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Modes of deposit-induced accelerated attack of MCrAlY systems at 1100 °C

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Abstract The reaction of cast NiCoCrAlY alloys with oxide-sulfate deposits in $\text{CO}_2\text{-H}_2\text{O-O}_2$ was studied at 1100 °C. The minimum Al concentration needed to form an external Al_2O_3 scale was increased compared with deposit-free exposures, as Al_2O_3 -forming compositions transitioned to internal Al_2O_3 and external Cr_2O_3 growth in the presence of certain deposits. Model deposits were used to investigate the role of each constituent in the complex reaction morphology observed with an industrial fly-ash. Two main modes of degradation were identified, which involved Al_2O_3 dissolution in molten Na silicate and solid-state Al_2O_3 reaction with CaO. Both led to enhanced Al consumption and promoted non-selective oxidation. Additions of Al_2O_3 or SiO_2 decreased the CaO reactivity due to the formation of aluminates or silicates, while Na_2SO_4 , on the contrary, enhanced the degradation by providing rapid mass transport in the molten state, and reduced alloy/scale adherence. A systematic study of the role of phase fractions and phase compositions in the $\gamma\text{-(Ni,Co)} + \beta\text{-(Ni,Co)Al}$ metal system is reported, with the aim of providing guidance in coating design. In particular, high γ fractions and Cr concentrations, which offer optimal hot corrosion resistance, were most susceptible to degradation by oxide-sulfate deposits.

Keywords MCrAlY coatings; Selective oxidation, Fly-ash; Silicate deposits

1 Introduction

Deposit-induced degradation concerns a variety of high-temperature processes, e.g., in aircraft, marine and land-based turbines, and in industrial boilers in general. Particulate matter ingested by an aircraft turbine via its air intake is generally described as calcium-magnesium alumino-silicate or CMAS. In marine engines, chlorides (e.g., NaCl, KCl) can combine with SO_x from the environment or produced by combustion of the kerosene to form sulfates (e.g., Na_2SO_4 , K_2SO_4). In waste or biomass incinerators, sulfur levels are usually low and alkali metals condense as chlorides. Integrated gasification combined cycle (IGCC) plants currently under development are designed to convert coal or a combination of coal and biomass into syngas, which then fuels a combustion turbine to generate electricity [1–3]. In addition to harsh gas environments (CO_2 , H_2O , SO_2), IGCC system turbine components are exposed to deposits of fly-ash which primarily contains SiO_2 , Al_2O_3 , CaO, MgO and Fe_2O_3 [4], but also K_2SO_4 and Na_2SO_4 as indicated above and FeS from the sulfidation of steel

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Figure 1: Schematic view of the temperature range and type of deposit relevant to the present work, in comparison with two typical modes of degradation, CMAS and hot corrosion.

components upstream [5]. The main source of particulate matter is the ambient air ingested by the turbine [6].

Particulate matter compositions vary widely depending on the fuel used and on the turbine location. Bituminous and anthracite coal, for example, tend to produce fly-ash rich in SiO_2 and Al_2O_3 , while fly-ash from subbituminous and lignite coals contain higher levels of CaO [7]. In addition, the nature of a deposit depends on the local temperature and gas composition. At high temperatures and low sulfur activities for example, alkali metals will tend to be present as silicates, while at lower temperatures and higher p_{SO_3} , alkaline earth metals such as Ca or Mg might form sulfates rather than silicates.

Metal coatings applied to impart corrosion resistance to Ni-based structural components in gas turbines include nickel aluminides $\beta\text{-NiAl}$ and MCrAlY ($\text{M}=\text{Ni, Co}$ or both), based on the B2 compound $\beta\text{-(Ni,Co)Al}$ and the fcc-Al solid solution $\gamma\text{-(Ni,Co)}$ [8,9]. Thermal barrier coatings (TBCs) are used on the hottest components, and include an yttria-stabilized zirconia (YSZ) ceramic topcoat for thermal insulation [10–14]. Since their inception, research on deposit-induced degradation of TBC systems has mostly focused on two aspects, CMAS and hot corrosion. At very high temperatures ($> 1200\text{ °C}$), CMAS deposits melt and infiltrate the YSZ, causing thermo-chemical and thermo-mechanical damage [4, 15–18]. Accelerated corrosion of the bondcoat may occur if the YSZ topcoat is removed or otherwise allows access to condensed species. Ni- and Co-base materials are particularly susceptible to hot corrosion, a potentially severe form of attack at relatively low temperatures ($700\text{--}900\text{ °C}$), where molten sulfates dissolve the thermally grown oxides and prevent the establishment of a protective scale [19–24].

Laboratory CMAS studies do not generally include alkali metal sulfates, because these rapidly volatilize at temperatures where the CMAS is molten ($> 1200\text{ °C}$). On the other hand, hot corrosion studies mostly do not consider oxides or silicates, because these do not melt at temperatures relevant to metal components ($700\text{--}900\text{ °C}$). However, depending on the operating conditions, deposits may contain both oxides and sulfates, and continuously increasing service temperatures imply that bondcoats will be exposed to these mixed deposits in an intermediate temperature range ($900\text{--}1100\text{ °C}$), where both solid and liquid phases may be of concern (Fig. 1).

This paper presents part of a broader study of deposit-induced accelerated corrosion of MCrAlY coatings in conditions relevant to IGCC systems. Ref. [25] addressed the reaction with pure CaO deposits at 1100 °C. The present paper aims at examining the modes of attack relevant to more complex and realistic oxide-sulfate deposits. In order to study the effect of coating microstructure in a wide composition range, a series of alloys were prepared to provide systematic variations of phase fractions and phase compositions. Cast versions were used in place of coatings. The effects of gas composition and temperature, as well as mechanistic aspects of the accelerated attack, are addressed in companion papers [26, 27].

