

Development of High Velocity Oxygen Fuel Corrosion Resistant Coatings; A Comparison between Novel High Entropy Alloy and Conventional Cermet Coatings for Geothermal Applications

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ABSTRACT

Corrosion damage of materials operating in the harsh geothermal environment with corrosive species, high temperatures and pressures necessitate the development of novel, cost-effective corrosion-resistant coatings to extend the service life of down-hole drilling equipment and power plant components. The thermal spraying process is a well-established and versatile method for producing thick coatings in terms of cost, wide range of powder selection, and high deposition efficiency. High Velocity Oxygen Fuel (HVOF) thermal spraying process has proven to be one of the most effective techniques for deposition of conventional cermet-carbide composite coatings improving their high-temperature oxidation corrosion, erosion, and wear resistance. The objective of this work focuses on testing the corrosion resistance of a CoCrFeNiMo_{0.85} high entropy alloy (HEA) coating fabricated by HVOF technique. Here we report the comparative analysis of corrosion resistance for the developed CoCrFeNiMo_{0.85} and CrC–NiCr, WC–Co carbide systems. The HEA and Cermets were immersed for 14 days in a simulated alkaline geothermal drilling environment at 120 °C and 50 bar. In addition, an electrochemical-accelerated corrosion test in a

3.5wt% NaCl was carried out at ambient temperature to investigate the behavior of the coatings in the presence of Cl-ions. The compositional effect of the microstructure on corrosion performance of the tested samples is discussed by analyzing corrosion damages and products using SEM/EDS analytical methods. The findings are essential to determine the suitability of HVOF as a fabrication method for CoCrFeNiMo_{0.85} HEA coatings and the candidacy of the resulting coating for corrosion protection of components used in geothermal energy production.

Key words: Thermal spray coatings; Corrosion resistant materials; Geothermal; Immersion test; Electrochemical corrosion; High Temperature.

INTRODUCTION

Several components in geothermal power plants need to be protected from the environment due to the corrosive nature of geothermal fluids used to generate the energy. Depending on the fluid properties for any location, the type of protection varies. In geothermal power plants, wear, erosion, corrosion, and scaling are all known problems¹. These issues can lead to a variety of outcomes, ranging from decreased plant efficiency to upstream component failure. Failure of a component is thus a significant challenge in the geothermal industry, where materials need to operate in high temperature and high pressure environments. A major cost factor is also linked to the drilling of geothermal wells, where cost rises due to increased depth/distance of drilling, increased trip times, higher high temperature and high-pressure conditions which can lead to increased wear and corrosion of the materials. To address the issue, coatings can be considered to be a potential solution to extend the service life of downhole equipment.

High velocity oxygen fuel (HVOF) spray is a well-used thermal spraying technique for metals, alloys, and carbide-based ceramic feedstock that can deposit dense and adherent coatings on surfaces. Because it has a higher velocity and lowers flame temperature than other thermal spray processes, it is primarily used for applying powder materials with a relatively low melting point and those that may degrade at high temperatures. The wear resistance of these coatings is well known. Many studies have shown that WC and CrC coatings have higher hardness, fracture toughness, and thus wear resistance than other carbides²⁻⁴. On the other hand, decarburization during manufacturing has been shown to have a negative impact on abrasive wear resistance of the coatings, owing to increased brittleness and a decrease in hard particle content; however, thermal spraying reduces the occurrence of this phenomenon⁵. Ductile cobalt (Co), Ni, or iron (Fe) binder is commonly used in WC coatings. The ductile binder adds toughness and strength to the carbide phase WC, which provides hardness and wear resistance. The chemical bond between WC and Co results has a very low interfacial energy in the solid-state, which gives excellent adhesion. In corrosive environments, the desire to improve the matrix contributes to localized corrosion⁶. To counteract this, the addition of chromium (Cr) has a significant impact on both the microstructure and, thus, the performance⁷.

