Reaction morphologies developed by nickel aluminides in type II hot corrosion conditions: the effect of chromium

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Abstract

The short-term reaction of Ni-36Al (at. %) and Ni-36Al-5Cr alloys with Na₂SO₄ in O₂-0.1 % SO₂ at 700 °C was studied by SEM and TEM. Local failure of the protective scale on NiAl led to nodule development via internal oxidation. Conversely, NiAlCr underwent a uniform attack involving internal sulfidation, porous scale growth, and NiO and Al₂O₃ dissolution into the sulfate. The roles of gas and sulfate compositions were studied by comparing exposures to Na₂SO₄, Na₂SO₄-MgSO₄ and Na₂SO₄-Cr₂O₃ deposits in air and O₂-0.1 % SO₂. The effect of Cr in preventing passivation during early-stage exposure was associated with a coupled dissolution of NiO and Cr₂O₃.

Keywords: A. molten salts; A. nickel; C. hot corrosion; C. selective oxidation; C. sulphidation

1 Introduction

Accelerated attack of high temperature alloys by molten sulfate deposits, generally referred to as hot corrosion, has long been recognized as an important concern in the operation of gas turbines for aircraft and marine propulsion systems [1,2]. Mechanistic aspects of the hot corrosion process, as well as alloy and coating compositional factors and mitigation strategies, have been reviewed multiple times, e.g. in Refs. [3-7], so that the subject is only briefly discussed here. Two temperature regimes are distinguished based on the melting point (T_m) of the deposited sulfate, typically Na₂SO₄ (T_m = 884 °C): type I at temperatures above T_m , and type II below T_m . In type II conditions, a minimum amount of SO₃ is required in the gas to stabilize a liquid sulfate [8]. No hot corrosion is expected below the eutectic temperature (e.g., T_e (Na₂SO₄-NiSO₄) = 671 °C, T_e (Na₂SO₄-CoSO₄) = 565 °C). Conversely, sulfates evaporate rapidly at elevated temperatures, such that dry corrosion (e.g. oxidation) prevails above about 1050 °C.

Hot corrosion essentially occurs as oxides, which would otherwise form a compact scale on an alloy surface, dissolve into the molten salt. In this regard, diagrams indicating which metal species will be most stable in given conditions of sulfate composition and temperature have proved useful in discussing reaction mechanisms. Following Goebel and Pettit [9], p_{SO_3} and p_{O_2} were used as coordinates to plot two-dimensional Na-M-O-S (M=Al, Ni and Cr) stability diagrams at 700 °C in Figure 1. The construction of such diagrams has

been discussed in detail by Li et al. [14]. Taking the example of Al, the basic and acidic reactions of Al_2O_3 with Na_2SO_4 are written

and

respectively, and represented by vertical lines ($p_{\text{SO}_3} = \text{constant}$) in Figure 1a, where the activity of all compounds is taken as unity. These p_{SO_3} values define whether a sulfate is considered acidic or basic, relative to a given metal oxide. The activities of SO_3 and Na_2O are related through the sulfate dissociation equilibrium

Metal cations and oxyanions have some solubility in solid and liquid Na_2SO_4 , and in the case of Al the basic and acidic dissolution reactions may be written

and

respectively (solutes are underlined). A relation between the activity of oxide ions and p_{SO_3} is obtained by considering the equilibrium

which is equivalent to Eq. (3).

The Ni and Co systems were studied in detail by Luthra and Shores [8] and Misra et al. [15]. As the concentration of metal sulfate in solid Na_2SO_4 reaches the solidus composition, and inasmuch as its activity is less than unity, a liquid is formed at a lower p_{SO_3} than that required to stabilize the pure metal sulfate. This behavior is particularly important in type II conditions and is illustrated for Ni in Figure 1b. In this figure, the dotted vertical line represents the p_{SO_3} at equilibrium between NiO (s), $\text{Na}_2\text{SO}_4\text{-NiSO}_4$ (s) and $\text{Na}_2\text{SO}_4\text{-NiSO}_4$ (l) estimated by Misra et al. [15] using a regular solution model for the liquid. The equilibrium p_{SO_3} in a $\text{O}_2\text{-0.1 \% SO}_2$ gas mixture at 700°C is not high enough to stabilize pure NiSO_4 (s), but will allow a liquid $\text{Na}_2\text{SO}_4\text{-NiSO}_4$ solution to form when NiO is contacted with Na_2SO_4 .

Another essential aspect is that dissolution or fluxing of an oxide, whether predominantly acidic or basic, will occur to some extent at any SO_3 level, with the solute activities being determined by the ambient p_{SO_3} . Solubility plots for various metal cations and oxyanions in molten Na_2SO_4 as a function of p_{SO_3} at 927°C were published by Rapp and coworkers [4]. Since the kinetics of dissolution processes are limited by ionic transport in the melt [16], activity gradients develop in the melt during hot corrosion of an alloy. In conditions where a negative solubility gradient [17] is established, the scale formed by oxidation of an alloy will dissolve at the oxide/melt interface and re-precipitate as a non-protective oxide within the melt.

Type I hot corrosion of Ni-base alloys proceeds according to two main modes of attack, as documented by Goebel et al. [2]. Adopting the terminology of Birks et al. [6], these are (i) basic fluxing, where the consumption of O and S at the oxide/melt interface due to oxidation and sulfidation leads to a local increase in the melt basicity, to a level where basic dissolution is significant; and (ii) alloy-induced acidic fluxing, where the dissolution of refractory metal oxides such as MoO_3 or WO_3 gives rise to locally acidic conditions, which destabilizes protective oxides such as NiO or Al_2O_3 .

More recently, the continuous increase of turbine service temperatures has led to type II hot corrosion of previously immune parts such as disks. The associated reaction mechanism, gas-phase induced acidic fluxing, is much less understood than type I mechanisms. Luthra [18,19] proposed a model for Co and Co-base alloys, but it is not directly applicable to Ni-base alloys. The work on Ni has mostly concerned gas atmospheres with SO₂-SO₃ contents much higher than would be found in a gas turbine. Lillerud and Kofstad [20] used an O₂-4 % SO₂ composition at different pressures at 700 °C, where Ni₃S₂ formed within the NiO scale, and rapid Ni diffusion in the sulfide caused high reaction rates, much like in gaseous oxidation-sulfidation processes [21]. A recent study [22] dealt with the reaction of Ni with and without Na₂SO₄ in O₂-0.1 % SO₂ at 700 °C, where NiSO₄ (s) is not stable but a liquid Na₂SO₄-NiSO₄ solution is formed. Little is known about the effect of alloying elements in these conditions. Recent work on Ni-base alloys at 700 °C concerned commercial materials, and focused on scale growth mechanisms [23], or on statistical lifetime models [24,25]; yet current mechanistic understanding remains limited.

