Study of fracture toughness and bend test morphologies of HVOF sprayed Cr$_3$C$_2$-25% NiCr coating after heat treatment

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Abstract: Majority of the industrial components are subjected to high temperature exposure, where crack propagation occurs due to shear failure. The paper involves the study of the fracture toughness of heat treated Cr$_3$C$_2$-NiCr coating at three different service temperatures (750°C, 850°C, and 950°C for 1-hour aging) using indentation techniques to measure the crack resistance of the coating. At 750°C and 850°C, the coating cracked at the bend area, but not spalled. At 950°C, the coating spalled and delaminated from the substrate indicating poor adhesion after prolonged exposure. The influence of heat treatment on the fracture toughness and adhesion properties of the Cr$_3$C$_2$-25%NiCr coating were also investigated. The high temperature exposure at 950°C, resulted in a shear failure of the coating due to the presence of splat contraction. The increase in temperature increases the fracture toughness $K_{IC}$ of the coating, with the decrease in hardness. It was observed that the oxidation levels enhanced on the top layer of the coating, which acted like a core region for crack initiation at 950°C resulting in shear failure during bend test.

1. Introduction

Majority of the power generation industries working under high temperature application suffer from deformation due to erosive wear and abrasion phenomenon. This decrease in thermal efficiency of the components leads to some of the failures in the system causing downtime error [1]. The failures like the erosive wear of the base material can also be witnessed in high power generation system. It is important to protect such erosive wear and increase the efficiency of the power generation system and also of the base material. Among the various thermal spray technologies, high velocity oxy-fuel (HVOF) offers excellent micro hardness, good adhesion of the splat particles and minimum porosity to the coated specimens. Chromium carbide powder has been extensively used to solve the problems of high temperature applications due to its erosion oxidation resistance as compared to the tungsten carbide based powders. Chromium carbide along with nickel chrome coatings are generally applied to heat treated components like the rolls and boiler tubes to combat against the highly erosive particles causing wear [2-3]. The chromium carbide coatings provide superior resistance to heat treatment at maximum service temperatures up to 750°C with improved microstructure, which occurs due to mechanical interaction of the splat particles with the base material and the oxidizing environment causing the reduced material loss. This material loss can be reflected in the decrease in the coating properties due to microstructural instability, and other properties like wear and hardness can also be affected. The formation of the Cr$_2$O$_3$ as a protective oxide layer is evidenced in most of the coating surface after high temperature exposure thereby, protecting the coating surface from oxidation [3]. By the heat treatment process, the properties of the Cr$_3$C$_2$-NiCr coating can be enhanced in-order to improve the erosion resistance of the coatings. The carbide dissolution has an important role in governing the hardness and the phases present in the coating. The super saturation of the NiCr binder matrix makes the carbide dissolution phase prone to brittle cracking and this cracking results in weak inter-splat adhesion, generation of cracks and development of oxide stringers. By heat treatment above 700°C, a microstructural change takes place involving the loss of initial carbide phase, carbide precipitation, and formation of shear crack networks where there is an absence of NiCr binder matrix [4-10].
The present study focusses on the study of the fracture toughness by the indentation test which is basically considered as a base test in determining the adhesive properties of the thermal spray coating. The study of the crack propagation that indeed resulted in the generation of the shear cracks during bend test was analyzed too. The measurement of the hardness was investigated and the corresponding fracture toughness is measured which is the decisive factor in case of erosive wear. The correlation between the heat treatment and the spallation resistance during bend testing is also investigated.

2. Materials and methods
The 75%Cr3C2-25%NiCr powder supplied by (M/s. H C Starck GmbH, made in Germany), Amperit code 588.074 was used as a feedstock powder. Agglomerated and sintered with the grain size -30/+5 µm alloy was used as a standard feedstock powder in the present investigation. The particles are spherical and irregular in morphology as they are identified using CAMSIZER X2 (M/s. Retsch Technologies GmbH, Germany) using the principle of Dynamic Image Analyzer as per ISO 13322-2. figure 1 indicates the average particle size X (µm) of the powder present with respect to the Percentage of Volume Q3 (%). The maximum range of the powder particles size lies in 90.0% having an average powder particle size of 33.2 µm. The HVOF coating were deposited using Hipojet-2700 thermal spray gun (Make: M/s. Metallizing Equipment Company Private Limited, India) using LPG as gaseous fuel. All the process parameters employed for the HVOF spray process was kept constant as per the standard prescribed by the manufacturer of the HVOF thermal spray equipment. The coating thickness was maintained in between 300 to 350 µm during thermal spraying and was constantly verified using coating thickness gauge (Model: Posit Ector 6000, Make: Defelsko, USA). The standard parameters adopted for HVOF-spraying are summarized in table 1. The 9Cr-1Mo substrate sample of size 50 x 50 x 5 mm size was grit-blasted with brown virgin alumina 16 mesh grit size to provide the optimum surface roughness between range Ra 6 to 8 µm, and in order to guarantee a strong mechanical bond between the coating and the substrate by the enhanced roughening of the substrate material. It is necessary to prepare the substrate by surface cleaning and desired roughness to achieve maximum coating bond strength. The surface after grit blasting has to be cleaned by dry compressed air free from any contaminates like debris and residual dust.