2 Materials and experiments

Three series of cast NiCoCrAlY alloys were used in this study. Nominal compositions are given in Table 1. First, a β -rich composition typical of bondcoats in plasma-sprayed TBCs was made with two Y levels, 0.3 and 0.1 at. % (all alloy compositions are given in at. %). Alloys UT3 to UT8 all have 30 Co and systematic variations of Al and Cr (12/16 Al, 27/30/33 Cr). A third series of alloys was designed to obtain independent variations of phase fractions and phase compositions in the γ - β field at 1100 °C. Alloy UT11 has a high β fraction, $f_\beta = 63$ vol. %, and a relatively low Cr concentration, 10 at. %. Alloy UT14 was designed to have the same f_β as UT4, but with the same phase compositions as UT11, that is, on the same tie-line. In the same way, UT15 was designed to have the same f_β as UT11, on the tie-line defined by UT4. Finally, UT12 and UT16 are the γ and β end-members of the tie-line defined by UT4, while UT13 and UT17 are the conjugate γ and β compositions for an equilibrated UT11. As shown in Fig. 2, this procedure provided two sets, each with four alloys on a particular tie-line, extending from single-phase γ to single-phase β . The alloys also form four sets of two alloys, each with a constant phase fraction but different phase compositions. All phase equilibrium calculations were done for $T = 1100$ °C, using the NIST database [28] in Thermo-Calc [29]. The later use of CRALDAD, a more recent database specifically developed for the Al–Co–Cr–Ni system [30, 31], showed that the alloys were in fact slightly off the tie-lines; nevertheless, the principle of independently varying phase fractions and phase compositions is still qualitatively valid. For clarity of reading, the alloys will be referred to using their β fraction (vol. %) and Cr concentration (at. %). For example, UT3 Ni–30Co–27Cr–12Al–0.1Y is abbreviated 13 β –27Cr.

Ingots were made by argon-arc melting, followed by drop casting into 10 mm diameter rods, which were then homogenized in vacuum for 6 h at 1200 °C plus another 48 h at 1150 °C. All processing was conducted at the Materials Preparation Center of the Ames Laboratory [32]. Specimens approximately 1 mm thick were cut from the heat-treated rods, ground using SiC paper to a P1200-grit finish, then degreased with detergent and ultrasonically cleaned in ethanol before exposure.

Microstructural characterization after further annealing at 1100 °C followed by air cooling confirmed the γ - β phase constitution. Some alloys also precipitated σ -CoCr: 1, 2 and 22 vol. % in 18 β –33Cr, 40 β –30Cr and 42 β –33Cr, respectively, as measured by image analysis. A thorough characterization of phase equilibria in the Al–Co–Cr–Ni system can be found in Ref. [30]. The alloys contained a small amount of yttrium-rich intermetallics (~ 0.1 vol. %), the value being slightly smaller

Table 1: Nominal composition of NiCoCrAlY alloys used in the present study (at. %). A number of alloys prepared by MPC at Ames Laboratory [32] were sent for ICP–OES analysis to Evans Analytical Group [33]. Measured concentrations were found to be within 0.5 at. % of nominal concentrations for Ni, Co, Cr, Al, and within 0.05 at. % for Y. Volume fractions of β , f_β , were measured by image analysis after annealing at 1100 °C for alloys UT2 to UT7, and calculated using the NIST database [28] for alloys UT11 to UT17 (see explanations in text).

#	Ref.	Elemental concentration (at. %)					f_β at 1100 °C (vol. %)
		Ni	Co	Cr	Al	Y	
UT1		42	19	15	24	0.3	
UT2	57 β –15Cr	42	19	15	24	0.1	57
UT3	13 β –27Cr	31	30	27	12	0.1	13
UT4	16 β –30Cr	28	30	30	12	0.1	16
UT5	18 β –33Cr	25	30	33	12	0.1	18
UT6	34 β –27Cr	27	30	27	16	0.1	34
UT7	40 β –30Cr	24	30	30	16	0.1	40
UT8	42 β –33Cr	21	30	33	16	0.1	42
UT11	63 β –10Cr	47	19	10	24	0.1	63
UT12	0 β –35Cr	25	33	35	7	0.1	0
UT13	0 β –19Cr	42	28	19	11	0.1	0
UT14	17 β –16Cr	44	26	16	14	0.1	17
UT15	63 β –18Cr	36	21	18	25	0.1	63
UT16	100 β –8Cr	43	15	8	34	0.1	100
UT17	100 β –5Cr	49	14	5	32	0.1	100

for γ -rich compositions.

Isothermal corrosion experiments were conducted at 1100 °C in flowing CO₂–20H₂O and CO₂–20H₂O–1.6O₂ (vol. %) mixtures, using a horizontal tube furnace. Gas flow rates were set to 100 ml/min, with a linear velocity of 2 mm/s at reaction temperature, and a total pressure slightly over 1 atm. To obtain a wet gas, CO₂ or CO₂–O₂ was bubbled through demineralised water set at 62 °C, thereby producing a mixture with slightly more than the desired 0.2 atm H₂O. The excess water vapor was subsequently condensed by cooling the wet gas in a distillation column at 60 °C. Prior to a given experiment, the furnace was stabilized at 1100 °C with the specimens positioned in a cold zone of the reaction tube, and the gas allowed to flow for 2 h. To start the experiment, the specimens were magnetically pushed into the hot zone.

Specimens were exposed to class C fly-ash deposit procured from a conventional coal-fired power plant (composition and source details in Table 2), as well as model deposits. The latter were prepared by grinding laboratory grade reagents using a mortar and pestle, and were given no heat treatment prior to corrosion testing. The powders were mixed with ethanol, and the resulting slurry was applied to one face of a given specimen using a dropper. The procedure was adjusted to produce approximately uniform 30 ± 5 mg/cm² deposits after evaporation of the ethanol.

Figure 2: Alloy compositions (atom fractions) projected on an isothermal ($T = 1100\text{ }^{\circ}\text{C}$), isoplethal ($x_{\text{Co}} = 0.3$) section of the Al–Co–Cr–Ni phase diagram calculated using the NIST database [28]. Alloys UT4 and UT11 to UT17 are along two tie-lines (see explanations in text). The projections of these tie-lines on the plane of constant $x_{\text{Co}} = 0.3$ are indicated by dashed lines.