In particular, the thermally sprayed CrC based coatings can be an excellent choice providing protection against localized corrosion and abrasive wear. Although CrC based coatings have lower hardness and wear resistance than WC coatings at lower temperatures, they outperform WC based coatings in high temperature wear. WC-based coatings are typically used at temperatures below 500 °C, whereas CrC-based coatings can operate at temperatures up to 900 °C⁸. They have a high melting point, which allows them to resist oxidation and corrosion better than other coatings. The wear resistance emerges from the carbide ceramic phase, while corrosion resistance from NiCr-binder⁹.

High entropy alloys (HEAs), a new class of materials, combine at least five elements to create a novel alloy with unique properties. The new approach to these HEAs has four main effects: the high-entropy effect, which stabilizes solid-solution-phases, the slow diffusion effect, which enhances nanoprecipitation and the severe lattice distortion effect, which is responsible for the high strength of HEAs; as well as the cocktail effect explaining the unexpected properties that can be obtained for HEAs. Recent studies have shown that many HEAs have high hardness, wear resistance and excellent corrosion resistance¹⁰⁻¹⁴.

The topic of this study was to test different coatings for different components of a novel down-the-hole (DTH) hammer with fluidic oscillator in simulated geothermal well environment. Advanced materials and coatings were developed for the testing including; cermet coatings, Nickel (Ni) -based coatings, nanocrystalline/amorphous coatings, and high entropy alloy (HEA) coatings to increase the lifetime of the component due to corrosion and wear. In this study, the results from corrosion testing in simulated high temperature and pressure drilling environment of developed high velocity oxygen fuel (HVOF) coating systems, including tungsten carbide (WC) coatings, chromium carbide (CrC) coatings, and high entropy alloy (HEA) coatings, are presented.

EXPERIMENTAL PROCEDURE

Materials and characterization

Through-hardened alloy steel was selected as a substrate which is one of the materials used in the drilling system. The steels were machined either disc as (30 x 3 mm) or rectangular (50 x 25 x 3 mm) shaped. The rectangular samples were fabricated with rounded edges to reduce the area of sharp edges, avoiding stress raisers at high temperatures, whereas the central position of the circular disc was exposed during the electrochemical room temperature test. Prior to coating, the substrates are generally prepared by cleaning to Sa 3 (white metal finish) in accordance with ISO 8501 ¹⁵ and profiled by grit blasting. Three powder feedstocks for developing the coatings included: Tungsten carbide cobalt-chromium (WC-Co-Cr) coatings, chromium carbide nickel (CrC/NiCr) coatings due to their commercial availability, known properties and application, and the novel CoCrFeNiMo_{0.85} HEA. The coatings were deposited by HVOF spraying (using JP5000® equipment) to offer corrosion and erosion resistance at elevated temperature (minimum 120°C) by achieving a dense structure and a relatively smooth surface finish. It is worth noting that the chosen carbide-based cermet coatings were previously investigated and have shown good sliding wear resistance⁴. The coatings were manufactured and provided by TWI Ltd. in Cambridge UK. The substrate steel specification is EN24T (BS 970:1955) or DIN 34CrNiMo6. The nominal (wt%) composition of the coating is listed in Table 1.

The surface finish was evaluated by the average roughness parameter (Ra) using an optical profilometer (ISO 13565 ¹⁶), taking the averaged value from six scans. The porosity of the coating was determined using the ASTM E2109-01 ¹⁷ standard. Optical microscopy was used to capture microstructure images of the polished cross-section surfaces. Using ImageJ® software averaged porosity was calculated using area fraction analysis and thresholding of at least twenty micrographs. A Vickers hardness tester was used to assess the microhardness of the coated cross-section surfaces that were generated. At least ten indents were created along the length of the coating using a 300g load. The hardness value was calculated as a mean with a standard deviation. A scanning electron microscope (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) was used to investigate the thickness and microstructures before and after the exposure test to demonstrate corrosion damages.

Table 1
The powder composition of WC-CoCr, CrC-NiCr - Cermets and CoCrFeNiMo_{0.85} - HEA coatings.

