



# Effects of water vapor on high temperature oxidation of cryomilled NiCoCrAlY coatings in air and low-SO<sub>2</sub> environments

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## ABSTRACT

Nanostructured NiCoCrAlY coatings were obtained through cryomilling and subsequent HVOF-spraying of the nanostructured powder onto copper substrates, followed by leaching of the Cu to obtain freestanding coatings. Oxidation tests in both air and an environment bearing 0.5% SO<sub>2</sub> with water vapor levels varying from 0 to 8% were conducted for 24 and 48 h at 1000 °C. It has been found that the oxides formed under all conditions are alumina followed by a spinel phase consisting primarily of cobalt aluminum oxide. In both air and the SO<sub>2</sub> environment an increase in total mass gain was seen up to 4% water vapor, followed by a decrease at 6 and 8%. This behavior is attributed to an extension of the transient oxidation stage, resulting first in a variation in scale thickness through increased spinel growth and second in a rise in internal oxidation caused by increased oxygen transport through the scale in the presence of water vapor. It would appear that above 4% water vapor the thickened spinel is able to compensate for alumina loss and create a diffusion barrier to internal oxidation, once again reducing mass gain.

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## 1. Introduction

The petrochemical industry can be a maintenance-intensive business due to various extreme conditions presented by the extraction and refining processes [1]. Corrosion in particular can be detrimental to many areas of the refinery and corrosion control can often account for 60% to 70% of a plant maintenance budget [2]. Sulfur is evolved from the refining process and is present in effluent gases as H<sub>2</sub>S, H<sub>2</sub>SO<sub>4</sub> and notably SO<sub>2</sub>. Combined with the high temperatures and presence of water vapor in boilers and other components, a significant maintenance issue arises. Current methods for dealing with corrosion include constant monitoring of equipment and use of corrosion resistant bulk materials or coatings [2].

One such coating that has been garnering interest is the MCrAlY system, NiCoCrAlY in particular. MCrAlY coating is typically used as the bond coat in a thermal barrier coating system because of their ability to grow oxide scales resulting in good thermal matchup between other coating layers [3]. These same oxide scales also produce substantial high temperature corrosion resistance [4]. Consequently NiCoCrAlY has been proposed as a stand-alone coating for certain hot-spot or high-corrosion/oxidation applications including key areas in oil refinery boilers.

NiCoCrAlY and MCrAlY's generally form a 2-phase structure of  $\gamma$ , a solid solution of Ni, Co and Cr, and  $\beta$  (NiAl), an aluminum-rich phase that feeds the oxide layer [5]. Depending on concentration, there is the possibility of a third  $\gamma'$  phase, coherent precipitates of Ni<sub>3</sub>Al that improve mechanical properties, although these precipitates are known to dissolve in the range of 800 to 950 °C [6,7]. Upon exposure to an oxidative environment at high temperature these alloys form an Al<sub>2</sub>O<sub>3</sub> scale, seeded by the  $\beta$  phase, followed by a mixed oxide layer that can contain Cr<sub>2</sub>O<sub>3</sub>, CoAl<sub>2</sub>O<sub>4</sub>, NiAl<sub>2</sub>O<sub>4</sub>, NiO and any number of other mixed oxides depending on the initial composition and microstructure of the MCrAlY. The formation of a dense, single-layer alumina scale is desirable for all applications.