Universally present in heat-resisting Ni-base materials, Cr has long been acknowledged as very beneficial to type I hot corrosion resistance, particularly when a high content is present in MCrAlY alloys [5]. A recent study [26] suggested that Cr may also be effective when added to β -NiAl in type II conditions. The present paper is aimed at further elucidating the role of Cr in the reaction mechanism of nickel aluminides in an oxygen-rich, O₂-0.1 % SO₂ gas mixture at 700 °C, with a focus on the early-stage reaction morphologies. We will demonstrate that:

1. Cr-free NiAl is not prone to hot corrosion at least initially, but is instead subject to localized internal oxidation aside protective Al₂O₃ scaling;
2. Cr-containing NiAl, by contrast, is unable to passivate and immediately undergoes uniform hot corrosion;
3. the effect of Cr in facilitating oxide dissolution in Na₂SO₄ prevails over its ability to promote Al₂O₃ scale establishment, as is observed in the absence of Na₂SO₄;
4. the gas p_{SO_3} is critical to the mode of attack, regardless of whether the applied deposit is initially solid or liquid; in basic conditions, applying a liquid deposit is necessary for the attack to occur, whereas in acidic conditions, where low-melting solutions can eventually form, applying a liquid deposit simply accelerates the attack without changing the mechanism.

2 Materials and experimental procedures

Model alloys of nominal compositions Ni-36Al and Ni-36Al-5Cr (at. %), referred to hereafter as NiAl and NiAlCr, were prepared at the Materials Preparation Center of Ames Laboratory [27] by Ar arc melting, followed by drop casting into 10 mm diameter rods, and then homogenizing for 6 h at 1200 °C and 48 h at 1150 °C in vacuum. Specimens approximately 1 mm thick were cut and ground to a P1200-grit finish using SiC paper, then degreased with detergent and ultrasonically cleaned in ethanol before exposure.

Isothermal corrosion experiments were conducted at 700 °C in a horizontal tube furnace, in flowing dry air and O₂-0.1 % SO₂ (referred to hereafter as O₂-0.1SO₂), with and without deposits. Gas flow rates were 30 ml min⁻¹, with a total pressure slightly over 1 atm.

The O₂-SO₂ mixture was passed through a platinized honeycomb catalyst located directly upstream of the specimens in the hot zone, allowing the otherwise sluggish reaction

to proceed, with an equilibrium p_{SO_3} calculated to be 7.1×10^{-4} atm at 700 °C from data in Ref. [10]. Deposits were prepared by mixing laboratory grade reagents in deionized water, and then applying the solution on the specimens using a dropper. Evaporation by heating the specimens on a hot plate produced approximately uniform 2.8 ± 0.5 mg cm⁻² deposits. In some instances deposits were applied by spraying the aqueous solution on preheated specimens. The deposition method was verified to have no significant effect on the corrosion behavior. The alloys were exposed to pure Na₂SO₄ and a Na₂SO₄-48 mol % MgSO₄ mixture, the latter of which is fully liquid at 700 °C [28].

Since hot corrosion processes are particularly prone to variability, experiments were run in duplicates or triplicates to ensure reproducibility of the results. After exposure, deposits were washed off from some specimens for surface SEM observations, FIB milling and TEM work. On other specimens, polished sections were prepared using water-free cutting fluid and polishing suspensions to retain any water-soluble products. In some cases, thin foils containing the metal, oxide and retained salt were prepared by FIB milling and observed by TEM.

Alloy phase constitutions before and after reaction were studied by XRD using a Panalytical Empyrean instrument, with Co radiation ($K_{\alpha 1}=1.789$ Å). Oxidized surfaces were examined by photo-stimulated luminescence spectroscopy (PSLS), which allows γ , θ and α polymorphs of Al₂O₃ to be distinguished [29], using a 633 nm HeNe laser in a Renishaw inVia Raman microscope. Reaction products were studied by SEM with a JEOL JSM 6510 instrument, equipped with an Oxford X-Max SDD EDS detector and INCA analysis software. Thin foils were prepared by FIB milling with a FEI Nova NanoLab 200 instrument, and TEM work was conducted on a Zeiss Libra 200FE instrument operated at 200 kV, equipped with HAADF and Si-Li EDS detectors.

3 Results

3.1 Phase constitution of the alloys and their oxidation products

Phase constitutions determined by XRD (Figure 2) and SEM before and after 20 h oxidation in dry air at 700 °C are given in Table 1, together with literature data. Slow cooling from the high annealing temperature (1150 °C), where the alloys fall within the single-phase β -NiAl region, produced L1₀ martensite and intergranular γ' -Ni₃Al in the NiAl alloy in the as-received condition. Oxidation to form Al₂O₃ scales caused Al depletion and γ' formation in the alloy subsurface for both compositions. During the 700 °C heat treatment, intergranular γ' precipitated in NiAlCr, but the grains retained their β structure. In contrast, the martensite present in NiAl decomposed into a very fine microstructure of Ni₅Al₃ and γ' precipitates in a β matrix, shown in Figure 3.

Due to the low oxide growth rate at the reaction temperature of 700 °C, the structure of the Al₂O₃ scales could not be determined with satisfactory reliability on the basis of the

XRD patterns recorded using grazing incidence: no α - Al_2O_3 reflections were clearly detected, while some small peaks compatible with θ - Al_2O_3 or γ - Al_2O_3 were found. Similarly, analysis of the oxidized sample surfaces by PSLS yielded no α - Al_2O_3 peaks, only faint θ - Al_2O_3 peaks and a broad low-intensity peak compatible with γ - Al_2O_3 . Given that α luminescence is intrinsically 10-12 times more intense than that of θ [29], and on the basis of both the PSLS and XRD results, it is concluded that the oxide scales grown on both alloys in air at 700 °C were mostly transition aluminas, γ or θ . This is consistent with earlier reports of γ - Al_2O_3 formation on equiatomic NiAl at this temperature [31].

