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Evaluation of Hot Corrosion Behavior of WC-Co-Cr Coatings Coated by the HVOF Method

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ABSTRACT: Thermal spray coating techniques have wide-ranging applications in various fields, including marine, automotive, biomedical, and aerospace industries. These methods are popularly used because materials coated with thermal spray coatings exhibit excellent resistance to oxidation, erosion, corrosion, and abrasive environments, particularly at high temperatures. The present study utilized the high-speed oxy-fuel (HVOF) technique, a state-of-the-art thermal spray coating method, to apply a hard cermet ceramic coating material consisting of WC-Co-Cr onto a 316L stainless steel substrate. Isothermal hot corrosion tests were also conducted at 750°C in the presence of 45% Na_2SO_4 and 55% V_2O_5 hot corrosion salts for 1, 3, and 5 hours. Advanced characterization techniques such as X-Ray Diffractometry (XRD), Energy Dispersive Spectrum (EDS), scanning electron microscopy (SEM), and elemental mapping analysis devices were used to characterize the samples coated with the HVOF technique before and after hot corrosion tests. The findings indicate that WC-Co-Cr hard coatings, which are known for their high resistance to abrasion, sustain severe damage at high temperatures. The coating was damaged after 5 hours in the hot corrosion tests performed in the presence of V_2O_5 and Na_2SO_4 molten salt at 750°C. In addition, due to the progressing corrosion process in the coating layer, spills and deterioration occurred. Due to the shedding of the coating layer, damage has occurred in the substrate material.

Keywords: WC-Co-Cr Hard Cermet Ceramic Material, Hot Corrosion, High-Velocity Oxy-Fuel (HVOF), Thermal Spray Coatings.

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HVOF Yöntemiyle Kaplanan WC-Co-Cr Kaplamaların Sıcak Korozyon Davranışının Değerlendirilmesi

ÖZET: Termal püskürtme kaplama teknikleri, denizcilik, otomotiv, biyomedikal ve özellikle havacılık endüstrisi gibi çeşitli alanlarda geniş kapsamlı uygulamalara sahiptir. Bu yöntemler, termal püskürtme kaplamalarla kaplanmış malzemelerin, özellikle yüksek sıcaklıklarda oksidasyona, erozyona, korozyona ve aşındırıcı ortamlara karşı mükemmel direnç göstermesi nedeniyle yaygın olarak kullanılmaktadır. Bu çalışmada, modern bir termal püskürtme kaplama yöntemi olan yüksek hızlı oksi-yakıt (HVOF) tekniği kullanılarak, WC-Co-Cr içeren sert sermet seramik kaplama malzemesi, 316L paslanmaz çelik bir alt tabaka üzerine kaplanmıştır. Ayrıca, 1, 3 ve 5 saat boyunca 750°C'de %45 Na_2SO_4 ve %55 V_2O_5 sıcak korozyon tuzları varlığında izotermal sıcak korozyon testleri yapılmıştır. HVOF tekniği kullanılarak kaplanmış örnekler, X-ışını Difraktometrisi (XRD), Enerji Dispersiyon Spektrometresi (EDS), taramalı elektron mikroskopisi (SEM) ve elementel haritalama analiz cihazları gibi gelişmiş karakterizasyon teknikleri kullanılarak sıcak korozyon testleri öncesi ve sonrasında karakterize edilmiştir. Bulgular, yüksek aşınma direnci ile bilinen WC-Co-Cr sert kaplamaların yüksek sıcaklıklarda ciddi hasar gördüğünü göstermektedir. Kaplama, 750°C'de V_2O_5 ve Na_2SO_4 erimiş tuz varlığında yapılan 5 saatlik sıcak korozyon testlerinden sonra hasar görmüştür. Ayrıca kaplama tabakasında ilerleyen korozyon sürecine bağlı olarak dökülmeler ve bozulmalar meydana gelmiştir. Kaplama tabakasının dökülmesinden dolayı da altlık malzemede hasarlar oluşmuştur.

Anahtar Kelimeler: WC-Co-Cr Sert Sermet Seramik Malzeme, Sıcak Korozyon, Yüksek Hızlı Oksi Yakıt (HVOF), Termal Sprey Kaplamalar.

1. INTRODUCTION

Hot corrosion, oxidation, and wear are the most common damage mechanisms that surface engineers encounter. It is of great importance that the materials produced and used in our daily lives are more durable in terms of less material and energy loss (Singh et al., 2022; Testa et al., 2022). It is necessary to protect these materials to have less loss of materials used in many application areas such as automotive, ship, aircraft, and medical. The longevity of the materials used in these sectors will reduce the production of new materials (Singh et al., 2022; Hu et al., 2021). Reducing material production will result in less energy and ore usage. Thus, it will contribute to the world economy and ecosystem. One of the works of surface engineers to reduce material losses and extend their life is to coat materials (Lashmi et al., 2019; Carpio et al., 2019). The coating process is the general name of the processes carried out to physically and chemically change the surface of a material. By coating the surface of a material, a more durable and economical material design is provided against aggressive environments that the substrate materials alone cannot resist (Ahmadi et al., 2019). Coating methods of materials, especially metals, are generally hot-dip, electroplating, mechanical coating, diffusion, and thermal spray coating methods. Thermal spray coating techniques are used to coat metals, particularly those utilized in high-temperature applications (Wiesner et al., 2020).

Substrat materials in thermal spray coating methods are high-temperature resistant materials such as cast irons, super alloy materials, and steels (Patil and Vagge, 2022). The basic goal of this technology is to melt a coating material that is stronger than the substrate material at high temperatures and send it as molten or semi-molten material to the surface of the substrate. Flame spray, arc spray, detonation gun, high-velocity oxy-fuel, cold gas dynamic spray, atmospheric plasma spray, vacuum plasma spray, and electron beams physical vapor deposition are a few thermal spray coating techniques. Among these methods, EB-PVD and APS methods are used to deposit coating materials with very high melting temperatures, such as ceramic materials, on the substrate surface (Ozgurluk et al., 2018). The HVOF method, on the other hand, is preferred for depositing metal coating materials with high melting temperatures on the substrate surface. According to other methods, since the melted coating material in this technique is sent to the substrate surface at supersonic speeds, the material to be coated has little contact with atmospheric conditions. Therefore, oxide and porosity in the coating microstructure are at a minimum level (Liu et al., 2022).