Table 2: Composition of the fly-ash used in the present study, as reported on the supplier’s certification report (wt. %). The ash originated from the Scherer, GA coal-fired power plant and was purchased from Boral (San Antonio, TX). It is classified class C according to ASTM C618 and AASHTO M295 standards.

SiO ₂	25.3
Al ₂ O ₃	19.2
Fe ₂ O ₃	5.8
CaO	32.0
MgO	7.7
SO ₃	3.2
Na ₂ O	2.2
K ₂ O	0.4

The phase constitution of the model mixtures was also studied by annealing in alumina crucibles with no alloy specimen.

After exposure, reaction products were examined by X-ray diffraction (XRD) using a Bruker D8 instrument with Cu radiation ($K_{\alpha 1} = 1.54\text{ }\text{\AA}$) and Panalytical HighScore Plus processing software. Metallographic cross-sections were first prepared using water-free cutting fluids and polishing suspensions to retain any water-soluble products such as Na₂SO₄. Preliminary observations showed the sulfate rapidly reacted or evaporated, and subsequent metallographic preparation was done with water-base products. Specimens were characterized by SEM with a JEOL JSM 6510, and in selected cases by electron probe micro-analysis (EPMA) using a JEOL JXA 8530F. Measured intensities were processed via a built-in ZAF calibration procedure using pure metals as standards.

3 Results

3.1 Oxidation with no deposit

All alloys (Table 1) were exposed to CO_2 – $20\text{H}_2\text{O}$ – 1.6O_2 with no deposit for 50 h and found to form external Al_2O_3 scales. Small amounts of Cr, Co or Ni oxide were present in the outermost part of the scales, depending on alloy composition. The alloy with lowest Al concentration, 0β –35Cr, was a borderline Al_2O_3 -former, in that it occasionally formed internal Al_2O_3 (and external Cr_2O_3) on the specimen edges.

3.2 Exposure to class C fly-ash

Alloys 57β –15Cr, 13β –27Cr, 16β –30Cr, 18β –33Cr, 34β –27Cr, 40β –30Cr and 42β –33Cr were exposed 50 h to the fly-ash in CO_2 – $20\text{H}_2\text{O}$. As a general observation, β -rich alloys were immune to the ash, growing external Al_2O_3 as they did in the absence of a deposit, while γ -rich alloys were susceptible to a localized type of degradation (Fig. 3). In the latter case the reaction morphology was complex and non-uniform. The attack varied in extent but was of a similar nature for the different alloys. In some regions, the alloys formed an external Al_2O_3 layer covered by oxides of variable composition, ranging from that of the applied ash (with little Cr, Co or Ni) to Cr_2O_3 . Other regions showed a more significant metal loss, as the corrosion product included an inner part of mixed Al-rich, Cr-rich and (Co,Ni)-rich oxides. Even then, a continuous Al_2O_3 layer was almost always present at the base of the scale (Fig. 3c). Photo-stimulated luminescence spectroscopy, which allows Al_2O_3 polymorphs to be distinguished [34], showed this oxide to be α - Al_2O_3 . In these regions, the outer part of the corrosion product was a mixed, but mostly Cr-rich, oxide. The concentration of alloy elements in the outer part showed local variations, and generally decreased with increasing distance from the specimen surface.

Given the varied nature of the corrosion products, no attempt was made at quantifying the metal loss. Qualitatively, the severity of the attack decreased with increasing Al concentration, and therefore β fraction, in the alloy; higher Cr appeared to make the attack more severe, but this was less marked.

The effect of Y concentration was tested using two versions of alloy 57β –15Cr, with 0.3 and 0.1 at. % Y. In the absence of a deposit, both versions formed Y–Al–O precipitates within the Al_2O_3 scale and intruding into the alloy. These were more numerous, larger and deeper in the 0.3 Y version. With the ash, while the 0.1 Y version formed external Al_2O_3 (Fig. 3a), the 0.3 Y version was susceptible to localized attack. As shown in Fig. 4, large Y–Al–O intrusions were found to disrupt the Al_2O_3 scale and to act as initiation sites for reaction of the alloy with the ash. This appeared to be short-lived, however, as a continuous Al_2O_3 layer was usually present at the base of the intrusions. In one specimen, zones of severe degradation ($> 15\text{ }\mu\text{m}$ deep metal loss) were observed, but corrosion tests conducted for several durations showed these to be isolated events.

3.3 Exposure to model deposits

In order to investigate the role of the deposit constituents in the corrosion process, further testing was conducted using model deposits. Fig. 5 shows γ -rich alloys after exposure to a model mixture with the same composition as the fly-ash used

Figure 3: Corrosion products observed after 50 h exposure to fly-ash (composition in Table 2) in $\text{CO}_2\text{-}20\text{H}_2\text{O}$ at 1100 °C. Alloys (a) 57 β -15Cr; (b) 40 β -30Cr; (c) 16 β -30Cr. The extent of degradation increases with decreasing alloy β fraction.

Figure 4: Alloy 57 β -15Cr with 0.3 at. % Y after 50 h exposure to fly-ash (Table 2) in $\text{CO}_2\text{-}20\text{H}_2\text{O}$ at 1100 °C. Where a large Y-Al-O intrusion was present, a mixed corrosion product formed which contained elements from both the ash and the alloy.

Figure 5: Local variations in corrosion product morphology observed on γ -rich alloys exposed to a model deposit with the same composition as the fly-ash (Table 2), 50 h at 1100 °C. The zone above the secondary Al_2O_3 layer is either (a) fully oxidized (alloy 16 β –30Cr in CO_2 –20 H_2O) or (b) contains a mixture of Al-rich oxide and Al-free metal (alloy 13 β –27Cr in CO_2 –20 H_2O). These two morphologies are occasionally observed side to side on a given specimen, as shown in (c) (alloy 16 β –30Cr in dry air).

Table 3: Composition of the model deposits used in this study (wt. %).