3.2 Exposure to Na_2SO_4 in O_2 -0.1 SO_2

After 2 h exposure to Na_2SO_4 in O_2 -0.1 SO_2 , NiAl formed a thin external scale and small intrusions (1 μm deep or less). As shown in Figure 4, the intrusions consisted of γ - Al_2O_3 and were enriched in S at the interface with the metal. The sulfate deposit was generally not adherent to the specimen after reaction, except where intrusions had formed, where it contained some Ni and Al (1-5 at. %). After 20 h, scattered nodules of varying size but equivalent morphology were observed (Figure 5). The bicone-shaped nodules consisted of internal γ - Al_2O_3 in an Al-depleted metal matrix near the reaction front, and a NiO-Ni Al_2O_4 mixture toward the surface. The oxides were identified by TEM-SAD (not shown here). A thin region of porous NiO was sometimes found at the surface of the largest nodules. The inter-particle region consisted of both γ and γ' , with compositions (12 and 26 at. % Al) consistent with γ - γ' equilibrium at 700 °C [30]. Traces of S (1 at. % or less) were sometimes detected in the oxide by SEM-EDS. No sign of repassivation was found at the reaction front of the smaller nodules; rather, local disruption of the protective scale and nodule development must have occurred continuously during the exposure. Regions were visible on the same sample where the internal attack was in a very early stage, as exemplified in the insert of Figure 5. Most of the surface was still covered by an external Al_2O_3 scale after 20 h.

In contrast, after 2 h reaction, the NiAlCr alloy was covered by a continuous, 2-5 μm mixed oxide scale (Figure 6a). The reaction product was Al-rich but also contained small amounts (2-5 at. %) of Cr, Ni, Na and S. Some regions were enriched in Ni and S. Chemical imaging (Figure 6b) revealed a considerable S enrichment in the oxide around the metal/oxide interface. This was much greater than in the Cr-free NiAl, as TEM-EDS analysis of the interfacial region after the same exposures yielded 24 at. % S for NiAlCr, compared to 3 at. % S for NiAl. In addition, NiAlCr developed internal Cr-rich sulfides. Variable amounts of Al and Ni (2-5 at. %) were found in the sulfate located directly above the scale. The corrosion products developed after 6.5 h and 20 h reaction (Figure 7) were similar to that observed after 2 h. Sodium and S were found throughout the Al-rich oxide scale, which also included Ni-rich sulfide regions. Ahead of the reaction front, sulfides identified as (Al,Cr) $_3\text{S}_4$ thiospinel by TEM precipitated in an Al-depleted γ' matrix. After 6.5 h, the sulfate deposit was separated in two distinct zones: near the scale surface, it contained relatively high amounts of Al and Ni (3-8 at. %), while outside and away from the scale surface, no significant Al was detected, and the Ni content was around 1 at. %. These Ni levels correspond to liquid and solid sulfate solutions, respectively (see Na_2SO_4 -Ni SO_4 phase diagram in Ref. [32]). Porous NiO was embedded in the sulfate near the scale surface. After

20 h, the sulfate deposit contained variable amounts of Ni (1-5 at. %), Al (1-15 at. %) and Cr (1-3 at. %). A porous oxide developed within the deposit both at the scale surface and at the interface with the gas. These oxide regions were rich in Ni and also contained some Al. The reaction morphologies observed after 20 h reaction of the NiAlCr specimens presented some local variations. The outermost oxide layer had thicknesses ranging from submicron (Figure 7b) to over 10 μm . In the latter case, little or no deposit was left, and both the inner oxide thickness and the internal sulfidation depth were greater (Figure 7c).

3.3 Exposure to $\text{Na}_2\text{SO}_4\text{-MgSO}_4$

Additional experiments were carried out to investigate the role played by the physical state (solid vs liquid) and chemistry (acid vs basic) of the deposit. Specifically, specimens of NiAl and NiAlCr were reacted with Na_2SO_4 in dry air, and with $\text{Na}_2\text{SO}_4\text{-MgSO}_4$ in dry air and $\text{O}_2\text{-0.1SO}_2$, all for 20 h. A eutectic $\text{Na}_2\text{SO}_4\text{-MgSO}_4$ mixture ($T_e = 670^\circ\text{C}$) was used to ensure that the deposit was liquid at the reaction temperature of 700°C .

Exposure of both NiAl and NiAlCr to Na_2SO_4 in dry air produced external Al_2O_3 scales, with scattered intrusions 1-2 μm deep (NiAl shown in Figure 8a). The sulfate deposit directly above the intrusions contained some Ni and Al (1-5 at. %). Under the $\text{Na}_2\text{SO}_4\text{-MgSO}_4$ deposit, NiAl formed an external Al_2O_3 scale with small intrusions and isolated nodules 20-30 μm deep in air (Figure 8b), but sustained massive degradation in $\text{O}_2\text{-0.1SO}_2$ (Figure 9a). The nodules formed in air comprised sulfides at the reaction front, Mg-rich aluminates toward the surface and an outermost MgO layer. In $\text{O}_2\text{-0.1SO}_2$, the corrosion product consisted of internal Al-rich oxide at the reaction front, and mixed Al-Ni oxides with S toward the surface (Figure 9a). The penetration depth was approximately uniform, but regions of non-oxidized alloy were also found within the internally oxidized zone. This corrosion product extended deeper but was of a similar constitution as the nodules formed under Na_2SO_4 in $\text{O}_2\text{-0.1SO}_2$.

Exposure of NiAlCr to $\text{Na}_2\text{SO}_4\text{-MgSO}_4$ resulted in external Al_2O_3 growth in air, while significant corrosion was observed in $\text{O}_2\text{-0.1SO}_2$ (Figure 9b). The reaction product was structurally similar to that formed with Na_2SO_4 in $\text{O}_2\text{-0.1SO}_2$ (compare with Figure 7), as it featured an outermost, porous Ni-rich oxide layer, an inner mixed oxide layer, and internal sulfides in an Al-depleted γ' matrix.

4 Discussion

The results obtained after relatively short-term exposure to Na_2SO_4 in $\text{O}_2\text{-0.1SO}_2$ indicated that alloying with Cr caused a substantial change in the reaction mechanism, from a localized internal oxidation type of attack (NiAl) to a relatively uniform hot corrosion process (NiAlCr). A remarkable manifestation of this change is the formation of a porous, mixed oxide layer within 2 h exposure on NiAlCr (Figure 6); while on NiAl, external Al_2O_3 formation persisted up to at least 100 h alongside the fast growing nodules. The simultaneous presence of both an external Al_2O_3 scale and nodules of various sizes on the binary alloy (Figure 5) indicates that new nodules nucleated continuously throughout the exposure, and that their growth remained rapid. In contrast, in the case of NiAlCr, external Al_2O_3 either did not form or failed within 2 h, but the extent of corrosion is relatively low in

the longer term. Indeed, in a recent study in which experiments were conducted in the same conditions [26], weight gains were found to be lower for NiAlCr than for NiAl after 100 h reaction. The present discussion is concerned with reaction morphologies and associated mechanistic aspects in the early stages, and less so with reaction kinetics or longer term performance.