The HVOF coating method, which has been used since the beginning of the 20th century, is one of the most important thermal spray coating techniques even today. Acetylene, propylene, and propane gases, as well as mixtures of these gases, are mostly preferred as flammable gases in the system. The procedure is started by sending an oxygen-rich gas mixture into the coating system. The coating process takes place under approximately 65-85 psi pressure (Wang et al., 2022; Testa et al., 2022). The thickness of the produced coatings varies between 0.1-1 mm. Combustion gas mixtures melt the coating material and send it to the substrate surface at supersonic speeds. The optimum distance of the coating torch from the substrate varies between 200-400mm. Coatings obtained after production have high adhesion strength, low porosity, and high density. The high temperatures used in the coating process ensure that the molten or semi-molten particles have significant thermal energy. The coating particles are delivered to the substrate surface at a rate of 500 to 800 m/s (Kalush et al., 2022; Doleker et al., 2018). The negative effects brought on by high temperatures are lessened by the fact that the temperature is lower than the plasma spray coating process. Additionally, due to the high speeds at which the materials to be coated are delivered to the substrate surface, even if the coating material is not melted, it can still cling to the substrate material because of the kinetic energy it possesses (Yang et al., 2022; Karaoglanli et al., 2017; Doleker et al., 2020). The excellent bond strength of the materials coated using the HVOF process is guaranteed by this adhesion property. Additionally, compared to the plasma spray coating technology, high-speed coatings and lower temperatures offer exceptional impact resistance in the coating layers. Additionally, many coatings created with this technique exhibit excellent slip, friction, and wear resistance. The drawback of this method is that ceramics with high melting temperatures cannot be used as coating materials, and the noise level is extremely high during production (Kiatisereekul et al., 2021; Doleker et al., 2021; Ozgurluk, 2022).

The HVOF technique, a cutting-edge thermal spray coating technique, demonstrates benefits like adaptability, continuity of the curing stage, and cheap cost when it comes to the deposition of WC-based materials. The HVOF-produced WC-Co-Cr coating materials have exceptional resistance to slip, wear, erosion, and friction. In particular, the high performance of WC-Co-Cr coatings at room temperature is supported by the studies available in the literature (Ma et al., 2014; Bolelli et al., 2014; Wood, 2014; Song et al., 2020). Tested the wear behavior of WC-Co-Cr and WC-CrxCy-Ni coatings produced by Song et al. In the study, it was observed that the Ni element added to the coating had a strength-enhancing effect at high temperatures. In addition, WC-Co-Cr coatings are the preferred material to prevent water droplet erosion in steam turbines. For this reason, WC-based coating with the HVOF technique is preferred as a promising approach in many areas (Vuoristo, 2007). The materials, which are typically coated using the WC-containing HVOF process, exhibit good high-temperature resistance and strength (Campo et al., 2009). The coatings coated with this approach exhibit very good behavior against wear and oxidation due to their low porosity and oxide content. Additionally, they are quite good at attaching the coating material to the substrate surface and resisting high temperatures (Ghadami., 2015; Niihara 1983).

In contrast to previous research, this study looked into the hot corrosion behavior of WC-Co-Cr coatings deposited on 316L stainless steel substrates using the HVOF process at high temperatures. Results of mapping analysis, SEM, XRD, and EDS performed after 750 °C hot corrosion tests were compared and analyzed.

2. MATERIALS AND METHODS

2.1 Materials

For the production of the coatings, firstly, 316L stainless steel substrate materials with the dimensions of 25x25x10mm^3 were procured. To prepare the substrate materials for the coating procedure, to clean the surfaces from dirt and oxide layers, and roughen them, they were sandblasted with the help of Al_2O_3 powder particles under approximately 2 bar pressure. Then, WC/Co/Cr coating powders with a purity of 99% at a mixing ratio of 86/10/4 by weight were obtained from the GTV company in the range of 5-25 µm. SEM image showing the spherical morphology of commercially obtained WC/Co/Cr powders is given in Figure 1. The substrate materials, which were sandblasted and made ready for the coating process, were placed in the Hipojet 2700-M (Mec, Jodhpur, India) branded HVOF coating unit and commercially obtained WC-Co-Cr powders were added to the powder feed unit. The spherical morphology of the powders provided a lot of convenience for the coating process. The parameters and carrier gases used in the HVOF coating process are given in Table 1.

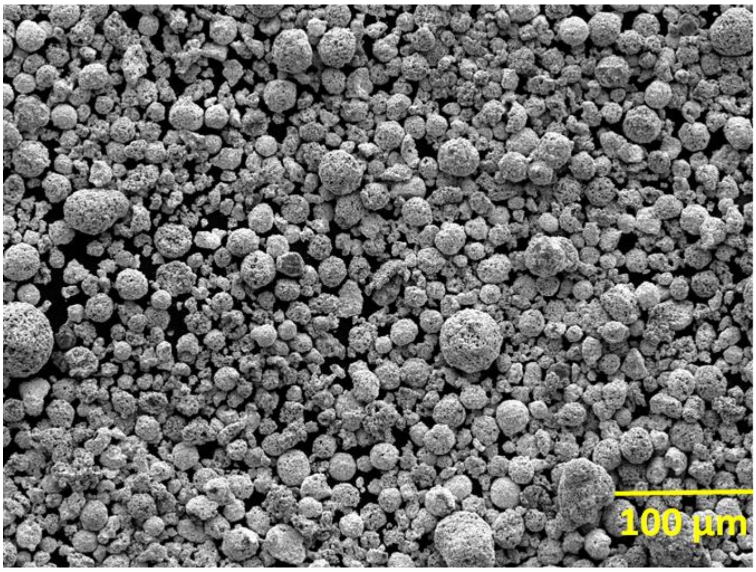


Figure 1. SEM image of WC-Co-Cr coating powders

Table 1. Parameters used in the HVOF thermal spray coating method

Materials	Combustible gases used in the method	Carrier gases used in the method	Material feed rate	Coating distance
WC-Co-Cr cermet powders	O_2 (230-240 slpm) CH_4 (85-90 slpm)	N_2 (5.5-6 slpm)	12.5-13 g/min.	250-260 mm

