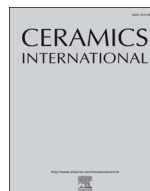




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High temperature corrosion resistant coatings for gas flare systems

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ABSTRACT

Gas flaring systems are used in processing plants to eliminate excess gases while serving as a safe pressure-relieving system. These systems are built using 310 stainless steel (SS310) thanks to its mechanical properties and performance under high temperature operating conditions. However, the findings have revealed that SS310 is susceptible to high temperature sulfidation when exposed to a corrosive environment. In the present work, SEM analysis has been conducted to investigate the causes of this type of failure. To tackle this problem, high velocity oxygen fuel (HVOF) thermal spraying was used to deposit a double-layer thermal barrier coatings, including a top yttria stabilized zirconia layer (TBC) and a bond coating CoNiCrAlY layer (BC) on SS310 substrates. The performance of the coatings was tested by exposing it to a high temperature corrosive environment. As a result, an improved resistance to corrosion was observed. This improved performance can be attributed to the absence of tetragonal to monoclinic phase change transformation, and to a decrease in the volume fraction of the monoclinic phase in yttria stabilized zirconia top coat, as indicated by XRD analysis.

1. Introduction

Oil producing companies generate a significant amount of waste gas mostly containing acidic gases such as CO₂ and H₂S. The presence of such gases at high temperatures causes severe damage to structural materials often resulting in loss of production and safety concerns. One example is the case of gas flaring systems, whose main purpose is pressure relief [1,2]. The flare tips are generally made from 310 stainless steel, which is an austenitic iron based alloy containing 19–22% nickel and 24–26% chromium [3,4]. Indeed, the presence of chromium provides the required corrosion protection through the formation of a protective chromium oxide layer, whereas the presence of nickel maintains the required strength and the mechanical properties at high temperature [5,6]. Despite these advantages, the extremely high temperatures and the presence of gaseous sulfides in the waste gas stream cause severe corrosion damage to flare tips. It was reported that the high percentage of nickel in 310 stainless steel increases its susceptibility to sulfidation attack, due to the high affinity between nickel and sulfur [7]. Consequently, this allows the formation of nickel sulfides, particularly Ni-Ni₃S₂, which melts at around 645 °C. This molten phase is a direct result of nickel depletion from the microstructure of 310 stainless steel. This leads to the loss of desired mechanical properties and the destruction of the chromium oxide protective layer [4,7]. A typical thermal barrier coatings consists of a thermally insulating ceramic top coating applied over an oxidation-resistant metallic bond coating. The 6–8 wt% yttria partially stabilized zirconia is used as a top

coating, due to its high temperature stability and low thermal conductivity [12,13]. The MCrAlY (M=Ni, and/or Co) bond coating provides high temperature corrosion protection and good thermal expansion between the ceramic top coat and steel substrate [8–11]. The purpose of adding yttrium to the coating is to increase the stability of zirconia at elevated temperature and adherence of the formed oxides to the coated substrate. The protection is achieved through the formation of aluminum oxide and inter-diffusion at the substrate/coating interface to the formation of depletion areas which increase with time and temperature [14,15]. Once the aluminum concentration on the surface reaches a critical minimum value, other oxides such as Cr₂O₃ will start to form under the aluminum oxide layer. The chromium oxide layer grows faster than aluminum oxide, which generates tensile stresses forming micro-cracks. The chromium oxide layer is usually imperfect and has some defects and cracks, and high temperature corrosion is expected to proceed and cause further damage to the coating [14,15]. Thermal barrier coatings are widely used by various industries, in applications such as gas-turbine engines for aircraft propulsion, and power generation due to its low thermal conductivity and high temperature stability. These thermal barrier coatings can be applied using several methods of spraying such as air plasma, high-velocity oxy-fuel (HVOF), low-pressure plasma and vacuum plasma. The use of HVOF method to deposit the thermal barrier coatings has attracted considerable attention due to the higher impact velocity of the inflight particles and the possibility to coat large surface areas. During the HVOF process, powder materials are melted and propelled at high-velocity towards the

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targeted surface producing low-porosity coatings, which have a high bond strength and fine as-sprayed surface finishes [16]. Additionally, it was reported that the coatings applied using HVOF process exhibited better oxidation resistance compared to other methods [17–19]. In the present work, the causes of cracks in the flare tip were investigated and discussed. The performance of a double-layer thermal barrier coatings deposit by HVOF process on 310 stainless steel was investigated under a high temperature corrosive environment.

2. Experimental

2.1. Materials and methods

The 310 stainless steel panels were obtained from the Metal Samples Company with dimensions 7.5×2.5 cm and chemical composition of C 0.25%, Cr 24–26%, Ni 19–22%, Mn 2%, Si 1.5%, P 0.45%, S 0.3%, Fe-Balance. A commercially available CoNiCrAlY powder (AMDRY 995 M, Sulzer Metco Inc. USA) with nominal composition of Ni-32, Cr-21, Al-8, Y-0.5, Co-balance (wt%) was used for spraying the bond coat of thermal barrier coatings. The ceramic powder used for top coat was ZrO_2 -8 wt% Y_2O_3 (Metco 204 NS) and was supplied by the same company. The substrate samples were first cleaned, blasted and immediately coated using the high-velocity oxy-fuel technique at ASWAN Company in the UAE. The bond coat thickness was ranging from 150 to 180 μm whereas the thickness of the top coat was 250 μm for all samples. To simulate the field operating conditions, the coated samples were exposed to 9.6% H_2S , 82% N_2 , 5% CO_2 and 3.6% of several different gases at 1020 $^\circ\text{C}$. The experiments were set up not to be continuous exposure tests. The heating cycles for all the samples started at room temperature and increased by 10 $^\circ\text{C}/\text{min}$ to reach 1020 $^\circ\text{C}$ then, the temperature was maintained constant for 12 h before cooling down to room temperature. Each sample was subjected to six cycles before visual inspection and Scanning Electron Microscopy (SEM) analysis was conducted. To further study the performance of the proposed thermal barrier coatings, one of the low-pressure flare tip with a diameter of 24 in. was coated and installed in an operating plant. The external coated area has a length of 2 m, while the length of the internal coated area was 1.5 m, with a bond coating thickness of 180 μm and 250 μm for the top coat. The area of the coating was determined based on the anticipated hot zone, which is where the flame was expected to reach and lick the metal during operation.