Ref.	SiO_2	Al_2O_3	CaO	Na_2SO_4
Al_2O_3 – CaO		60	40	
SiO_2 – CaO	60		40	
CaO – Na_2SO_4			90	10
Al_2O_3 – Na_2SO_4		90		10
SiO_2 – Na_2SO_4	90			10
Al_2O_3 – CaO – Na_2SO_4		50	40	10
SiO_2 – CaO – Na_2SO_4	50		40	10
SiO_2 – Al_2O_3 – CaO – Na_2SO_4	25	25	40	10

previously (Table 2). The reaction morphology was also non-uniform. In some regions (Fig. 5a), it was identical to that observed with the fly-ash. In other regions (Fig. 5b), the inner part consisted of a mixture of Al-rich oxide and Al-free metal. As discussed later, these are stages of the same process: the fully-oxidized type is simply a more advanced state of the internally-oxidized type. The two morphologies were occasionally observed side-by-side on a given specimen, as shown in Fig. 5c. The similarity in results obtained with the fly-ash and the model deposit validates the use of the latter to study the relevant reaction mechanisms.

A first screening of alloy-oxide interactions was done by reacting a γ -rich alloy, 18 β –33Cr, and a β -rich alloy, 57 β –15Cr, 50 h in dry air with the following individual oxide deposits: SiO_2 , Al_2O_3 , Fe_2O_3 , CaO and MgO . When contacted with SiO_2 , Al_2O_3 and Fe_2O_3 , both alloys formed an Al_2O_3 scale, not significantly different from those grown in the absence of a deposit. Reaction with CaO and MgO produced Ca and Mg aluminates in addition to Al_2O_3 ; with CaO , the γ -rich alloy also formed a liquid Ca chromate before passivating [25]. Based on these results, model deposits were designed as combinations of three types of constituents: Al_2O_3 or SiO_2 as a relatively acidic oxide; CaO as a basic oxide; Na_2SO_4 as an alkali metal sulfate. Corrosion tests using the deposit compositions given in Table 3 were conducted for 50 h in CO_2 –20 H_2O –1.6 O_2 on selected γ -rich alloys. The following focuses on alloys 13 β –27Cr and 0 β –35Cr.

Figure 6: Corrosion products observed on alloy 13 β -27Cr after 50 h reaction in CO₂-20H₂O-1.6O₂ at 1100 °C with (a) Al₂O₃-40CaO; (b) Al₂O₃-40CaO-10Na₂SO₄. Mixed compound notation: C: CaO; A: Al₂O₃; S̄: SO₃.

Figure 7: Corrosion products observed on alloy 13 β -27Cr after 50 h reaction in CO₂-20H₂O-1.6O₂ at 1100 °C with CaO-10Na₂SO₄. Mixed compound notation: C: CaO; A: Al₂O₃; Cr: Cr₂O₃.

3.4 13 β -27Cr (Ni-30Co-27Cr-12Al-0.1Y)

Upon reaction with an Al₂O₃-CaO deposit, alloy 13 β -27Cr formed a scale of Ca aluminates (denoted C_xA_y) and Al₂O₃ (Fig. 6a). Little Ca chromate (denoted CCr) was observed. The deposit consisted of C_xA_y and some untransformed Al₂O₃ and CaO. Adding Na₂SO₄ to Al₂O₃-CaO resulted in a thicker C_xA_y scale, with more transient oxides at its surface, i.e., (Ni,Co)O, CoCr₂O₄, and calcium sulfo-aluminate C₄A₃S̄ as shown in Fig. 6b. The scale had poor adherence to the alloy. Exposure to CaO-Na₂SO₄ produced similar results, but the chromate was formed in greater quantity, and while an external C_xA_y-Al₂O₃ scale developed in some regions, in others C_xA_y was embedded in CCr and Al oxidized internally (Fig. 7). The scale was mostly detached from the alloy. Exposure to Al₂O₃-Na₂SO₄ produced external Al₂O₃, also with poor adherence.

Reaction with SiO₂-CaO produced a C_xA_y-Al₂O₃ scale, with some CCr, mixed Co-Ni-Cr oxide, and Ca aluminosilicate (Fig. 8). Calcium silicates also formed in the deposit. In contrast to Na₂O-Al₂O₃, the Na₂O-SiO₂ system has a large liquid region at 1100 °C [35], and indeed, when mixed with SiO₂, Na₂SO₄ reacted to form

Figure 8: Corrosion products observed on alloy 13 β –27Cr after 50 h reaction in CO₂–20H₂O–1.6O₂ at 1100 °C with SiO₂–40CaO. Mixed compound notation: C: CaO; A: Al₂O₃; S: SiO₂.

a molten Na silicate (denoted NS) on the specimen. The solubility of Al₂O₃ in this liquid is large [35], and indeed large amounts of Al (~ 10 at. %) were found by SEM–EDS in the silicate near the specimen surface. The alloy mainly formed an external Al₂O₃ scale; in some locations, however, Al₂O₃ intrusions and external Cr₂O₃ were observed instead, as shown in Fig. 9a. Chromium was then found in the silicate, but mostly in the form of precipitated Cr₂O₃ — the concentration of dissolved Cr was about 0.5–1 at. %. The Al₂O₃ intrusions depth and Cr₂O₃ layer thickness were variable but generally limited to a few μm .

With the SiO₂–CaO–Na₂SO₄ mixture, the bulk of the deposit consisted of SiO₂ and CaSiO₃, while liquid Na₂O–CaO–SiO₂ formed in contact with the specimen. The molten silicate also dissolved significant Al₂O₃. The alloy locally underwent internal oxidation (Fig. 9b). Some variability was observed in the morphology of these regions, as the reaction product above the internal Al₂O₃ consisted of either C_xA_y layers, typical of reaction with CaO, or of Cr₂O₃ embedded in Na₂O–CaO–Al₂O₃–SiO₂, similar to what was observed with SiO₂–Na₂SO₄.

Finally, reaction with a SiO₂–Al₂O₃–CaO–Na₂SO₄ deposit resulted in almost uniform internal Al₂O₃ with external Cr₂O₃ (Fig. 9c). A continuous Al₂O₃ layer was found at the internal oxidation front. The deposit in contact with the specimen surface consisted of mixed alumino-silicate of varying composition. This reaction morphology resembled that observed with the fly-ash, shown in Fig. 5b.