Coatings produced by the HVOF method are more environmentally friendly and perform better than coatings coated with the electrolysis method. In addition, the choice of coating material in this method includes a wide range. Cermet coatings produced by the HVOF method, such as WC-Co-Cr, are replacing many coating methods (Pulsford et al., 2019). Due to the nature of the HVOF method, coating large and complex-shaped parts was not possible. Thanks to the new generation of spray torches developed, the surfaces of narrower areas began to be effectively coated from shorter distances (Lyphout and Björklund 2014). Thus, the contact of molten particles with the atmosphere in coating processes carried out from shorter distances is also minimized (Zhao et al., 2019). During the coating processes, which sequentially take place from a shorter distance, the heated coating particles reach the substrate material without losing their heat. With this effect, complete melting may not occur in the particles reaching the substrate. As a result, low plastic deformation and poor bonding ocur. Considering all the positive and negative effects of the new generation HVOF method, materials produced using optimum coating parameters exhibit superior properties compared to materials produced by other methods. In this study, the coating parameters specified in Table 1 are the optimum values for WC-Co-Cr coating material.

The surface roughness, hardness, and porosity of the WC-Co-Cr hard cermet material deposited on the 316L stainless steel substrate using the HVOF technique, a new thermal spray coating method, were measured prior to high-temperature testing. The results of the measurements, conducted using a Mitutoyo SJ-310 (Japan) device for surface roughness, a Qness Q10 (Austria) device for hardness, and the Image-J porosity measurement program for porosity, are presented in Table 2. All values shown in Table 2 are values obtained before the hot corrosion of coating samples. After the sanding and polishing stages of the samples, which were mounted for hardness, the hardness value was measured from 5 different regions in the microhardness device. For porosity, cross-sectional SEM images were taken from the samples taken from the bakelite. Average porosity values from 5 different cross-sections SEM images are added to the table. For the roughness value, the average of the values taken from 5 different regions from the top surface of the pre-corrosion coating sample was determined.

Table 2. The roughness, porosity, and hardness values of WC-Co-Cr hard cermet coating materials, which were coated using the HVOF technique, one of the thermal spray coating methods

	Hardness (Hv)	**Porosity (%)**	**Roughness (Ra µm)**
WC-Co-Cr material	1565-1570	0.49±0.17	3.17-3.20

2.2 Hot Corrosion tests

Hot corrosion is a type of damage that occurs at high temperatures due to the presence of impurities in fuels used in various industrial sectors, such as NaCl, V_2O_5, Na_2SO_4, and KCl. These impurities melt at high temperatures and diffuse into the coating materials, causing damage. There are two types of hot corrosion damage: Type-I at high temperatures of 850-1000°C and Type-II at lower temperatures of 600-850°C. This study investigated Type-II hot corrosion damage of WC-Co-Cr coating material by sprinkling 55% V_2O_5 and 45% Na_2SO_4 salt mixtures on the coating materials, which were then subjected to isothermal hot corrosion tests for 1, 3, and 5 hours at 750°C. The samples were analyzed using advanced techniques such as SEM, XRD, EDS, and mapping before and after the tests to investigate their behavior against hot corrosion. Approximately 20mg/cm^2 of hot corrosion salts were sprinkled on each sample, and they were placed in an electric furnace operating at 750°C under open atmospheric conditions.

The diagram showing the time-dependent damage effect of hot corrosion damage mechanisms is given in Figure 2.

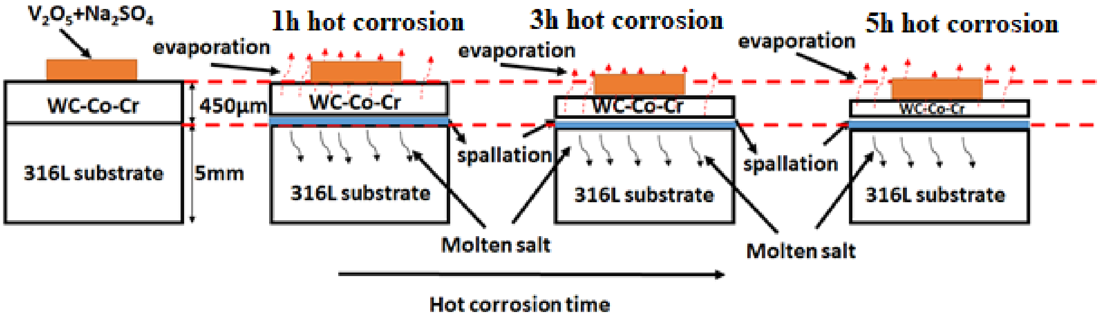


Figure 2. Time-dependent damage effect of hot corrosion damage mechanisms

After the hot corrosion tests, each sample was first taken from the oven that cooled down to room temperature for microscopic analysis. All samples taken from the furnace were individually embedded in cold bakelite. The samples taken for mounting were sanded for approximately 3 minutes on 60, 80, 100, 120, 300, 400, 600, 800, 1000, 1200, and 2000 mesh-size sandpapers, respectively. All the sanded samples were then polished with the diamond solution in 3µm, 1µm, and 0.25µm cloths and made ready for microscopic analysis.

3. RESULTS AND DISCUSSION

3.1 Characterization of as-sprayed WC-Co-Cr advanced ceramic cermet coatings

The HVOF coating method, which is widely used in many sectors such as aviation, space, ship, and automotive, provides an oxide-free, porosity-free, and dense coating layer. In Figure 3, a cross-section SEM image of 316L stainless steel material coated with WC-Co-Cr advanced ceramic cermet material by the HVOF method is given. It is seen that the coating layer completely exhibits the characteristic features of the HVOF method. As a result of the measurements made from 4 regions of the produced coating thickness, it is seen that it is approximately 450 µm. The coating layer with WC-Co-Cr content provides the 316L stainless steel substrate material with hardness and strength, as well as oxidation and corrosion resistance.