![Figure 1: Average particle size of Cr3C2-25%NiCr powder having a 33.2 µm particle size.](image_url)

3. Characterization techniques
The as-sprayed samples were heat treated at three different temperatures (750°C, 850°C and 950°C in air for 1-hour exposure) inside a laboratory muffle furnace (Make: M/s. Bionics Scientific Technologies (P) Ltd, India). This temperature was selected in order to evaluate the fracture toughness and residual stress measurement of the Cr3C2-NiCr coating in the actual boiler working temperatures. The scanning electron microscope (SEM) (Make: Carl Zeiss Model: Evo18, Germany) equipped with energy dispersive spectrometry (EDS) (Make: Oxford Instruments, United Kingdom) was used to obtain the back scattered electron (BSE) microstructures of as-sprayed and heat treated samples were carried
out. The average coating thickness was reconfirmed by taking a mean of 10 measurements for each coating area during the SEM investigation.

Table 1. HVOF Hipojet-2700 parameter.

| Parameters          | Standard observed reading |
|---------------------|---------------------------|
| Oxygen flow rate    | 260 slpm                  |
| Fuel (LPG) flow rate| 65 slpm                   |
| Air flow rate       | 650 slpm                  |
| Spray Distance      | 8 inch                    |
| Powder Feed rate    | 60 gram/min               |
| Fuel Pressure       | 7.0 kg/cm²                |
| Oxygen pressure     | 10.0 kg/cm²               |
| Air pressure        | 6.0 kg/cm²                |

4. Results & Discussion

4.1 Microstructural investigation of as-sprayed and heat treated samples

Figure 2, shows the SEM images of the as-sprayed samples with some presence of alumina grit particles entrapped at the coating-substrate interface. The SEM concludes a 280 to 310 µm coating thickness on the mild steel substrate. Multiple spray passes are used to obtain the required thickness of the coating, which led to the development of a lamellar structure in the coatings. The SEM coating morphology showed a general characteristic splat like layered deposition and re-solidification of molten particles. The coating is free from any cracks. SEM-EDS confirms the presence of dark and light grey regions indicating chromium rich phase corresponding to Cr₃C₂ grains [11-12]. The SEM microstructure confirms the presence of micro-pores that are evenly distributed throughout the coating area, as identified as black dots. Figure 2 shows the top view of the Cr₃C₂-25%NiCr coating indicating the uniform homogenous distribution of the Cr₃C₂ matrix in white color and the dark spots of NiCr matrix grey in color. The coatings indicated a uniform distribution of Cr and Ni elements along with carbide content as per the Cr₃C₂-25%NiCr powder composition. The Cr₃C₂ as the main phase is surrounded by the NiCr matrix from the top surface view of the coating as shown in figure 2. The EDS analysis shows the presence of Ni, Cr, C and few traces of Fe, the presence of Fe in the coating area, is due to inter-diffusion of the Fe which is predominant in the 9Cr-1Mo substrate material. The SEM microstructure showed the lowest level of porosity along with homogenous carbide dissolution. The as-sprayed coating was held in the laboratory muffle furnace at 750°C, 850°C and 950°C for 1 hour aging. Figure 2, shows the SEM images after prolonged aging of the coating with micron level layer of oxidation formed after high temperature exposure. The appearance of the as-sprayed Cr₃C₂-25%NiCr coating is initially grey in color after aging. The SEM images indicates no signs of micro cracks generation during heat treatment process.
4.2 Fracture toughness measurement

The process of application of major load results in causing of catastrophic failure of the coating and of the base material. Evans and Charles characterized the surface generated cracks on the brittle surface using micro hardness, young’s modulus and crack length as these parameters help to determine the fracture toughness value [12].

The fracture toughness is calculated from the following Charles and Evan equation

$$K_{IC} = 0.016 \left( \frac{E}{H} \right)^{1/2} \times \left( \frac{F}{C^{3/2}} \right)$$

Figure 2: As-sprayed SEM of the Cr$_3$C$_2$-25%NiCr coating and top view of coating.