3.5 0 β –35Cr (Ni–33Co–35Cr–7Al–0.1Y)

Reaction of alloy 0 β –35Cr with all tested deposits resulted in internal oxidation of Al, albeit with differences depending on deposit composition. Exposure to Al₂O₃–CaO led to uniform, relatively deep internal oxidation of Al and thick external Cr₂O₃ (Fig. 10a). A continuous Al₂O₃ layer was present at the reaction front. Adding Na₂SO₄ to Al₂O₃–CaO led to a similar reaction morphology, although the depth of internal oxidation was locally reduced, and in some regions an external Al₂O₃ scale was present (Fig. 10b). Mixed Ca–Cr aluminate and CCr formed near the specimen surface.

Figure 9: Corrosion products observed on alloy 13 β -27Cr after 50 h reaction in CO₂–20H₂O–1.6O₂ at 1100 °C with (a) SiO₂–10Na₂SO₄; (b) SiO₂–40CaO–10Na₂SO₄; (c) SiO₂–25Al₂O₃–40CaO–10Na₂SO₄. Mixed compound notation: C: CaO; A: Al₂O₃; N: Na₂O; S: SiO₂.

Exposure to SiO₂–CaO resulted in a reaction morphology similar to that observed with Al₂O₃–CaO, with the main difference being that the external scale was made of mixed Ca–Cr silicates; it contained Cr₂O₃ too, but not as a continuous layer. Furthermore, no Al₂O₃ layer formed at the internal oxidation front.

The SiO₂–Na₂SO₄ deposit produced a molten silicate, which again dissolved large amounts of Al₂O₃. A thick Cr₂O₃ layer was present above most of the internal Al₂O₃ (left panel of Fig. 10d), but in some locations there appeared to be no external scale, and instead Cr₂O₃ was found dispersed in the silicate (right panel of Fig. 10d). An external Al₂O₃ scale was present locally.

With the SiO₂–CaO–Na₂SO₄ mixture, a relatively thick scale formed, which contained various phases such as Ca–Cr silicate, C_xA_y, Ca–Cr sulfo-aluminate, Cr₂O₃ or CoCr₂O₄. Underneath, internal oxidation was relatively shallow and locally an external Al₂O₃ layer was present (Fig. 10e).

Finally, exposure to SiO₂–Al₂O₃–CaO–Na₂SO₄ resulted in both regions of external Al₂O₃ scaling and regions of internal oxidation (Fig. 10f). In the latter case, the affected depth was variable, as was the morphology of the reaction front, which locally featured a continuous Al₂O₃ layer. The corrosion product also contained an external, more or less continuous scale of mixed alumino-silicate, Cr-rich silicate and Cr₂O₃.

Figure 10: Corrosion products observed on alloy 0β-35Cr after 50 h reaction in $\text{CO}_2\text{-}20\text{H}_2\text{O-}1.6\text{O}_2$ at 1100 °C with (a) $\text{Al}_2\text{O}_3\text{-}40\text{CaO}$; (b) $\text{Al}_2\text{O}_3\text{-}40\text{CaO-}10\text{Na}_2\text{SO}_4$; (c) $\text{SiO}_2\text{-}40\text{CaO}$; (d) $\text{SiO}_2\text{-}10\text{Na}_2\text{SO}_4$; (e) $\text{SiO}_2\text{-}40\text{CaO-}10\text{Na}_2\text{SO}_4$; (f) $\text{SiO}_2\text{-}25\text{Al}_2\text{O}_3\text{-}40\text{CaO-}10\text{Na}_2\text{SO}_4$. Mixed compound notation: C: CaO; A: Al_2O_3 ; Cr: Cr_2O_3 ; N: Na_2O ; S: SiO_2 .

Figure 11: Corrosion products observed on alloy 0 β –19Cr after 50 h reaction in CO₂–20H₂O–1.6O₂ at 1100 °C with (a) SiO₂–10Na₂SO₄; (b) SiO₂–40CaO–10Na₂SO₄. Mixed compound notation: C: CaO; A: Al₂O₃; Cr: Cr₂O₃; N: Na₂O; S: SiO₂; $\bar{S}$: SO₃.

3.6 Additional exposures to model deposits

In order to better understand the effects of alloy phase fraction and phase composition on deposit-induced corrosion, alloys 0 β –19Cr, 0 β –35Cr, 17 β –16Cr, 16 β –30Cr, 63 β –10Cr, 63 β –18Cr, 100 β –5Cr and 100 β –8Cr were exposed to the SiO₂–Al₂O₃–CaO–Na₂SO₄ mixture and to the fly-ash (Table 2). With both deposits, only the alloys 16 β –30Cr (similar to 13 β –27Cr studied above) and 0 β –35Cr (see above) alloys experienced internal oxidation, while all others formed external Al₂O₃. Thus the β -rich compositions were immune, and in the γ -rich region, only alloys with high Cr levels were susceptible to degradation.

The same eight alloys were exposed to pure CaO. The β -rich alloys (63 β and 100 β) only formed C_xA_y–Al₂O₃ scales, while the γ -rich alloys (0 β and 16 β) also produced molten CCr. As could be expected, the quantity of CCr increased with increasing Cr and decreasing Al concentration in the alloy.

The alloy sensitivity to molten NS was studied using alloy 0 β –19Cr. Exposure to SiO₂–Na₂SO₄ resulted in external Al₂O₃ formation (Fig. 11a). As observed for alloys 13 β –27Cr and 0 β –35Cr, large amounts of Al were dissolved in the silicate; yet this did not lead to Al₂O₃ breakdown, despite the alloy having a lower Al concentration than 13 β –27Cr. Alloy 0 β –19Cr was also exposed to SiO₂–CaO–Na₂SO₄, which involved reaction with both CaO and NS. The alloy produced a thick C_xA_y scale with Cr₂O₃ and (Co,Ni)O embedded, and a continuous Al₂O₃ layer at the base (Fig. 11b). Internal oxidation of Al occurred in a few isolated cases, but mostly the alloy passivated.