3. Results and discussion

To understand the main cause of failure in the 310 stainless steel, SEM study on structurally damaged uncoated sample from a failed low-pressure flare tip in the field was conducted. The sample was mechanically cut using a precision cutting saw and then cold mounted before it was grinded, polished and cleaned using deionized water and acetone to remove any contamination on the surface before the SEM was conducted. The Fig. 1 shows that the failed flare tip suffered from severe cracking and significant distortion after two years of operation. Additionally, it has suffered high-pressure spider-type attack at the grain boundaries as a result of exposure to a sour environment.

To analyze the failed flare tip substrate sample elemental composition, microanalysis was carried out on one of the attacked grain boundaries using line-scan technique as illustrated in Fig. 2. The line-scan microanalysis revealed the presence of alternating layers of iron sulfide and chromium sulfide. In addition, the absence of nickel indicates its depletion from the 310 stainless steel sample. It can be postulated that when the flare tip was exposed to hydrogen sulfide, oxygen in the atmosphere reacted with the surface of the steel forming chromium oxide, which is considered to be a protective layer. During the formation of this oxide, defects and cracks are usually developed due to the stresses that build up within the layer as a result of its fast growth. Consequently, these cracks act as short circuit paths for the

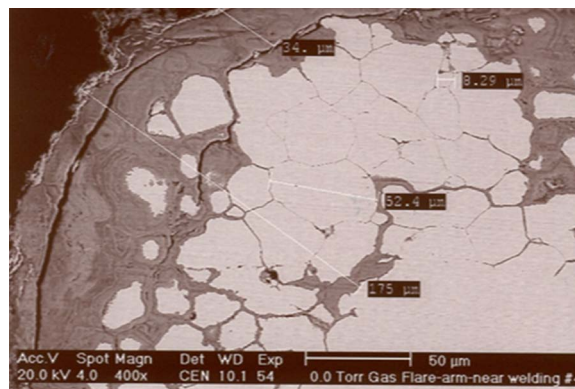


Fig. 1. SEM image of sample taken from a cracked area of the failed flare tip.

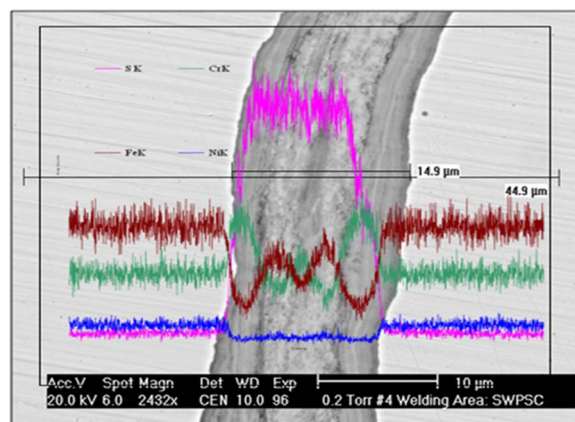


Fig. 2. EDS microanalysis conducted on grain boundaries of the sample shown in Fig. 1.

sulfur to diffuse inward and reach the metal surface. Due to the depletion of chromium from surface, the formation of iron sulfide will be thermodynamically favorable and, therefore, a layer of iron sulfide will form at the chromium oxide/metal interface. At high temperature, iron sulfide is not protective and further diffusion of sulfur is expected. The progress of sulfur diffusion and the depletion of chromium and iron make the formation of nickel sulfide more thermodynamically favorable. At this stage, nickel-nickel sulfide phase forms within the steel. This phase usually melts at 645 $^\circ\text{C}$, which is below the operating temperature of the flare tip. This leads to significant depletion of nickel from the stainless steel. As the nickel is consumed, sulfur reacts with chromium to form chromium sulfide, which is thermodynamically stable at this stage. Gradually, the chromium will be consumed and the formation of iron sulfide will be dominant resulting in the loss of steel high temperature strength that is provided by the nickel present in the 310 stainless steel composition. Simultaneously, the grain boundaries of the steel are attacked by the sulfidation processes [17–23]. With this combination of changes along with the high temperatures, the stainless steel underwent significant degradation, which was observed in the case of the failed flare tip. The uncoated flare tip 310 stainless steel substrate failure mechanism is illustrated in Fig. 3.

After understanding the failure mechanism of the 310 stainless steel, the application of a double-layer thermal barrier coatings was adopted. Experimental samples were prepared and exposed to 1020 $^\circ\text{C}$ for six thermal cycles in the lab to simulate the real environment in the field. The surface morphologies of uncoated sample, coated sample only with BC, and coated sample with BC + TBC are illustrated in Fig. 4.

In Fig. 5, SEM micrograph of the uncoated SS310 sample exposed to a thermally corrosive atmosphere showed the formation of a cracked chromium rich oxide layer, instead of a well-adhered protective layer on the surface of the metal. As a result and due to the formation of the

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