In Ref. [26], the better resistance of NiAlCr over NiAl was tentatively attributed to the ability of Cr to exclude transient oxidation of Ni and favor the rapid establishment of Al_2O_3 during the early stage of the exposure. Although this may be the case in the absence of a deposit, it does not in fact apply to type II hot corrosion conditions, as shown by the present results. Instead of oxidation-related arguments, the present discussion considers the acid-base chemistry of the sulfate deposit – a standpoint which has so far mostly been limited to type I conditions [4], but will be shown here to be also useful in describing type II processes.

4.1 Reactivity of NiAl

The reaction of NiAl with Na_2SO_4 in O_2 -0.1 SO_2 resulted in the local development of bicone-shaped nodules of internal Al_2O_3 (Figure 5). Such nodules were reported by previous investigators after oxidation of β -NiAl alloys in quartz ampoules in the presence of buffer metal-oxide mixtures (Cu-CuO₂, Ni-NiO, ...) in the temperature range 500-1000 °C [33], or in H_2 - H_2S - H_2O gas mixtures at 900 °C [34]. In both cases the inability of the alloy to maintain a protective Al_2O_3 scale was attributed to the reaction of Al with S [35], although the underlying mechanism was not discussed in detail. Similar nodules were also observed after oxidation in O_2 at 1000 °C of presulfidized β -NiAl [36]. The formation of porous, internal Al_2O_3 was attributed by the latter authors to the oxidation of internal Al_2S_3 that had formed during the presulfidation treatment. According to the interpretation presented, the reaction would generate SO_2 and disrupt the Al_2O_3 , preventing its growth as a compact layer. However, no Al_2S_3 was found in the present study despite careful TEM examination of the nodules. Smialek [37] reported the rapid growth of porous Al_2O_3 on highly S- and Zr-doped NiAl in air at 1200 °C. An open network of submicron microchannels was argued to allow rapid gas transport. This is a different mode of propagation, but Smialek also concluded that the widespread porosity was due to SO_2 evolution. This conclusion could be neither confirmed nor disproved here, but the S enrichment at the bottom of the Al-rich oxide intrusions formed in the presence of Na_2SO_4 (Figure 4) did seem essential to the internal oxidation process.

The importance of S was confirmed by reacting a NiAl specimen with Na_2SO_4 in O_2 -0.1 SO_2 for 20 h, then washing off the deposit, and heat-treating the specimen again in air with no deposit, all at 700 °C. Successive surface micrographs of the same region are shown in Figure 10: the nodules formed during the sulfate exposure are seen to grow only slightly during the first 20 h heat-treatment in air, and to not grow significantly thereafter. It is therefore concluded that the process leading to internal, porous γ - Al_2O_3 formation is not self-sustaining, and that a continuous supply of S is required. The exact nature of the interaction between S and Al is not fully understood at present, and deserves further investigation.

The absence of a significant fluxing process is in itself informative. After 2 h reaction with Na_2SO_4 in O_2 -0.1 SO_2 , small but significant amounts (1-5 at. %) of Al and Ni were measured in the sulfate in contact with the oxide intrusions, and less than 1 at. % were present in the rest of the deposit. Solubility curves such as those established by Rapp and co-workers [4] at 927 °C are not available at 700 °C, and it is not known whether the predominant aluminum solute in Na_2SO_4 equilibrated with O_2 -0.1 SO_2 at this temperature ($p_{\text{SO}_3} = 7.1 \times 10^{-4}$ atm) is Al^{3+} or AlO_2^- . Lawson et al. [38] reported a slow acidic dissolution of bulk Al_2O_3 with an O_2 -1 SO_2 mixture at 700 °C ($p_{\text{SO}_3} = 7.1 \times 10^{-3}$ atm), whereas there was less reaction under basic conditions. The solubility minimum is at $p_{\text{SO}_3} = 5 \times 10^{-2}$ atm at 927 °C [39]. With a decrease in temperature, p_{SO_3} for the $\text{NaAlO}_2/\text{Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3/\text{Al}_2(\text{SO}_4)_3$ equilibria decreases, and the minimum solubility shifts towards lower p_{SO_3} values. Based on the Gibbs free energy of reactions (1) and (2), it is expected that a p_{SO_3} of 7.1×10^{-4} atm will be near the solubility minimum at 700 °C. Thus, the dissolution of Al_2O_3 could be either acidic or basic, depending on the local sulfate chemistry; the discussion will return to this point when addressing the NiAlCr alloy. If one only considers the Na_2SO_4 - NiSO_4 solution, the solidus composition contains 3 at. % Ni at 700 °C [32]. It is therefore concluded that some liquid sulfate was locally present in contact with the oxide intrusions. Even so, the long-term persistence of an Al_2O_3 scale alongside the nodules indicates that Al_2O_3 was relatively stable with respect to dissolved Al.

In Na_2SO_4 equilibrated with O_2 -0.1 SO_2 at 700 °C, NiO undergoes acidic dissolution to form a liquid NiSO_4 - Na_2SO_4 solution [22]. As a consequence, the absence of significant NiO dissolution during the reaction of NiAl with Na_2SO_4 in O_2 -0.1 SO_2 indicates that little NiO was formed. In other words, even though the alloy likely produced some transient NiO, its dissolution was not rapid enough to disrupt the establishment of an external Al_2O_3 scale. Furthermore, wherever this scale lost its protective character and a nodule developed, a relatively low p_{O_2} was maintained at the nodule surface, such that the activity of NiO in the mixed oxide was too low for its acidic dissolution to proceed significantly. The observation that some porous NiO was present at the surface of the largest nodules indicates that as nodules developed, the oxide in their upper part tended to get enriched in Ni, until eventually NiO could form and react with Na_2SO_4 – this segregation simply reflects the relative stabilities of Al and Ni oxide, as in the non-selective oxidation of dilute alloys.

During exposure to the liquid Na_2SO_4 - MgSO_4 in O_2 -0.1 SO_2 , local Al_2O_3 failure also resulted in internal oxidation (Figure 9a). The semi-continuous, deep corrosion product evolved from a localized type of attack. Indeed, longer exposure to Na_2SO_4 (100 h, not shown here) eventually produced larger, semi-continuous nodules, suggesting that the liquid deposit simply accelerated the internal attack. As mentioned above, Ni segregation within the nodule eventually led to NiO formation and dissolution in the sulfate, but an important conclusion here is that the initial reaction process of NiAl exposed to a sulfate in mildly acidic conditions at 700 °C is not one of hot corrosion. Rather, it is internal oxidation assisted by S, even when the applied sulfate is liquid.