The deposits used so far had relatively large concentrations of CaO (40 wt. %) or Na₂SO₄ (10 wt. %). While these levels are relevant to some industrial deposits, e.g., class C fly-ash, they are large relative to other applications such as

aero engines, where the CMAS tend to be much richer in SiO_2 . An additional series of experiments was conducted using alloy 13 β –27Cr and deposits covering a broader range of compositions. Briefly, these included mixtures based on SiO_2 –25 Al_2O_3 –10CaO–10 Fe_2O_3 –5MgO, with or without 5 wt. % K_2SO_4 , or with CaO concentrations varying up to 46 wt. %, the other constituents being kept in constant proportions. Also tested was a mixture with the same composition as the fly-ash used previously, but with no sulfate. None of these deposits led to significant degradation of the alloy: variable amounts of Cr-rich oxide formed, but always above an external Al_2O_3 scale, no internal oxidation occurred.

4 Discussion

The present results show that NiCoCrAlY alloys that are intrinsically Al_2O_3 -formers (i.e., when free of a deposit) are at risk of switching to internal Al_2O_3 and external Cr_2O_3 formation when exposed to certain types of oxide-sulfate deposits at 1100 °C. The attack is localized, and its severity depends on both deposit and alloy composition.

The processes underlying this deposit-induced attack can ultimately be understood in terms of primary reaction modes involving CaO, SiO_2 and Na_2SO_4 . The reaction of CaO with Cr to form a liquid chromate rapidly consumes the Cr-rich γ phase, while its reaction with Al_2O_3 to form Ca aluminates results in enhanced Al depletion [25]. On the other hand, SiO_2 and Na_2SO_4 form a molten silicate with high Al solubility. The dissolution of thermally grown Al_2O_3 in this phase has the same effect as C_xA_y formation: reducing the Al_2O_3 thickness causes an increased oxidation rate, and a greater Al flux is required to sustain external scaling, which the alloy may fail to accommodate. Variations of these primary modes are observed in multi-component deposits due to interactions between constituents. In particular, SiO_2 and Na_2SO_4 affect CCr and C_xA_y formation, in different ways. These interactions are schematically summarized in Fig. 12, which maps the nature and potential severity of γ -rich alloy degradation as a function of deposit composition. The influence of each constituent will be discussed in subsequent sections.

Regarding the metal system, alloys with both high Cr and high γ fractions were most affected by the deposits. This is related to the nature of the processes identified above: the reaction of thermally grown Al_2O_3 with either CaO or NS affects the Al mass balance, and is therefore most detrimental to γ -rich alloys, which have a smaller Al reservoir. Similarly, CCr formation is a concern for these alloys both because it preferentially consumes the Cr-rich γ -phase, and because it does so as long as no continuous Al_2O_3 layer is established, which again depends on the Al content. The importance of the attack can be conveniently described in terms of a shift in the minimum Al concentration required to form an external Al_2O_3 scale. This is done in Fig. 13, which was inspired by the oxide map developed by Giggins and Pettit for the oxidation of NiCrAl alloys [36]. As indicated in this figure, an expanded internal/external Al_2O_3 transition region exists in the presence of the oxide-sulfate deposit. In addition, a slight increase in the Y concentration, from 0.1 to 0.3 at. %, triggered localized attack of the 57 β –15Cr alloy exposed to the fly-ash. This was due to the increased number and size of Y–Al–O precipitates, which served as initiation sites for accelerated reaction (Fig. 4). Local Al_2O_3 scale disruption due

Figure 12: Schematic map of primary reaction modes involved in the deposit-induced attack of Cr-rich, γ -rich NiCoCrAlY alloys at 1100 °C. The map represents the alloy-deposit reaction products (aluminates, aluminosilicates, and chromates) in a composition space defined by three deposit constituents: SiO_2 , CaO , and Na_2SO_4 . Deposit compositions causing internal oxidation are represented by hatching.

to highly reactive Y-rich oxide particles was previously reported for MCrAlY alloys exposed to Na_2SO_4 in type II hot corrosion conditions [37].

The reaction mechanism associated with multi-component deposits is best described from the morphologies developed after varying durations. This is discussed in detail in Ref. [26], in which results obtained for exposure times ranging from 20 min to 250 h are reported. As an example, Fig. 14 shows alloy 13 β –27Cr after 1 h exposure to the model deposit with the same composition as the fly-ash (Table 2). An external Al_2O_3 scale is seen to have formed initially, and failed locally. The scale is still present but lost its protective character, as oxides of Cr, Ni and Co are found above it in quantities larger than had formed initially. Alumina intrusions are seen to grow from the scale into the alloy. Due to the localized nature of the attack, several evolutionary stages are visible on the same micrograph: the intrusions develop into the internal oxidation morphology typical of longer exposures, with Cr_2O_3 growing as an external layer and the internal oxide particles coalescing into a continuous Al_2O_3 layer at the reaction front. This morphology reflects a steady-state and was not seen to evolve further, at least up to 250 h in isothermal conditions, although in some cases the Al-free metal between the internal Al_2O_3 also oxidized (Fig. 5). Excepting the latter aspect, the morphology is quite similar to that developed by certain wrought austenitic Ni-base alloys classified as “marginal Al_2O_3 -formers”. In general, these alloys grow external Al_2O_3 at low temperatures and internal Al_2O_3 plus external Cr_2O_3 at higher temperatures. Recently published studies of alloy 602 CA [39, 40], for example, illustrate these similarities. Although the present NiCoCrAlY alloys had higher Al and Cr concentrations, the resemblance with 602 CA reflects the effect of the deposits on the oxide map (Fig. 13).

The link between primary reaction modes identified using unary or binary de-

Figure 13: Map showing the effect of sulfate-oxide deposits on the oxidation of NiCoCrAlY alloys at 1100 °C. The boundaries were determined from work by Giggins and Pettit [36] and our work [38] on NiCrAl alloys. “NiO” denotes alloy compositions which form external NiO and internal Al_2O_3 and Cr_2O_3 ; “ Cr_2O_3 ” denotes compositions which form external Cr_2O_3 and internal Al_2O_3 ; “ Al_2O_3 ” denotes compositions which form external Al_2O_3 exclusively; “transition” denotes compositions subject to localized internal oxidation of Al. The alloy map is superimposed on an isothermal section of the NiCoCrAl system with a constant 30 at. % Co, generated with the CRALDAD database [30].