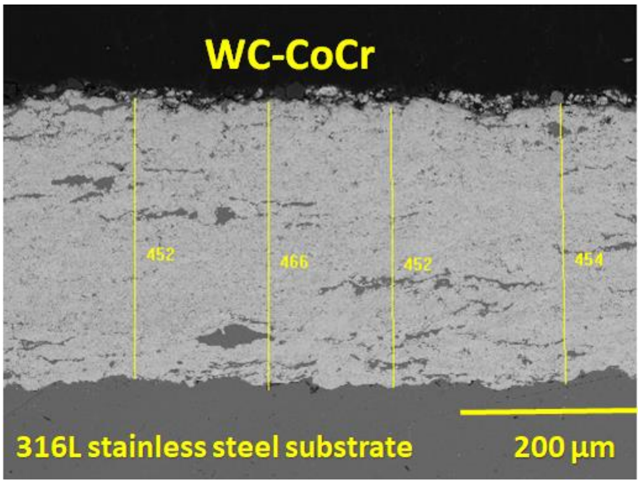


Figure 3. As-sprayed cross-section SEM image of 316L stainless steel material coated with WC-Co-Cr

Figure 4 presents the elemental mapping analysis results of the WC-Co-Cr coating system deposited by the HVOF technique. The coating content mainly consists of W, C, Co, and Cr elements, while the 316L stainless steel substrate contains Fe, C, Cr, and Co elements. The coating layer exhibits an oxide-free, non-porous, and compact microstructure, which is a characteristic feature of the HVOF technique. These results are consistent with our previous studies that also utilized the HVOF method (Doleker et al., 2018; Doleker et al., 2021).

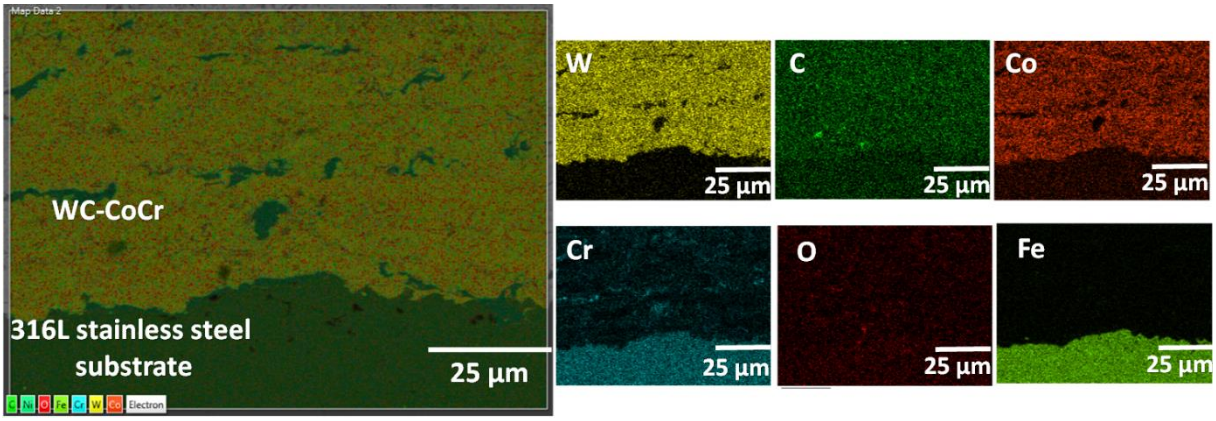


Figure 4. As-sprayed cross-section mapping analysis of WC-Co-Cr coated 316L stainless steel material

The XRD phase analysis results from the top surface of the WC-Co-Cr cermet coating layer are presented in Figure 5, which reveals the presence of WC, W2C, and Co phase structures in the coating system manufactured using the HVOF method.

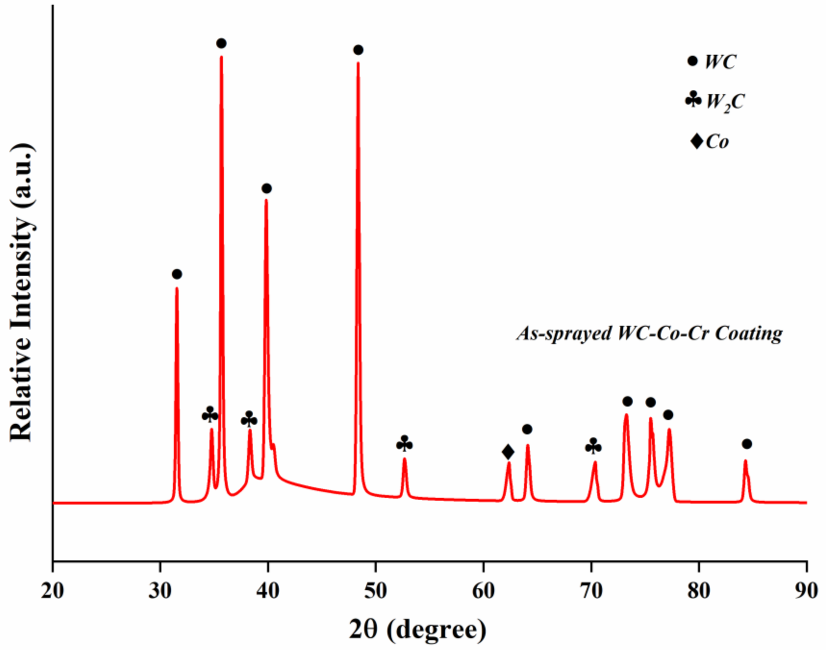


Figure 5. XRD analysis of the as-sprayed WC-Co-Cr coating system

3.2 Hot corrosion effect on WC-Co-Cr advanced ceramic cermet coatings

As it is known, if the hot corrosion damage mechanism occurs between 850-1000°C, it is called high-temperature hot corrosion (type1), if it occurs between 650-850°C, it is called low-temperature hot corrosion (type2). Since WC-Co-Cr coating system tests are carried out at 750°C in the presence of 55%V_2O_5 and 45% Na_2SO_4 corrosion salts, it is in type 2 corrosion type. In this damage mechanism, corrosion salts melt with the effect of temperature and interact with the coating system. The reactions present in the damage mechanism begin as follows:

$$V_2O_5 + Na_2SO_4 = 2(NaVO_3) + SO_3 \quad (1)$$

$$Na_2O\ (\text{base}) + V_2O_5\ (\text{acid}) = 2NaVO_3\ (\text{salt}) \quad (2)$$

In the hot corrosion event, V_2O_5 and Na_2SO_4 corrosion salts begin to melt under the influence of temperature, leak into the coating through micro-cracks and pores and move toward the lower layers. Hot corrosion damage mechanism occurs with various reactions. The corrosion salts that melt at high temperatures react with each other to form the $NaVO_3$ phase first (Peng et al., 2012; Habibi et al., 2013; Saremi et al., 2013).