Now turning to air exposures, the continued presence of a thin Al_2O_3 scale after reaction with Na_2SO_4 - MgSO_4 indicates that the solubility of Al_2O_3 in the melt was low in these relatively basic conditions, in agreement with previous findings [38]. Some isolated nodules were formed (Figure 8b); their constitution (internal sulfides at the reaction front, aluminates towards the surface) is consistent with a process of basic fluxing, while the non-

uniform reaction morphology points to local disruptions of the generally protective Al_2O_3 scale. In line with mechanistic descriptions of basic fluxing during type I hot corrosion [2], it is inferred that the protective regime is only maintained so long as sulfidation of the alloy by a locally oxygen-deprived melt is prevented: when the Al_2O_3 scale locally fails, sulfidation consumes SO_3 , and the increased basicity destabilizes Al and Ni oxides. Even then, the solubility of the aluminate and nickelate ions must have remained relatively low (or, rather, must have rapidly returned to a low level), as most intrusions reached 1-2 μm deep and repassivated, without forming larger nodules such as that shown in Figure 8b.

In the absence of SO_3 in the gas, the $\text{Na}_2\text{SO}_4\text{-MgSO}_4$ solution itself was relatively unstable, as indicated by the precipitation of MgO (the p_{SO_3} for MgO/MgSO_4 equilibrium, both taken as solid phases at unit activity, is calculated to be 2.2×10^{-6} atm at 700 °C from data in Ref. [10], which is much higher than the $\text{Na}_2\text{O/Na}_2\text{SO}_4$ value of 6.6×10^{-23} atm, and apparently higher than was present in the air cylinder). Rahmel and coworkers [40,41] previously discussed the consequences of the low stability of MgSO_4 , suggesting that the precipitation of a continuous MgO layer on the corrosion product would inhibit hot corrosion in basic conditions. This may have limited the size of the nodules observed here.

In light of these observations, the absence of nodules after reaction of NiAl with Na_2SO_4 alone in air is readily understood. Local breakdown of the Al_2O_3 scale resulted in 1-2 μm intrusions of Al oxide (Figure 8a), but in the absence of an extended liquid phase, basic fluxing did not proceed further. We conclude that NiAl may be subject to limited basic fluxing in air at 700 °C, but this requires the continued presence of a liquid deposit.

4.2 Reactivity of NiAlCr; effect of Cr

Starting with the relatively basic conditions, the absence of nodules or of any other sign of accelerated attack of NiAlCr after exposure to the liquid $\text{Na}_2\text{SO}_4\text{-MgSO}_4$ deposit in air indicates that either the Al_2O_3 scale did not experience local failure, or that the solubilities of nickelate and aluminate ions in the liquid melt were negligibly small. Chromia readily dissolves in basic sulfate melts, which is known to increase the melt acidity and hamper the basic dissolution of NiO and Al_2O_3 [2]. This may possibly explain the absence of hot corrosion of NiAlCr in air.

The addition of SO_3 in the gas caused a substantial change, as NiAlCr samples exposed to Na_2SO_4 and $\text{Na}_2\text{SO}_4\text{-MgSO}_4$ deposits in $\text{O}_2\text{-0.1SO}_2$ suffered uniform accelerated attack. After reaction, the Na_2SO_4 deposit contained significant amounts of Al, Cr and Ni, and a porous oxide developed at the sulfate/gas interface (Figure 7). Acidification of the sulfate by the gas apparently triggered a fluxing type reaction mechanism, which emphasizes the critical role played by salt chemistry (that is, in terms of its acidity; our results suggest that MgSO_4 has no significant effect in acidic conditions, which is consistent with findings by Rahmel and coworkers [40,41] from polarization studies at higher temperatures). Conversely, the fact that similar morphologies and extents of reaction were observed with the initially solid Na_2SO_4 and the liquid $\text{Na}_2\text{SO}_4\text{-MgSO}_4$ deposits indicates that insofar as the ambient p_{SO_3} allows the formation of a liquid $\text{Na}_2\text{SO}_4\text{-NiSO}_4$ solution, the initial state of the deposit (solid or liquid) is not decisive.

The critical question here is how the addition of 5 at. % Cr to NiAl could trigger a fluxing-type mechanism that was absent for the binary alloy. This encompasses two issues,

(i) the inability of the Cr-bearing alloy to establish a protective Al_2O_3 scale, and (ii) the tendency for Al, Cr and Ni oxides to dissolve in the sulfate and precipitate at its surface. During oxidation in air with no deposit at 700 °C, the NiAlCr alloy formed less transient NiO than NiAl did [26]. Yet this did not have the expected beneficial effect in the presence of a deposit, which, as will be argued now, is related to the influence of Cr on the sulfate chemistry.

As discussed in Section 4.1, the solubility of Al in Na_2SO_4 at 700 °C is not known, but it is estimated to be close to its minimum at the p_{SO_3} of interest, 7.1×10^{-4} atm. The case of Cr is similar: no data are available at 700 °C, but measurements by Zhang [42] place the solubility minimum at $p_{\text{SO}_3} = 4 \times 10^{-2}$ atm at 927 °C, and considering the thermodynamics of the $\text{Na}_2\text{CrO}_4/\text{Cr}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3/\text{Cr}_2(\text{SO}_4)_3$ equilibria, the solubility is thought to be close to its minimum in the present experimental conditions. (Since the degree of oxidation of Cr changes from +III in Cr_2O_3 to +VI in CrO_4^{2-} , the solubility of chromate ions varies with p_{O_2} ; however, Zhang's measurements show that CrO_2^- rapidly predominates in the basic regime as p_{O_2} decreases, and overall the influence of p_{O_2} on the minimum solubility is marginal, until Cr^{2+} ($\underline{\text{CrS}}$) is prevalent at a very low p_{O_2} .) Hence the predominant solutes of Al and Cr are undetermined *a priori*, and will depend on local variations of the sulfate chemistry away from its equilibrium composition (i.e., that defined by the gas p_{SO_3}). Since the consumption of O and S by reaction with the alloy tends to lower the p_{SO_3} , basic dissolution appears more likely.