Figure 14: Corrosion product formed on alloy 13β-27Cr exposed 1 h to a model deposit with the same composition as the fly-ash (Table 2) in CO_2 -20 H_2O at 1100 °C.

posits and the corrosion process associated with higher-order deposits is deduced from the composition of the latter. Specifically, in the case of the 13 β –27Cr alloy: (i) the lowest order mixture causing internal oxidation was the ternary SiO₂–CaO–Na₂SO₄; (ii) in higher order deposits, only those with both a high CaO concentration and some Na₂SO₄ caused internal oxidation; (iii) in those cases, the corrosion products were similar in nature and morphology to those observed with SiO₂–CaO–Na₂SO₄. It follows that for this particular alloy composition, the co-occurrence of reaction modes involving CaO and NS was necessary to induce Al₂O₃ failure. This was not the case for alloy 0 β –35Cr, which is closer to the threshold for external Al₂O₃ formation and where each reaction mode separately caused internal oxidation. Another consequence is that corrosion by multi-component deposits can be analyzed in terms of the interactions between thermally grown Al₂O₃ and deposit constituents, and the consequences thereof on the Al mass balance and Al₂O₃ stability.

4.1 Thermodynamic considerations

At 1100 °C, the p_{SO_3} corresponding to CaO/CaSO₄ equilibrium is calculated using data compiled by Barin [41] to be 9×10^{-7} atm, so that CaO should be stable under the current testing conditions. Analysis by XRD of powders reacted in CO₂–H₂O–O₂ confirmed that CaO was indeed the predominant species. Sodium sulfate, in comparison, is much more stable relative to Na₂O, as the p_{SO_3} for Na₂O/Na₂SO₄ equilibrium is 2×10^{-14} atm, a figure smaller than the impurity level in the reaction gas — no Na₂O was detected in the reacted samples. However, in the presence of oxides such as SiO₂, the relative stability of Na₂SO₄ is reduced: for example, the p_{SO_3} associated with the equilibrium

is 5×10^{-6} atm, which is significant, and indeed Na₂SO₄ reacted to form Na₂SiO₃. Incomplete thermodynamic data do not allow accurate calculation at 1100 °C, but extrapolation from lower temperatures yields an even higher p_{SO_3} value if Na₂Si₃O₇, which is closer to measured silicate compositions, is considered instead of Na₂SiO₃. Thus, either a significant p_{SO_3} or a very low SiO₂ activity would be needed to prevent the formation of the liquid silicate.

In conditions where Na is present as a sulfate, the question of its interaction with the other deposit constituents is of interest. With CaO being a very basic oxide, its reaction with Na₂SO₄ involves CaSO₄. As noted above, the latter is not stable at unit activity in a low p_{SO_3} gas. However, CaO may dissolve in liquid Na₂SO₄: the equilibrium CaSO₄ fraction in the Na₂SO₄–CaSO₄ solution, which is wide at 1100 °C [42], depends on the environmental SO₃ level. Alumina is amphoteric, and is expected to form NaAlO₂ in a basic environment [43]. The p_{SO_3} associated with the equilibrium

is 8×10^{-9} atm, which is small and suggests that NaAlO₂ would not exist at unit activity in the present conditions. The Na₂O–NaAlO₂ system contains a liquid aluminate, but the eutectic temperature (1132 °C at 5 mol. % Al₂O₃ [35]) is slightly higher than the present reaction temperature. Results on hot corrosion of Al₂O₃ at 1000 °C [44] also indicate that the aluminate solubility in molten Na₂SO₄ is low,

Figure 15: Analysis of $x\text{CaO} + y\text{Al}_2\text{O}_3 = \text{C}_x\text{A}_y$ reaction kinetics during annealing of $\text{Al}_2\text{O}_3\text{--}40\text{CaO}$ and $\text{Al}_2\text{O}_3\text{--}40\text{CaO}\text{--}10\text{Na}_2\text{SO}_4$ powder mixtures in air at 1100 °C. (a) Example of XRD pattern ($\text{Al}_2\text{O}_3\text{--}40\text{CaO}$, 8.5 h); (b) extent of completion calculated by adding the mole fractions of all C_xA_y compounds, determined from XRD patterns.

although it can be increased by the simultaneous dissolution of SiO_2 . Indeed, alloy 13 β –27Cr was exposed to pure Na_2SO_4 in dry air, and formed a stable Al_2O_3 scale — no hot corrosion was observed.

4.2 Role of Na_2SO_4 in the reaction process

Despite the absence of an Na_2SO_4 -induced hot-corrosion process, the addition of Na_2SO_4 to $\text{Al}_2\text{O}_3\text{--CaO}$ did increase the reactivity of CaO, in that it resulted in a thicker C_xA_y scale on alloy 13 β –27Cr (Fig. 6). In order to examine the role of Na_2SO_4 , $\text{Al}_2\text{O}_3\text{--CaO}$ and $\text{Al}_2\text{O}_3\text{--CaO--Na}_2\text{SO}_4$ powder mixtures were annealed at 1100 °C in Al_2O_3 crucibles, with no metal specimen, and the evolution of phase constitution was studied by XRD. Fig. 15a shows a typical diffraction pattern, where reactants (CaO , Al_2O_3) and products (C_xA_y) are identified. Semi-quantitative analysis of patterns recorded after several reaction times using a built-in tool in the XRD processing software provided an estimation of the powder compositions. The mole fractions of all C_xA_y compounds were added to determine an accumulated extent of completion for the $x\text{CaO} + y\text{Al}_2\text{O}_3 = \text{C}_x\text{A}_y$ reactions. This extent is also defined as $1 - x_{\text{Al}_2\text{O}_3} - x_{\text{CaO}} - x_{\text{Na}_2\text{SO}_4}$, where x_i is the mole fraction of phase i . Extents of completion are plotted as a function of reaction time for both powder mixtures in Fig. 15b. The plots indicate that adding Na_2SO_4 significantly accelerated the reaction of CaO with Al_2O_3 to form C_xA_y phases. As a further study, Al_2O_3 and CaO powders were mixed in a large excess of Na_2SO_4 and annealed 20 h at 1100 °C. The molten sulfate was found by SEM–EDS to contain no measurable Al but on average 1 at. % Ca, i.e., about 8 mol. % CaSO_4 in Na_2SO_4 . Based on this observation, it is concluded that the molten sulfate mediated the conversion of CaO and Al_2O_3 to C_xA_y by facilitating Ca transport. This occurs even though pure CaSO_4 is not stable relative to CaO; rather, CaSO_4 exists at activity less than one as a solute in Na_2SO_4 .