Coating	Elemental and phase composition				
WC-CoCr	WC = 86.0		Co = 10.0		Cr = 4.0
CrC-NiCr	NiCr= 25.0		Cr ₃ C ₂ = 75.0		-
CoCrFeNiMo _{0.85}	Co = 19.19	Cr = 16.94	Fe = 18.19	Ni = 19.12	Mo = 26.56

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Simulated geothermal drilling test environment

Table 2 shows the experimental conditions in the autoclave high temperature and pressure (HTHP) test, simulating drilling environment, with conditions used in Iceland. In geothermal drilling the cooling fluid (mud) used is commonly water based with high pH (9) to avoid corrosion. Icelandic tap water is used in drilling¹⁸ and thus, used to simulate drilling environment for the corrosion tests. The tap water has a pH around 9 at room temperature since it flows through basaltic rocks. The rectangular coupon samples were weighed before being placed in the vertical sample holder supports. The vessel was filled with 2 L of tap water. The water was alkaline, with a filling pH of 9 (see table 2), which is typical of Icelandic drinking water. The test samples were immersed in the liquid for the entire 14-day period of exposure. For safety reasons, the autoclave was then pressurized to a gauge pressure of 50 bar with nitrogen at 25 °C for one day to check for leakage. The rotational speed of the stirrer was set to 60 RPM. During the leakage test, the data logging system recorded the pressure and temperature readings. After the leakage test was successful, the autoclave vessel was pressurized to 33.6 bar gauge at 27.6°C with N₂ and heated to 120 °C at a rate of 25 °C/h, with a lower heating rate as the temperature approached 120 °C. Brooks® mass flow controllers control the filling rate of the gas components as they pass through the gas filling panel. Linde Gas® supplied the gas used in the experiment, which had a purity of 99.5%. After each experiment, the autoclave was slowly depressurized, and the remnant solution was discarded after cooling from the experimental temperature to room temperature at a rate of 25 °C/h. The reactor is then cleaned with deionized water, ethanol and/or acetone.

Electrochemical testing

The electrochemical test is designed to determine the corrosion kinetics of these coatings as well as the effect of Cl⁻ on the corrosion process. The temperature and pressure rise dramatically with salinity at increasing depth of geothermal wells. In the case of a geothermal reservoir, lithostatic pressure will reach the critical pressure of the fluid at a depth of 2.3 km or 3 km, assuming seawater salinity¹⁹.

For the electrochemical test, 2.5 cm of the coated disc surfaces were exposed to the electrolyte. Before testing, the samples were ultrasonically cleaned in ethanol. All tests were carried out at room temperature. The experiments were carried out in a 3.5 wt. % NaCl solution using a three-electrode electrochemical cell setup with saturated Ag/AgCl as a reference and a graphite rod as a counter electrode. The experiments and data logging were carried out using a Princeton Applied Research® Potentiostat (VersaSTAT 4) and versaSTUDIO® electrochemical software (version 2.54). In all cases, the open circuit potential (OCP) was measured and recorded for 1 hour. Polarization measurements were performed at a scan rate of 0.167 mVs⁻¹ at a potential ranging from -1000 mV to +1000 mV versus OCP. The reported electrochemical potentials in the study are against an Ag/AgCl electrode.

Table 2
Test conditions for WC-CoCr, CrC-NiCr and CoCrFeNiMo_{0.85} corrosion experiments

Test type	T (°C)	P (bar)	Electrolyte used	pH at 22.3 °C	Time (hours)
Autoclave	120	50	Tap water and N ₂	9.0	336
Potentiodynamic	25	1.01	3.5wt% NaCl	7,1	<24

RESULTS AND DISCUSSION

Microstructural and chemical composition analysis before corrosion testing

Similar to HVOF sprayed coatings²⁰, all three coatings in the study are characterized by a mechanical bond between the coating, a dense microstructure and a relatively smooth surface finish. When deposited under various oxygen and fuel flow rates, a small amount of oxygen was introduced into all three coatings (Table 3), where the highest was observed for HEA (3.6 wt%). This can be explained by the high reactivity

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