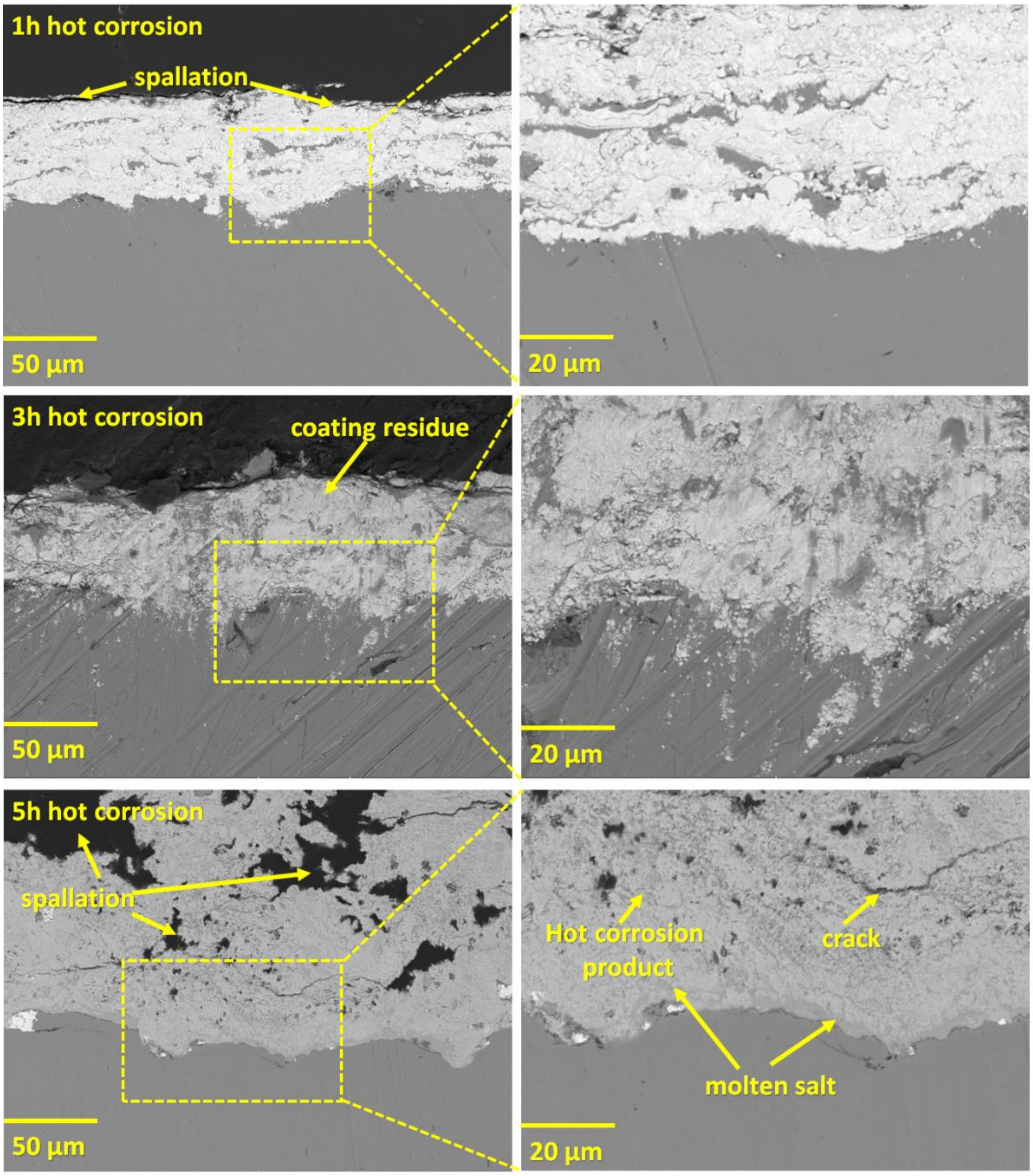


Figure 6. Cross-section SEM images of WC-Co-Cr coating system after hot corrosion test

In Figure 6, cross-section SEM images obtained after isothermal hot corrosion tests of the WC-Co-Cr coating system are given. In this study, in which the low-temperature hot corrosion damage mechanism was realized, molten corrosion salts formed reactions with the coating layer and caused the layer to be damaged. Parts of the coating layer interacting with corrosion salts were separated from the structure and a significant decrease in coating thickness was observed. After the first 1-hour hot corrosion test, the porosity structure with the top parts of the substrate material was observed. After the corrosion test of 3 and 5 hours, the existing porosities in the structure were closed with the effect of sintering. The coating thickness continued to decrease as the hot corrosion process progressed. After the corrosion test was conducted for 3 and 5 hours, the existing porosities in the structure were closed with the effect of sintering. This indicates that the high temperature and pressure conditions of the hot corrosion process caused the coating material to fuse together, filling in any pores or voids that were previously present. This effect is known as sintering. The coating thickness continued to decrease as the hot corrosion process progressed. This suggests that the hot corrosion process was causing the coating material to wear away or dissolve, potentially exposing the underlying substrate material to further damage (Chen et al., 2018; Habibi et al., 2013). Overall, these results suggest that the hot corrosion process can have significant effects on the structure and properties of coated substrate materials, and further research may be needed to better understand and mitigate these effects (Kim et al., 2017).

In Figure 7, there are SEM images of the surface obtained after the hot corrosion tests of the WC-Co-Cr coating system at different magnifications. On the top surface, there are long bar structures formed by coating layers interacting with corrosion salts. It is thought that the V element causes these long rod structures. Similar long rod-like structures were seen in previous hot corrosion studies (Ozgurluk et al., 2018). In this study, long rod-like structures were formed as a result of the reaction of melting corrosion salts with the coating layer.