The simultaneous presence of Al, Cr and Ni in the sulfate after reaction of NiAlCr in O_2 -0.1 SO_2 is indicative of a coupled acid-base dissolution phenomenon. Acidic dissolution of NiO itself is relatively slow in the conditions of interest, in particular too slow to disrupt the establishment of Al_2O_3 on NiAl. This is presumably due to slow SO_3 transport (as $\text{S}_2\text{O}_7^{2-}$) in the sulfate, which would both limit the dissolution kinetics and lower its driving force. Indeed if mass transport is slow, acidic dissolution causes a local rise in basicity, and Ni^{2+} solubility is decreased. In the presence of Cr, however, basic dissolution of Cr_2O_3 provides a local source of SO_3 , facilitating the acidic dissolution of NiO:

The rapid exchange of ions would also allow the basic dissolution of Al_2O_3 ,

which otherwise is very slow, to proceed.

This process of synergistic dissolution, in which the SO_3 required for acidic dissolution of a basic oxide (here NiO) is provided by the basic dissolution of a more acidic oxide (Cr_2O_3 , Al_2O_3), has been documented by previous investigators [4]. In particular, Hwang and Rapp [16] monitored the sulfate chemistry during individual and coupled dissolution of Fe_2O_3 and Cr_2O_3 , and showed that coupled reactions were faster than individual ones. The authors noted that Al_2O_3 - or Cr_2O_3 -forming alloys that failed to exclude transient oxidation of Ni or Co would be particularly susceptible to hot corrosion because of synergistic dissolution. Here, we propose that as a result of the local SO_3 exchange, accelerated NiO dissolution in the presence of Cr_2O_3 prevented the establishment of an external Al_2O_3 scale. This is plausible inasmuch as dissolution kinetics are controlled by ionic transport in the

melt, which was verified in Ref. [16] in the case of Cr_2O_3 and Fe_2O_3 . The dissolution process apparently overcame the ability of Cr to mitigate transient NiO formation.

The fact that a coupled dissolution process occurred in NiAlCr and not in NiAl suggests that the solubility of CrO_4^{2-} (or CrO_2^-) is greater than that of AlO_2^- in these mildly acidic conditions. Solubility measurements compiled in Ref. [4] indicate that this is indeed the case in the range of p_{SO_3} investigated at 927 °C. In electrochemical polarization studies at 900 °C, Fukumoto et al. [43] also reported this trend in a central potential range, but the solubility of Al reached much higher values at very anodic and very cathodic potentials. Solubility data at 700 °C would be very useful here to facilitate a more detailed discussion.

In order to test, qualitatively, the proposed interpretation, specimens of NiAl were exposed to mixed Na_2SO_4 - $x\text{Cr}_2\text{O}_3$ deposits ($x = 5 \times 10^{-3}$, 5×10^{-2} and 0.5 mol %) in O_2 -0.1 SO_2 . Basic dissolution of Cr_2O_3 in molten Na_2SO_4 equilibrated with O_2 -1 SO_2 at 927 °C was measured in Ref. [16] to be rather slow, reaching 50 % of saturation in about 10 h, and should be even slower if not negligible in solid Na_2SO_4 at 700 °C. Thus dissolution is mainly expected to occur if and where a liquid Na_2SO_4 -NiSO₄ solution is formed by reaction with the alloy.

With 5×10^{-3} % Cr_2O_3 added to the Na_2SO_4 , nodules of internal Al-rich oxide developed, with the same morphology as those found after exposure to pure Na_2SO_4 . However, these covered almost the entire alloy surface, and porous NiO was present on most of the nodules, including small ones (Figure 11a). With 5×10^{-2} % Cr_2O_3 , nodules covered the whole surface, while at 0.5 % the corrosion product had turned into a semi-continuous scale of Al-rich oxide, with a porous NiO layer at its surface, and internal sulfides ahead of the oxidation front (Figure 11b). While deposits were only applied to the flat surfaces, the sides of the specimens exposed to the Na_2SO_4 - Cr_2O_3 mixtures were heavily corroded, which suggests that a liquid sulfate had formed. This was not the case for the pure Na_2SO_4 deposit.

The higher nodule densities observed with Na_2SO_4 - Cr_2O_3 mixtures are indicative of nucleation events being more frequent: defects naturally occurring in the growing Al_2O_3 scale were more likely to lead to local breakdown and internal oxidation in the presence of Cr_2O_3 . This result is consistent with the proposed interpretation of the effect of alloying NiAl with Cr. Specifically, the dissolution of Cr_2O_3 enhances the dissolution of NiO and Al_2O_3 , likely through a process of acid-base coupling, which prevents effective alloy passivation (or repassivation).

In analyzing the effects of the gas and sulfate chemistry on the stability of thermally grown oxides, it is useful to consider two limiting situations. If mass transport in the sulfate were very rapid compared to dissolution reactions, the gas phase conditions (p_{O_2} , p_{SO_3}) would prevail everywhere in the sulfate, regardless of dissolution reactions, which would proceed independently from each other. If, on the other hand, mass transport were very slow, the sulfate chemistry near the oxide/sulfate interface, initially set by equilibrium with the gas, would be affected by dissolution reactions, and acid-base coupling would be significant. In this latter case, the chemistry of sulfate solutions may be conveniently analyzed in a manner analogous to that of aqueous solutions. Consider for example the individual dissolution of Cr_2O_3 . In a relatively acidic sulfate, the solubility of CrO_2^- is small, Cr_2O_3 does not dissolve significantly, and the ambient p_{SO_3} is not affected. In a more basic sulfate however, a larger amount of CrO_2^- is produced, which leads to a local increase of p_{SO_3} until an equilibrium is reached. In this case, the $\text{Cr}_2\text{O}_3/\text{CrO}_2^-$ couple acts as a buffer for the

p_{SO_3} , in the same way as large concentrations of an acid and its conjugate base buffer the pH of an aqueous solution. The analysis is developed in detail in the Appendix. In particular, we show that in a certain range of initial sulfate compositions, the coupled dissolution of Cr_2O_3 and NiO would locally buffer a p_{SO_3} intermediate between those individually established by the $\text{Cr}_2\text{O}_3/\text{CrO}_2^-$ and $\text{NiO}/\text{Ni}^{2+}$ couples. This buffered p_{SO_3} is determined by the equilibrium constants of the dissolution reactions, and is independent of the starting p_{SO_3} . In other words, in this regime, oxide solubilities are independent of the gas composition.