Research to date has been primarily focused on oxidation behavior of NiCoCrAlY, however there have been only a small number of studies in environments bearing water vapor or sulfur. Leyens et al. studied the effect of a range of H<sub>2</sub>/H<sub>2</sub>O atmospheres on the oxidation of an electron-beam physical vapor deposited NiCoCrAlY coating heat treated at 1100 °C and found that the presence of water vapor led to an increase of up to 25% in total mass gain over 28 h of oxidation at 1080 and 1100 °C [8]. Similar results were found by Zhou et al. in the testing of a NiCrAlY coating deposited by low pressure plasma spray; in this case 50% greater mass gain at 100 h and 100% greater mass gain at 400 h were found with 5% water vapor as opposed to dry air at 1050 °C [9]. A review by Saunders et al. of oxidation in atmospheres containing water vapor found that across a number of studies MCrAlY's sometimes show an increase in oxidation rate due to the presence of water vapor, but in some cases did not form alumina at all. In general it was found that the effect of water vapor was more

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pronounced in the initial stages of oxidation as water vapor has a greater effect on the stability of transient alumina phases as opposed to the diffusion processes in an established, protective alumina layer [10]. Most recently, Subanovic et al. studied the effects of H<sub>2</sub>/H<sub>2</sub>O vapor systems on NiCoCrAlY, which resulted in the formation of large blisters and internal oxidation of the coating [11]. Finally Godlewska et. al. have studied the effect of NiCoCrAlY exposure to various H<sub>2</sub>/H<sub>2</sub>S pressures at high temperature [12]. In this case the coating evolved a sulfide scale rather than an oxide scale but otherwise followed similar, although faster, growth kinetics. To date no studies have been performed in gaseous SO<sub>2</sub>-bearing environments or on combined oxidation and sulfidation of MCrAlY's.

Nanostructuring is thought to have a significant effect on the oxidation of MCrAlY's. Generally speaking, nanostructured coatings are thought to produce a more consistent and better-adhered alumina layer than their conventional counterparts [13,14]. This is due to increased grain boundary area allowing for greater Al diffusion [13] to the scale and the formation of small amounts of aluminum oxide within the cryomilled powder and subsequent coating [15]. These oxides give nucleating points for a denser alumina scale. Mercier et. al. have found that nanostructuring speeds up the transition from  $\theta$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and results in a denser, slow-growing  $\alpha$ -alumina layer that serves as a diffusion barrier to the formation of the second spinel layer [16]. This effect can however be negated by surface oxides formed in the thermal spray process used if samples are not surface-treated prior to oxidation.

The purpose of this study is to investigate the behavior of nanostructured NiCoCrAlY coatings in an environment containing O<sub>2</sub>, SO<sub>2</sub> and water vapor. The environment chosen is representative of an oil refinery boiler, which typically operates at temperatures around 800 °C, with localized hot spots as high as 1000 °C [2]. Samples of high-velocity oxy-fuel sprayed (HVOF), nanostructured NiCoCrAlY were selected as HVOF is a relatively easy, low-cost deposition method that is known to preserve nanostructure from feedstock to coating [17].

## 2. Experimental procedures

The NiCoCrAlY coatings were produced from commercially available gas atomized –325 mesh Amdry 9951 powder from Sulzer Metco. Initial powder composition can be found in Table 1.

Nanostructure was obtained through cryomilling for 16 h in a Union Process 1-S attrition mill at 180 rpm. The ball to powder ratio was 30:1. Liquid nitrogen levels were maintained through continuous addition to the vessel and 0.2% stearic acid was added to the powder to prevent the particles from coating the steel balls and the vessel. The nanostructured powder was then deposited onto a copper substrate via HVOF, resulting in a coating 470  $\mu$ m thick, on average. Freestanding coatings were obtained by leaching away the copper substrate in nitric acid. Transmission electron microscopy of the same samples conducted previously shows that nanostructure was indeed preserved with an average grain size of 10.5  $\pm$  5.5 nm, for the as-sprayed coating [18].

A first cycle of oxidation testing was conducted in a controlled environment custom-built tube furnace mated to a Cahn D-100 balance for thermogravimetric analysis (TGA), shielded with helium. Samples were placed on an alumina plate suspended from the balance into the furnace, the system was closed and heated to 1000 °C at 4.2 °C/min in argon. Once at temperature and stable, the Ar was replaced with

flowing air for 48 h followed by another Ar purge and cooling. Prior to entering the furnace, the air was bubbled through water at varying temperatures to pick up 0, 4 or 8% water vapor. Calculation of parabolic rate constants ( $k_p$ ) was performed using the method described by Pierraggi [19].

