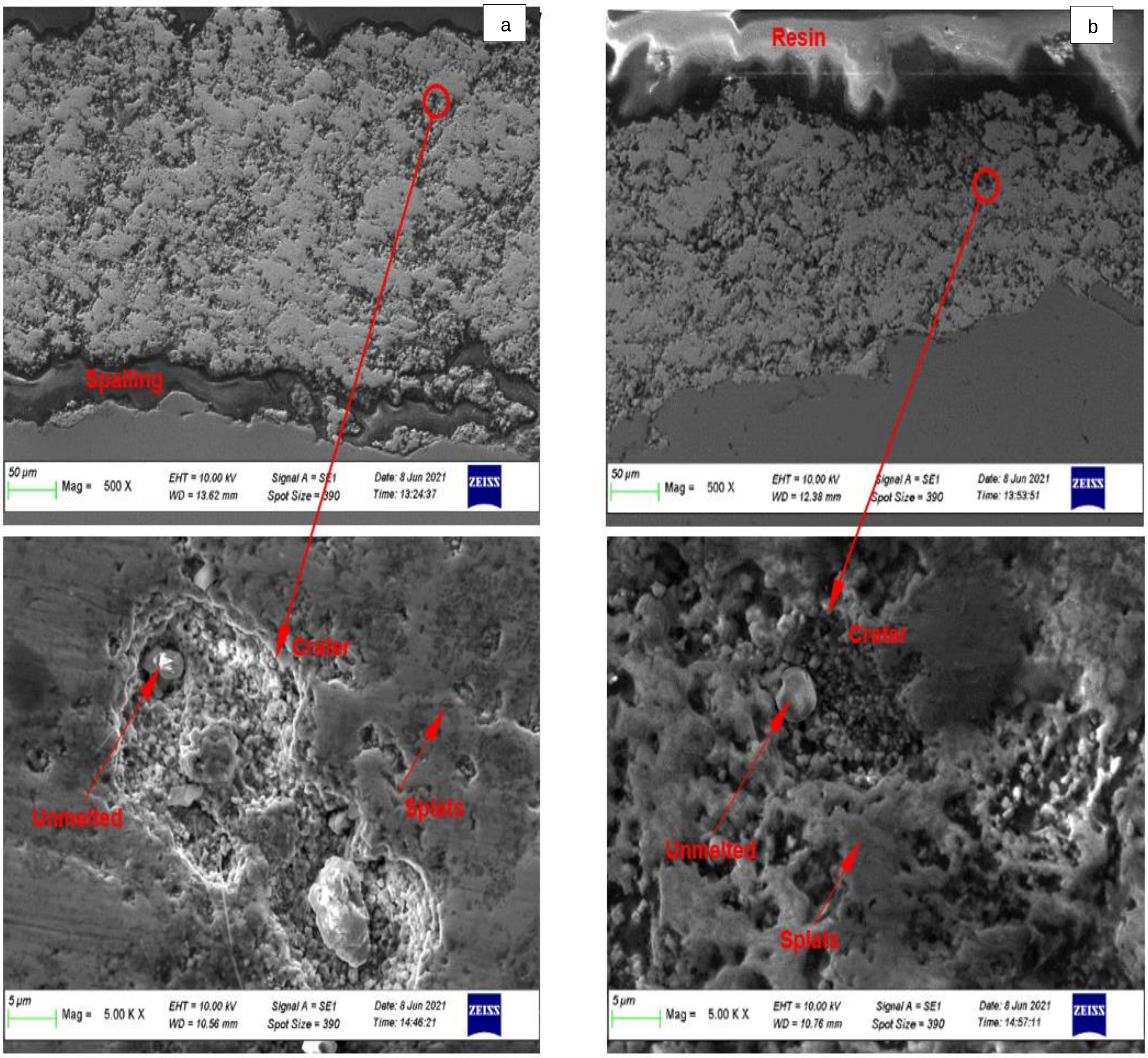

Figure 5. The micrograph of coating degradation after the 4th cycle in temperature of 500°C. (a) WC10Co4Cr, (b) WC17Co.

CONCLUSION

From this study, some conclusions can be drawn as follows:

1. Deposition of WC10Co4Cr cermet using HVOF thermal spray coating on substrate AISI 1045 steel has a coating hardness value of 1011.25 HVN, where the Cr element contributes to the increase in the coating hardness. However, WC17Co coatings have a lower hardness of 996.34 HVN.
2. The results of the oxidation test at the elevated temperature showed that WC17Co coatings were preferred over the WC16Co4Cr with some advantages i.e.: better microstructure integrity, stable oxidation rate, and lower accumulation of oxide thickness.
3. The oxide formation of Cr_2O_3 had risks in the characteristics of WC16Co4Cr coatings, and yet the impact has become detrimental to coating integrity at elevated temperatures. However, some mitigation could be done by applying a bond coat layer on the substrate before cermet spraying and employing a post-spray coating process, including heat treatment and sealing.

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