A NiAl specimen was reacted with Na_2SO_4 -5 % Cr_2O_3 in air and no accelerated corrosion of any sort was observed. Similarly, no hot corrosion occurred when NiAlCr was exposed to Na_2SO_4 or even Na_2SO_4 - MgSO_4 in air. Thus local equilibria in air and in O_2 -0.1 SO_2 did not in fact buffer the same p_{SO_3} . However, the presence of Cr_2O_3 did have a significant effect on tests conducted in O_2 -0.1 SO_2 . The apparent contradiction is most likely due to the complex interplay between the reaction kinetics on the one hand, and the chemistry, physical state (solid vs liquid) and transport properties of the sulfate on the other hand. We conclude that mass transport proceeded at an intermediate rate, allowing both the gas composition and the dissolution reactions to affect the sulfate chemistry. It is noted that in Hwang and Rapp's synergistic dissolution experiments [16], the salt p_{SO_3} was not significantly affected by Cr_2O_3 dissolution, whether individual or coupled with that of Fe_2O_3 . Instead coupled dissolution kinetics were controlled by the Fe_2O_3 reaction, and the salt p_{SO_3} by the $\text{Fe}_2\text{O}_3/\text{Fe}^{3+}, \text{Fe}^{2+}$ equilibrium, until no oxide was left and it returned to the value set by the gas. The key aspect is that Cr_2O_3 may not be acidic enough to establish high p_{SO_3} levels, sufficient to trigger NiO dissolution for example, but Cr_2O_3 dissolution will allow a short-range exchange of SO_3 which will facilitate NiO dissolution so long as the ambient p_{SO_3} is acidic with respect to NiO. Thus, the effect of Cr is primarily kinetic in nature, but has the consequence of changing the mode of attack.

4.3 *Comments on the effect of Cr*

Chromium has been widely recognized as very beneficial to resistance against hot corrosion. For example, Goward suggested in a 1986 review of protective coatings [44] that 15-20 % Cr were required for protection in type II conditions, and works reviewed in Ref. [5] showed that 30-35 % Cr offered yet superior resistance. Several studies of cyclic, type I hot corrosion of Ni aluminides [45-47] showed that small Cr additions were beneficial, more so than Pt additions for example. An extensive study of NiCrAl alloys at 900-1100 °C [48] also showed a beneficial effect of Cr in the β - γ region. In this context, the observation reported here that Cr triggers a fluxing-type mechanism, which is typically associated with high corrosion rates, may seem unsettling at first. However, the results mentioned above concern either increased Cr levels in MCrAlY alloys already containing Cr, or type I conditions, or both, whereas the present work concerns small Cr additions to Cr-free NiAl in type II conditions. As will be argued here, the apparent variance resides in the fact that hot corrosion in various conditions of temperature and alloy and gas composition involves distinct mechanisms, which are differently affected by the Cr concentration.

It is first noted that direct comparisons between short term, isothermal exposures discussed here and long term, cyclic tests (e.g. Ref. [47]) or even burner rig tests (e.g. Ref. [46]) should be made with caution. Indeed, alloy performances in thermal cycling are influenced by their resistance to spallation and their inherent ability to re-form protective Al_2O_3 scales (which benefits from Cr additions) as much as by the reaction with the sulfate deposit. The sulfate chemistry may vary during the test and go through successive steady-states as the deposit interacts with the sample, is removed because of evaporation or scale spallation, and is re-applied. This obviously makes mechanistic analyses extremely challenging.

Perhaps the best understood aspect of alloying with Cr is that the basic dissolution of Cr_2O_3 to form chromate ions (or chromite, depending on the local p_{O_2} [42]) reduces the melt basicity to a level where basic dissolution of NiO or Al_2O_3 is avoided [2]. This is mostly relevant to type I conditions, where basic fluxing is a problem. Although Cr_2O_3 is acidic like oxides of other refractory metals such as W or Mo, the formation of CrO_2^- will not by itself induce acidic dissolution of Al_2O_3 , whereas that of WO_4^{2-} or MoO_4^{2-} will [2]. Thus the $\text{Cr}_2\text{O}_3/\text{CrO}_2^-$ couple tends to buffer the melt in a region of NiO and Al_2O_3 stability, hampering basic fluxing but not causing alloy-induced acidic fluxing in basic environments.

For alloys with high Cr contents but little or no Al, which rely on Cr_2O_3 for corrosion resistance, increasing the Cr concentration will reduce the extent of transient oxidation, i.e., the amount of Ni or Co oxide exposed to Na_2SO_4 . In this case higher Cr contents are very beneficial, particularly in type II conditions as observed by Luthra [49] in the Co-Cr system. In electrochemical polarization studies, Fukumoto et al. [43] found that the solubility of Al_2O_3 became much greater than that of Cr_2O_3 at very low and very high potentials. This is to be related with the earlier work by Wu et al. [50], who showed that the breakdown potential (past which oxide dissolution and rapid corrosion occur) of Cr_2O_3 was more negative than that of Al_2O_3 in basic conditions, and more positive in acidic conditions, i.e., the passive range of Cr_2O_3 was wider. The authors linked this to the superior resistance of commercial Cr_2O_3 -forming alloys over Al_2O_3 -forming alloys. Furthermore, as argued by Luthra [49] and Rapp [4], the fact that solid-state diffusion is much faster in Cr_2O_3 than in Al_2O_3 may be an advantage for hot corrosion resistance, as a continuous scale would be established more rapidly, more effectively preventing exposure of the base metal. This is thought to be particularly significant at 600-800 °C, where transient oxidation is more important on Al_2O_3 -formers than on Cr_2O_3 -formers [51]. Both the more rapid growth and the wider passive range explain why increasing the Cr content of a marginal Al_2O_3 -former, switching to Cr_2O_3 formation, can be beneficial. The cases of Cr_2O_3 -formers or marginal Al_2O_3 formers are very different from the present situation, where Cr was added to NiAl in a small quantity, and the alloy remained an Al_2O_3 -former.

Finally, it is noted that while producing Cr-free diffusion coatings is impractical because most substrates would contain Cr, it is not necessarily desirable. As mentioned earlier, the types of attack observed on NiAl and NiAlCr were very different in nature, and also in terms of kinetics, such that longer term (100 h) exposure led to locally deeper metal loss for the binary alloy than for NiAlCr. Since local failure of a protective scale can hardly be avoided during service, Cr may provide some degree of protection on the long term, even in type II conditions.

5 Conclusions

The short term exposure of NiAl and NiAlCr to Na_2SO_4 in O_2 -0.1 SO_2 at 700 °C produced two distinct reaction morphologies, resulting from distinct mechanisms. The NiAl alloy was able to form an external Al_2O_3 scale, but local scale failure led to internal oxidation and rapid nodule development. Both the nucleation of Al_2O_3 intrusions and the subsequent propagation of the internal oxidation front were associated with the presence of S at the metal/oxide interface. The reaction mechanism did not involve significant oxide dissolution in the sulfate. In particular, the Al_2O_3 remained chemically stable even when a liquid Na_2SO_4 - MgSO_4 deposit was used. Nevertheless, scale failure and nodule development did require the presence of an acidified sulfate deposit.