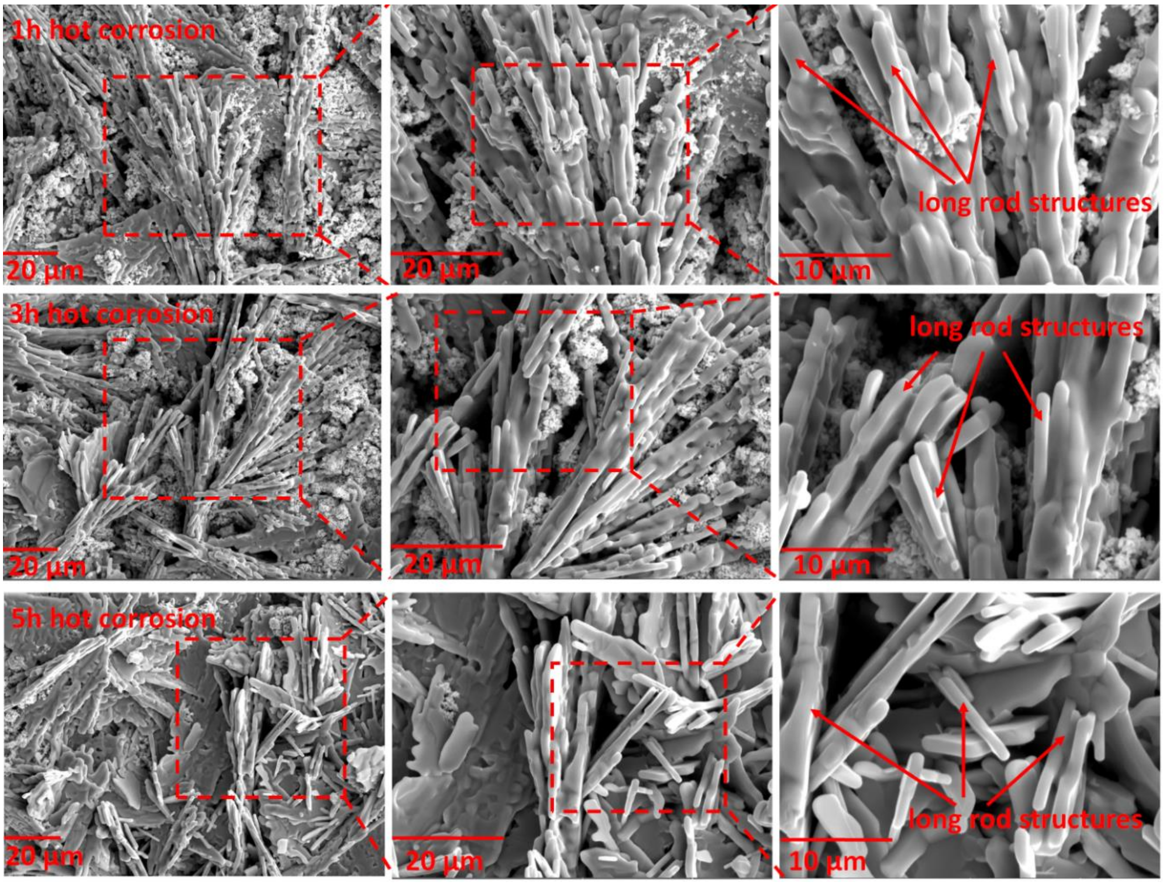


Figure 7. SEM images of the top surface of the WC-Co-Cr coating system after the hot corrosion test

The coating layer reacted with the molten salts and started to separate into layers after 1 hour of hot corrosion and after 5 hours of corrosion test, it almost completely detached from the substrate material. The cross-section images in Figure 6 were obtained from the coating residues on the substrate surface after the tests. Similar to this study, the tribocorrosion behavior of three WC-based coatings prepared by the HVOF method was carried out in a 3.5% NaCl solution. Unlike hot corrosion, the effect of corrosion and wear was investigated in the study, which was carried out with the help of an abrasive at room temperature. These three coatings were Co, CoCr, and Cr-7Ni matrix WC cermets. According to the experimental results, it has been observed that the binding phases greatly affect the corrosion and wear performances. Among the coatings, WC-12Co content exhibited very low corrosion resistance, while coatings with WC-10Co$_4$Cr and WC-Cr_3C_2-Ni contents showed higher corrosion resistance. Similar to this study, in other studies in the literature, it was observed that the added Cr element in addition to the Co element increased the corrosion resistance (Zou et al., 2015).

The results of the elemental mapping analysis conducted after the hot corrosion test are presented in Figure 8. The hot corrosion tests were performed in open atmospheric conditions, which resulted in the simultaneous occurrence of both oxidation and hot corrosion damage mechanisms in the coating materials. The mapping analysis clearly illustrates the infiltration of the V_2O_5 and Na_2SO_4 salt mixtures, which melt at high temperatures, into the inner regions of the coating layer.