This method involves the determination of the value of the half diagonal and the crack length generated at the coating area. During indentation, the total volume of the pore in the stress field of indenter has zero hardness and thus does not resist material plastic flow [13-14]. The load of 2.0 kgf was applied on the heat treated Cr$_3$C$_2$-25%NiCr coating at 750°C to generate sufficient crack. The crack lengths were measured for the corresponding hardness taken near the epoxy, mid-center of the coating and near the coating-substrate interface and the estimate of the fracture toughness were done, and majority of the cracks generated were running parallel to the substrate area. Few cracks were produced near to the impression of the indent diagonal corners. The coating showed traverse cracks in the majority of the optical images taken during indentation loading. No delamination or induced metallurgical transformation between the coating and the substrate was observed.

The fracture toughness of the coating was calculated from the measurements of Vickers indentation cracks as shown in Table2 using Eqn.1. The presence of NiCr matrix which is tough and hard reinforced with Cr$_3$C$_2$ particles can accumulate the kinetic energy of the counter striking particles and thus minimize the chances of cracking after exposure to the high temperature after 850°C [13-14]. The fracture toughness ($K_{IC}$) for a minimum crack length (42.93 µm near coating-epoxy resin for 750°C heat treatment) and the maximum crack length (124.64 µm near coating-epoxy resin interface for 850°C heat treatment) are shown in Table2. The fracture toughness value ($K_{IC}$) decreases after 950°C and also the generation of the cracks are minimum after 850°C, thereby making the carbide coating more plastic. The ductility of the NiCr alloy has improved the fracture behavior and generation of the cracks at high temperature exposure. The good ductility of the NiCr matrix prevented the localized stresses to minimize the cracks inside coating. The lamella bonding was improved at 950°C which restricted the cracks to penetrate inside the coating. The probable reason might be due to carbide dissolution effect which makes more difficult for the cracks to grow until the desired toughness of the lamella boundary region has been reached. The coatings have a minimum porosity that have hindered the generation of the cracks at high temperature exposure during indentation, the fracture toughness values ranged from 1.857 MPa.m$^{1/2}$ to 4.833 MPa.m$^{1/2}$ with the rise in temperature from 750°C to 950°C.
Table 2. Fracture toughness values, crack length at the corresponding Micro Vickers hardness.

| Test trials | Temperature (°C) | Position of indenter near to | $K_Ic$ Value ($x10^{-3}$) MPa m$^{1/2}$ | Crack length in (µm) | Micro hardness (HV 2.0) |
|-------------|-----------------|-----------------------------|-------------------------------------------|----------------------|------------------------|
| 1           | 750             | Epoxy                       | 4.895                                     | 42.93                | 912                    |
| 2           | 750             | Mid-coating                 | 2.964                                     | 59.22                | 946                    |
| 3           |                 | substrate                   | 1.857                                     | 79.87                | 978                    |
| 4           | 850             | Epoxy                       | 1.014                                     | 124.64               | 856                    |
| 5           | 850             | Mid-coating                 | 1.691                                     | 88.34                | 878                    |
4.3 Bend test measurement

Coated strips were evaluated to test the coating integrity to check whether the coating would spall or delaminate from the substrate before the cohesive failure. The coated specimens were as-sprayed up to a coating thickness of 150 to 200 µm. The coated specimens were heat treated at 750°C, 850°C and 950°C for 1 hour and bend test as per ASTM E-290 (2014) standard were performed. All the three specimens were investigated for the HVOF sprayed coating under standard operating parameters. The 750°C exposure sample showed a light greyish colour appearance, after elevated exposure to 850°C and 950°C, the colour changes to dark greyish due to higher oxidation during exposure. It is known that the spallation of the coating tends to degrade the fatigue properties of the coating so, the present study involves the bend testing of the heat treated coated specimen using a mandrel. The coated specimens are bent to 180° by applying force. After bend test the cracks were visible on the coating surface, these surface cracks were visible through the naked eye. The cracks originated from the top surface and later it propagated through the substrate. The cracks in the Cr₃C₂NiCr coating generally were straight enough and the opening of the cracks was measured using SEM as shown in figure 3. Figure 4 shows the SEM of the crack generation at 750°C and 850°C exposure, where the spallation nucleate from the top surface.
and later spread whole towards the coating. The width of each cracks were approximately 44 to 52 µm each. At 950°C, it was observed that the coating spalled from the substrate. The coating was not able to sustain thermal shock and fatigue at 950°C resulting in cohesive failure. The presence of irregularities like the porosity at the interface between the carbide matrix and the substrate leads to the propagation of the cracks.