A second cycle of static oxidation tests were conducted in a similar custom-built tube furnace without TGA. Samples were placed in the tube on an alumina refractory sample holder then closed and heated to 1000 °C at 8 °C/min in air. Once the desired temperature was reached air or a mixture containing 0.5% SO<sub>2</sub> described in Table 2 was introduced. In this case a wider range of water vapor levels was used: 0, 2, 4, 6 or 8%. TGA tests indicated that under all conditions stable oxidation following a parabolic rate law was established within 6 h. Consequently, tests of 24-hour durations were run; in each case the system was purged with air on completion of the test and furnace-cooled.

Mass of samples for the oxidation tests was measured before and after testing using a Sartorius BP 110S Scale. X-ray diffraction (XRD) patterns were obtained with a Philips PW1070 X-Ray Diffractometer with a scan angle ranging from 30 to 80 (2 $\theta$ ), step size of 0.005 (2 $\theta$ ) and dwell time of 0.5 s. Phase identification was completed using X'Pert HighScore software. Scanning electron microscope (SEM) observations and energy-dispersive spectroscopy (EDS) were carried out on a Philips XL-30 FE-SEM with EDAX EDS.

A thermodynamic study of the system was also conducted using FactSage thermochemical software. In oxidation of alumina-forming alloys, the oxygen partial pressure can vary through the thermally grown oxide layers. At the metal interface, the oxygen partial pressure is low and the system is considered to be in metallic saturation. A gradient of oxygen partial pressure exists across the oxide layer, and the gas interface can be considered in relative oxygen saturation. Calculations using the FACT53, FTOxid and SGTE databases were conducted to determine the oxide layers present at equilibrium in the SO<sub>2</sub>-bearing environment with 4% water vapor. The thermodynamic calculations do not account for the kinetic effects of diffusion and also assume the entire metallic substrate reacted to form oxide.

## 3. Results

Fig. 1 shows the calculated oxidation behavior of the NiCoCrAlY coating at 1000 °C. Thermodynamic modeling indicates that on a substrate consisting of FCC  $\gamma$ -phase and BCC NiAl intermetallic  $\beta$ -phase the initial layer formed is an Al<sub>2</sub>O<sub>3</sub> corundum phase evolving into an (Al,Cr)<sub>2</sub>O<sub>3</sub> corundum phase at increase oxygen partial pressure. Depletion of aluminum in the substrate from corundum formation results in a second spinel-phase layer comprised primarily of NiAl<sub>2</sub>O<sub>4</sub>, CoAl<sub>2</sub>O<sub>4</sub> and other similar oxides. FactSage also indicates the thermodynamic possibility of forming a third NiO or CoO layer, upon depletion of all other constituents, but this does not take into account the diffusion limiting effect of the previous oxide layers formed. Consequently this third layer has not been seen in many studies. It is important to note that from a thermodynamic standpoint the presence of 0.5% SO<sub>2</sub> do not have any substantial effect on the type of oxides that form.

XRD patterns for samples oxidized in Air and the 0.5% SO<sub>2</sub> environment at both 0 and 8% water vapor are presented in Fig. 2. The tallest peaks correspond with the  $\gamma$ -phase (JCPDS #001-1258) and in all cases the surface oxides formed are alumina (JCPDS #011-0661)

**Table 1**  
Chemical composition of the NiCoCrAlY powder.

Alloy composition (mass%)				
Ni	Co	Cr	Al	Y
46.5	23	17	13	0.5

**Table 2**  
Composition of the SO<sub>2</sub>-bearing environment.

Gas composition (mass%)			
N <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	SO <sub>2</sub>
82.5	12	5	0.5

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