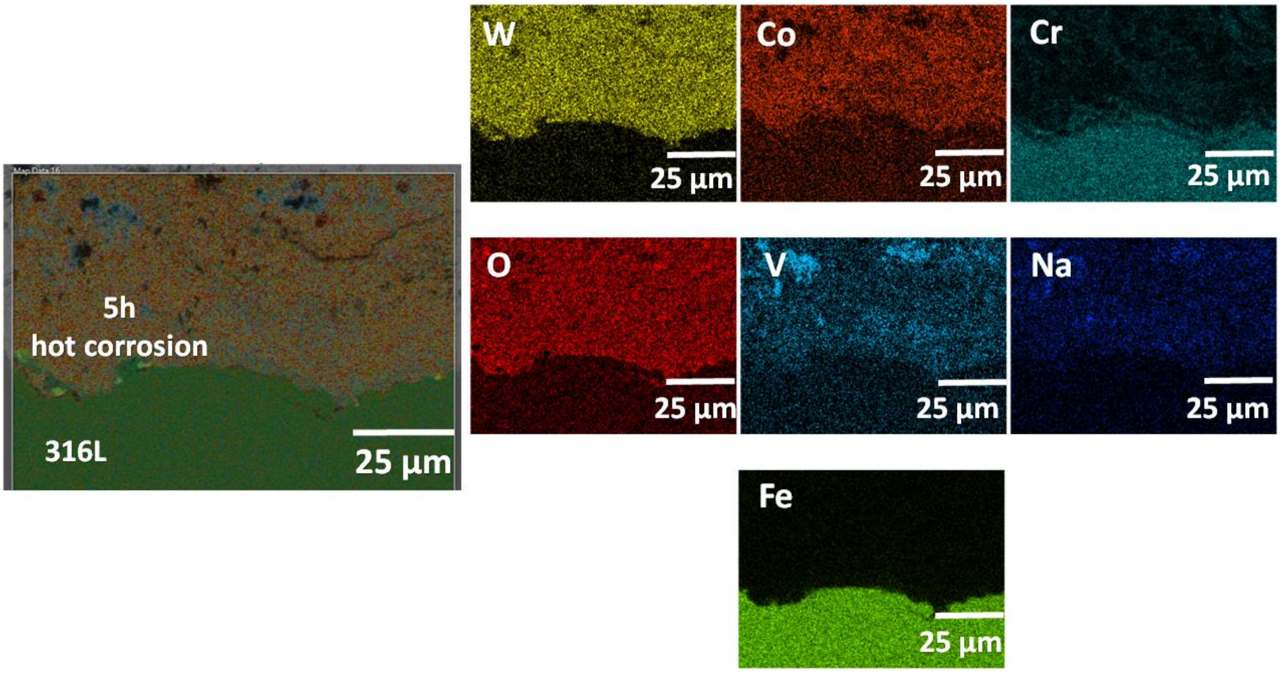
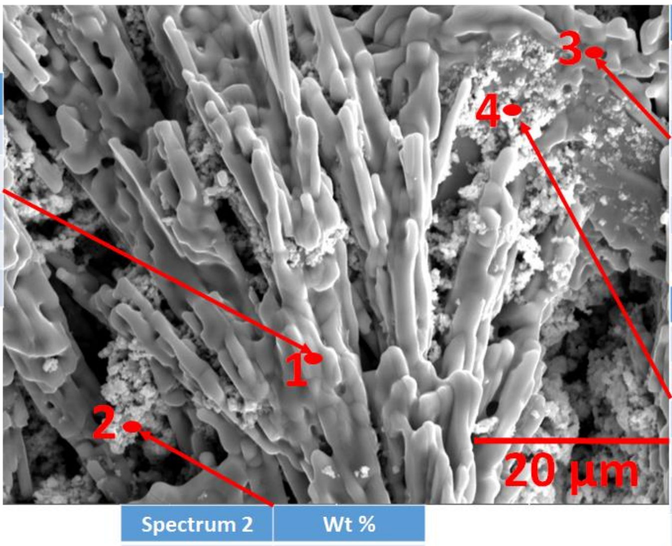


Figure 8. Cross-section elemental mapping analysis of WC-Co-Cr coating system after hot corrosion test

Unlike in this study, Kaur et al. used the HVOF technique to coat Cr_3C_2-NiCr on SAE-347H boiler steel. Kaur et al., who performed cyclic hot corrosion experiments in the presence of Na_2SO_4-$Fe_2(SO_4)$ corrosion salts at approximately 700°C, stated that the oxidized structure of the rich Cr content increased the hot corrosion and oxidation resistance (Kaur et al., 2009). Similarly, corrosion resistance of materials coated with the HVOF method on mild steel substrate using NiCr powders was tested. It was observed that the corrosion resistance of the samples whose SEM and XRD analyzes were performed before and after the corrosion tests were also increased (Aalamialeagha et al., 2003). Sundararajan et al. coated the coating material containing 80Ni-20Cr and 50Ni-50Cr on a steel substrate surface using both HVOF and APS methods. In the oxidation tests performed at 650°C for 100, 1000, and 3000 hours, they stated that all coatings produced by the HVOF method were more durable than the coatings produced by the APS method (Sundararajan et al., 2005). Sidhu et al. produced Cr_2O_3-NiCr, WC-12Co, Stalite 6, and Ni-20Cr coatings on ASTM-SA210 GrAl boiler tube steel using the HVOF method. In the cyclic hot corrosion tests carried out in the presence of 60% V_2O_5 and 40% Na_2SO_4 salts at 900°C, it was observed that the corrosion resistance of the coatings formed a protective oxide layer was better. In densely layered structures, an increase in corrosion resistance has been observed since oxygen and molten corrosion salts have to travel a long way along grain boundaries (Sidhu et al., 2006). In another study, the behavior of T11 and T22 boiler pipe steels against oxidation was investigated by coating with NiCrFeSiB alloy by the HVOF method. It has been observed that the superior oxidation performance of the NiCrFeSiB coating is due to the amorphous SiO_2 and protective Cr_2O_3 layer formed on the top surface (Mahesh et al., 2009). In a work in which 347H boiler steel was coated with Ni-20Cr with the HVOF technique, the oxidation resistance of coated and uncoated steels at 700°C was investigated. As a result of cyclic oxidation tests, it was observed that the coated samples were highly resistant to oxide flaking (Kaushal et al., 2011). Similar results were also seen in our study.



Spectrum 1	Wt %
W	54.6
C	20.3
V	16.8
Na	7.3
Co	1.1

Spectrum 2	Wt %
W	56.9
C	21.1
Co	10.4
V	3.9
Cr	3.5
Ni	3.2
Fe	1.0

Spectrum 3	Wt %
W	52.7
C	21.3
V	15.9
Na	7.7
Co	1.6
Cr	0.7

Spectrum 4	Wt %
W	54.2
C	25.4
Co	9.4
V	4.0
Ni	3.5
Cr	1.6
Na	1.2
Fe	0.7

Figure 9. Top surface EDS analysis after hot corrosion test of WC-Co-Cr coating system

Unlike other studies, in our hot corrosion study, EDS analyzes were performed on the top surfaces of the WC-Co-Cr coating system after the hot corrosion tests. The result of this EDS analysis obtained from the top surface is given in Figure 9. Elemental point analysis was carried out in 4 different regions. The effects of V_2O_5 and Na_2SO_4, which are hot corrosion salts, are observed at every point where the analyzes are performed. Analysis 1 was performed from the long rod-like structures present on the top surface. As an elemental distribution, in addition to W, C, and Co elements, V and Na elements were also encountered. It has been observed that the Cr element in the coating structure is not present in the long rod-like structures. Point analysis number 2 was carried out from the sedimentary structures present on the coating surface. In addition to W, C, Co, and Cr elements in the elemental distribution of sediment-shaped structures, V elements from corrosion salts and Ni and Fe elements present in the substrate material components were also encountered. EDS analysis results from 3 and 4 contain similar contents to the results of EDS analysis 2. According to the results of 4 different EDS analyses, it was observed that long rod-like structures were first formed in the structure in the hot corrosion damage of the WC-Co-Cr coating system. It was understood that the long rod-like structures were separated from the top surface together with the coating layer, depending on the progressive corrosion time.