**Figure 3:** Bend strip coated sample after bend test, 950°C heat treated sample showing coating failure.

**Figure 4:** SEM image of bend strip coated sample after bend test at 750°C, 850°C

5. **Conclusions**

The experimental study of the Cr₃C₂-25%NiCr coating by HVOF is deposited on the 9Cr-1Mo steel substrate and the investigation of the fracture toughness are measured. The heat treatment of the coated sample at 750°C, 850°C, and 950°C resulted in an increase in the micro Vickers hardness for as-sprayed coatings from 748 ± 56 HV to 978 ± 38 HV for 750°C and later decrease in micro Vickers hardness was observed. The decrease in this trend is probably due to hardening phenomenon, where the carbide dissolution takes place at high temperature causing lesser micro Vickers hardness. The crack length for 750°C heat treated coated sample is minimum about 42.93 µm for HV2.0 indent loading, and maximum for 850°C heat treated coated sample having 124.64 µm. The reason being the NiCr alloy has increased the ductility of the alloy matrix and reduced the generation of the cracks after high temperature exposure. The absence porosity (less than 1.5%) and reduced surface roughness has hindered the growth of the cracks after elevated temperature exposure. The K IC values ranged from 1.857 MPa.m¹/² to 4.833 MPa.m¹/² with rise in temperature from 750°C to 950°C. The adhesion strength and bend test of the heat treated coated sample was observed on a decreasing trend due to deteriorating adhesion after thermal exposure.
References

[1]. Bansal P, Shipway P H and Leen S B 2007 “Residual stresses in high-velocity oxy-fuel thermally sprayed coatings – Modelling the effect of particle velocity and temperature during the spraying process” ActaMaterialia55.

[2]. Beshish G K, Florey C W, Worza Af J and Lenling W J March 1993 “Fracture Toughness of Thermal Spray Ceramic Coatings Determined by the Indentation Technique” Journal of Thermal Spray Technology Volume 2(1).

[3]. Chicot D, Demareaux P, Lesage J 1996 “Apparent interface toughness of substrate and coating couples from indentation tests” Thin Solid Films 283.

[4]. ChicotD, Pertuz A, Roudet F, Staia M H and Lesage J 2004 “New developments for fracture toughness determination by Vickers indentation” DOI: 10.1179/026708304225017427 Materials Science and Technology Vol. 20.

[5]. Demareaux P, Chicot D and Lesage J 1996 “Interface indentation test for the determination of adhesive properties of thermal sprayed coatings” Journal of Materials Science Letters 15

[6]. Chicot D, Marot G, Araujo P, Horny N, Tricoteaux A, Staia M H and Lesage J 2006 “Effect of some thermal treatments on interface adhesion toughness of various thick thermal spray coatings” Surface Engineering Vol. 22 No 5.

[7]. Chicot D, Araujo P, Horny N, Tricoteaux A and Lesage TJ 2005 “Application of the interfacial indentation test for adhesion toughness determination” Surface & Coatings Technology

[8]. Yamazaki Y, Arai M, Miyashita Y, Waki H and Suzuki M 2013 “Determination of Interfacial Fracture Toughness of Thermal Spray Coatings by Indentation” Journal of Thermal Spray Technology Volume 22(8) 1358-1365.

[9]. Gariboldi E, Rovatti L, Lecis N, Mondora L and Mondora G A 2016, Tribological and mechanical behaviour of Cr3C2–NiCr thermally sprayed coatings after prolonged ageing, Surface & Coatings Technology.

[10]. Lesage J and Chicot D 2002 “Role of residual stresses on interface toughness of thermally sprayed Coatings” Thin Solid Films 415 143–150.

[11]. Kuroda S, et.al. 2001 “Peening action and residual stresses in high-velocity oxygen fuel thermal spraying of 3161 stainless steel” Journal of Thermal Spray Technology Volume 10(2) 367-374.

[12]. Lopez E, Cantera, Mellor B G 1998 “Fracture toughness and crack morphologies in eroded WC–Co–Cr thermally sprayed coatings” Materials Letters 37201–210.

[13]. Houdkova S and Kasparova M 2013 “Experimental study of indentation fracture toughness in HVOF sprayed hard-metal coatings” Engineering Fracture Mechanics 110 468–476.

[14]. Ghabchi A et al 2014 “Damage mechanisms and cracking behavior of thermal sprayed WC-Co-Cr coating under scratch testing” Wear 313 97–105.