Exposure of alloy 13 β –27Cr to $\text{CaO--Na}_2\text{SO}_4$ locally led to internal oxidation (Fig. 7), which was not observed with CaO alone. Exactly how Na_2SO_4 triggered internal oxidation is not clear at this stage, since the activity of pure CaO cannot be

increased, but this result further exemplifies the detrimental effect molten Na_2SO_4 can have on CaO-induced attack. Remarkably, in the case of alloy 0 β –35Cr, while exposure to Al_2O_3 –CaO or SiO_2 –CaO led to uniform internal oxidation, the addition of Na_2SO_4 to either deposit tended to reduce the internal oxidation depth, to the point where Al_2O_3 was locally present as an external scale (compare Figs. 10a–b, and Figs. 10c–e). How Na_2SO_4 favored passivation in this case requires further study.

The presence of Na_2SO_4 also led to the establishment of a locally elevated S activity at the metal surface, as shown by the occasional presence of internal Y sulfides (for example in Fig. 11b). This had important implications in the early-stage reaction, which are presented in a companion publication [26]. In the presence of an excess of SiO_2 , Na_2SO_4 effects can only be short-lived, since Na_2SO_4 is eventually consumed to form Na silicate. With SiO_2 -free deposits, however, Na_2SO_4 additions lead to enhanced Al_2O_3 spallation (Figs. 6 and 7) due to the presence of sulfur, which is known to reduce scale adherence [45–47].

4.3 Effects of Al_2O_3 and SiO_2

The addition of Al_2O_3 or SiO_2 to CaO reduced the quantity of CCr formed on alloy 13 β –27Cr prior to the establishment of external C_xA_y – Al_2O_3 . This mitigating effect was greater yet in the case of alloy 0 β –35Cr, as CCr consumed over 150 μm of metal during reaction with CaO [25], but was not observed here with Al_2O_3 –CaO or SiO_2 –CaO. This can be associated with a reduced reactivity of CaO toward the alloy, due to the formation of Ca aluminate or silicate in the deposit.

However, Al_2O_3 and SiO_2 do not have equivalent effects. For instance, on alloy 0 β –35Cr exposed to Al_2O_3 –CaO, an external Cr_2O_3 layer was formed above the internal oxidation zone, and the alloy eventually repassivated (Fig. 10a). With SiO_2 –CaO, both Cr_2O_3 and Ca–Cr silicates formed, but not as a continuous layer (Fig. 10c). In this case the alloy did not repassivate, and internal oxidation penetrated deeper. It is concluded that, when present as a continuous layer, Cr_2O_3 lowered the p_{O_2} at the metal surface, which resulted in a reduced inward O flux, and favored the establishment of a new Al_2O_3 layer, as opposed to continued internal oxidation. In the presence of SiO_2 , the formation of a Ca–Cr silicate, likely uvarovite $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ [48], prevented the establishment of a continuous Cr_2O_3 layer, and therefore repassivation. A pseudo-ternary compound exists in the CaO– Al_2O_3 – Cr_2O_3 system (chromate aluminate sodalite $\text{Ca}_8[\text{Al}_{12}\text{O}_{24}](\text{CrO}_4)_2$ [49, 50], but was not observed to form here.

5 Conclusions

Applying sulfate-oxide deposits to Al_2O_3 -forming NiCoCrAlY alloys led to enhanced degradation due to the presence of CaO, SiO_2 and Na_2SO_4 . The Cr-rich γ -phase initially reacted with CaO to form a molten Ca chromate, Ca aluminates and Ni and Co oxides. Once an external Al_2O_3 scale was established, it either reacted with CaO to form Ca aluminates, or dissolved in molten Na silicate. In both cases, this increased Al consumption, promoting Al_2O_3 failure for γ -rich alloys. These primary reaction modes were affected by the deposit compositions: SiO_2 and Al_2O_3 were found to reduce the reactivity of CaO, due to the formation of Ca aluminates

and silicates in the deposit. Sodium sulfate, on the other hand, provided faster Ca transport and enhanced its reactivity toward the alloys. It also produced a locally high sulfur activity at the metal/oxide interface, and reduced scale adherence.

In service conditions, alkali metals may be present either as sulfates or as silicates, depending on the gas and deposit compositions. The present study shows that they can play an important role in the corrosion process either way, and even in successive ways. Indeed, changes in service conditions may lead to the deposition of Na_2SO_4 , for instance, and its subsequent reaction with SiO_2 to form a silicate, as was the case here.

Within the range of compositions studied, only deposits rich in CaO or those containing Na_2SO_4 and SiO_2 proved potentially aggressive, and they mostly affected γ -rich, Cr-rich alloys. Both aspects are due to the nature of the primary reaction modes. In an alloy with relatively low Al and high Cr, each reaction mode individually triggered internal oxidation, while with more Al and less Cr, the reaction with CaO and the dissolution in Na silicate each consumed Al_2O_3 , but its stability as an external scale was only compromised when the two modes were concurrent. Essentially, the deposits raised the minimum Al concentration required to maintain an external Al_2O_3 scale, to an extent increasing with increasing Cr level.

The present results indicate that with most deposits of realistic compositions, any Al_2O_3 -forming alloy which would suffer internal oxidation is expected to repassivate eventually, in isothermal conditions. However, given the low adherence of the scales formed with the deposits and the enhanced Al depletion, thermal cycling would certainly have severe consequences, in particular if more deposit is applied periodically.

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