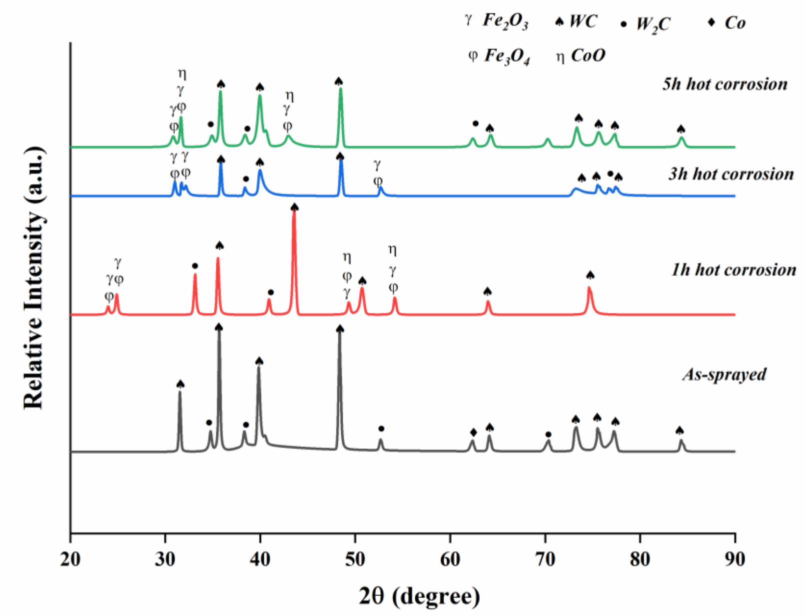


Figure 10. Top surface EDS analysis after hot corrosion test of WC-Co-Cr coating system

We can also see the results of the XRD analyses performed, where the coating layer is damaged and separated from the structure. The XRD analyses performed after each hot corrosion test are given in Figure 10 by superimposing them. As a result of isothermally performed hot corrosion tests, it is seen that phase separation occurs in the WC layer in the WC-Co-Cr coating layer inside the structure. While the WC layer transforms into the W_2C phase, it is seen that the element Co, which has a high affinity for oxygen, also turns into the CoO phase. As a result of the separations in the coating layer and the migration of the base material components towards the top part, oxidized phases of the Fe element were also encountered. The elements V and Na, which are hot corrosion salts, were not encountered in the XRD phases. The reason for this is thought to be that these corrosion salts are very low compared to other composition elements and that the long rod-like structures that perform phase transformation are separated from the coating surface. X-ray diffraction (XRD) is a powerful technique used to analyze the crystal structure and chemical composition of materials. However, the XRD analysis can only detect the elements and compounds that are present in sufficient quantities and within the detection limit of the technique. In the case of hot corrosion salts, such as V and Na, their concentrations in the coating material may be relatively low compared to other elements, which makes them difficult to detect using XRD. Moreover, the long rod-like structures that perform phase transformation during hot corrosion may be located deep within the coating material and separated from the coating surface. This can also make it difficult for XRD to detect the presence of these structures, as the technique is typically surface-sensitive and may not penetrate deeply into the material. Other analytical techniques, such as scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), or transmission electron microscopy (TEM), may be more suitable for detecting and characterizing the hot corrosion salts and the rod-like structures in the coating material. These techniques can provide higher resolution and depth of analysis, which can be used to locate and identify the hot corrosion products and understand their mechanisms of formation.

In addition to phase transformations such as WC, W_2C, it is possible to talk about the presence of iron oxide phase structures such as Fe_2O_3 and Fe_3O_4 in the XRD analysis results. No iron-containing compounds are present in the coating layer. The reason why these phase structures are encountered in the XRD analysis is due to the shedding of the coating layer in some regions and the emergence of ferrous compounds in the base material, stainless steel. These results were also seen in the hot corrosion studies carried out before (Kiatisereekul et al., 2021; Doleker et al., 2021; Ozgurluk, 2022).

4. CONCLUSION

Isothermal hot corrosion tests were conducted on the WC-Co-Cr hard cermet coating materials deposited on a substrate of 316L stainless steel using the HVOF technique, which is one of the thermal spray coating methods, at a temperature of 750 °C. The results were analyzed in accordance with the existing literature and presented below.

- WC-Co-Cr advanced hard cermet coating materials were deposited successfully on a 316L stainless steel substrate using the innovative thermal spray coating method, HVOF. The resulting coating microstructure is characterized as dense, non-porous, and oxide-free.
- Hot molten corrosion salts formed long rod-like structures on the top surface of the WC-Co-Cr coating layer. Since long rod-like structures cause volume increases in the coating layer, thermal expansion mismatches have occurred in the coating layer and some parts of the coating layer have been spilled.
- As a result of XRD analysis, it was observed that oxidized compounds of Fe element occur in a hot corrosion damage mechanism.
- It has been observed that the behavior of WC-Co-Cr hard cermet material, which is known to be resistant to abrasion, against hot corrosion is quite weak.
- In the XRD analysis results, phases such as Fe_2O_3 and Fe_3O_4 were found in addition to the phase structures in the coating. The appearance of these phases indicates that shedding has occurred in the coating layer.

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6. CONFLICT OF INTEREST

The authors confirm that, to the best of their knowledge, there are no conflicts of interest or competing interests with any institution, organization, or individual that could influence the review process of the paper.

7. AUTHOR CONTRIBUTION

Yasin ÖZGÜRLÜK contributed to the conceptualization and management of the research, design of the research and management of the project, data analysis and interpretation of the results, critical review of the intellectual content, preparation of the manuscript, and final approval and overall responsibility for the paper.

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