The addition of Cr to the alloy led to a uniform type of attack where NiO and Al_2O_3 dissolved significantly in the sulfate, a porous, non-protective scale formed, and the alloy was internally sulfidized. A similar reaction morphology was observed when a Na_2SO_4 - MgSO_4 deposit was used, but not when the reaction was conducted in air, with either of the deposits. Furthermore, the addition of Cr_2O_3 to Na_2SO_4 enhanced nodule development on NiAl in O_2 -0.1 SO_2 . These results were analyzed by considering the role of the gas composition and of the dissolution reactions on the sulfate chemistry. The acidic dissolution of NiO is made thermodynamically possible by the acidification of the sulfate through equilibrium with the gas phase. This occurs independently of whether the applied sulfate is solid or liquid. While selective oxidation initially protects the binary alloy, the dissolution of Cr_2O_3 at the surface of the NiAlCr alloy causes a rapid local exchange of SO_3 , which allows NiO dissolution to proceed more rapidly than an external Al_2O_3 scale can establish.

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7 Appendix

The dissolution of oxides in Na_2SO_4 is studied here by analogy with acid-base equilibria in aqueous solutions. We consider a situation where transport in the sulfate is slow, to the extent that the sulfate chemistry at the oxide/sulfate interface is locally controlled by the equilibria associated with oxide dissolution. Three cases are studied: independent dissolution of acidic and basic oxides, and coupled dissolution.

7.1 *Independent dissolution of an acidic oxide*

Let AO be an acidic oxide, which reacts to produce Na_2AO_2 in solution in Na_2SO_4 . Initially, the sulfate does not contain any Na_2AO_2 , and its p_{SO_3} is set through equilibrium with the gas. The equilibrium Na_2AO_2 activity as a function of the initial p_{SO_3} is calculated by considering the following mass balances:

$$\begin{array}{lcl} & \text{AO} & + \quad \text{Na}_2\text{O} \quad = \quad \text{Na}_2\text{AO}_2 \quad (\text{A1}) \\ \text{initial} & n_{\text{AO}}^i & \quad n_{\text{Na}_2\text{O}}^i \quad \quad 0 \\ \text{equilibrium} & n_{\text{AO}}^i - x & \quad n_{\text{Na}_2\text{O}}^i - x \quad \quad x \end{array}$$

$$\begin{array}{lcl} & \text{Na}_2\text{SO}_4 & = \quad \text{Na}_2\text{O} \quad + \quad \text{SO}_3 \quad (\text{A2}) \\ \text{initial} & n_{\text{Na}_2\text{SO}_4}^i & \quad n_{\text{Na}_2\text{O}}^i \quad \quad n_{\text{SO}_3}^i \\ \text{equilibrium} & n_{\text{Na}_2\text{SO}_4}^i - z & \quad n_{\text{Na}_2\text{O}}^i + z \quad \quad n_{\text{SO}_3}^i + z \end{array}$$

where n_j^i is the initial amount of substance j in a given unit volume, and x and z are the extents of reactions (A1) and (A2), respectively. The equilibrium constants associated with reactions (A1) and (A2) are defined as:

$$K_A = \frac{a_{\text{Na}_2\text{AO}_2}}{a_{\text{Na}_2\text{O}}} \quad (\text{A3})$$

and

$$K = a_{\text{Na}_2\text{O}} \cdot p_{\text{SO}_3} \quad (\text{A4})$$

where the activities of the solid oxide AO and the solvent Na_2SO_4 are set to unity. The quantity of Na_2SO_4 is assumed constant and much larger than that of all other species. Thus the total number of moles in the unit volume is approximately constant, and concentrations equal number of moles directly obtained from the mass balances. For example, since Na_2O is consumed by reaction (A1) and produced by reaction (A2), the equilibrium Na_2O concentration is $C_{\text{Na}_2\text{O}} = n_{\text{Na}_2\text{O}}^i - x + z$. Activity coefficients are further assumed to be constant and equal to one for all species, such that activities are equated with concentrations. We obtain the following system:

$$K_A = \frac{x}{a_{\text{Na}_2\text{O}}^i - x + z} \quad (\text{A5})$$

$$K = (a_{\text{Na}_2\text{O}}^i - x + z) \cdot (p_{\text{SO}_3}^i + z) \quad (\text{A6})$$

which is solved to yield:

$$x = \frac{K_A}{2(1 + K_A)} \left(\alpha + \frac{K}{p_{\text{SO}_3}^i} - p_{\text{SO}_3}^i \right) \quad (\text{A7})$$

$$z = \frac{1}{2} \left(\alpha - \frac{K}{p_{\text{SO}_3}^i} - p_{\text{SO}_3}^i \right) \quad (\text{A8})$$

where $\alpha = \sqrt{\left(\frac{K}{p_{\text{SO}_3}^i} - p_{\text{SO}_3}^i \right)^2 + 4K(1 + K_A)}$, and the relationship $K = a_{\text{Na}_2\text{O}}^i \cdot p_{\text{SO}_3}^i$ has been used assuming equilibrium in the sulfate prior to AO dissolution. The equilibrium activities $a_{\text{Na}_2\text{AO}_2} = x$ and $p_{\text{SO}_3} = p_{\text{SO}_3}^i + z$ are plotted as a function of $p_{\text{SO}_3}^i$ in Figure A1.

Three distinct regimes are identified. For $p_{\text{SO}_3}^i \gg 2\sqrt{K_A K}$ (regime R1), α can be approximated as $\alpha = p_{\text{SO}_3}^i$, which yields $z = 0$, and $p_{\text{SO}_3} = p_{\text{SO}_3}^i$. Using Eqs. (A3) and (A4), we find $a_{\text{Na}_2\text{AO}_2} = \frac{K_A K}{p_{\text{SO}_3}^i}$. In this acidic regime, the solubility of AO is small. Thus reaction (A1) does not proceed significantly to the right, little Na_2AO_2 is produced and the ambient p_{SO_3} is not affected.

For $\frac{1}{2}\sqrt{\frac{K}{K_A}} \ll p_{\text{SO}_3}^i \ll 2\sqrt{K_A K}$ (regime R2), α is approximated as $\alpha = 2\sqrt{K_A K}$, which yields $a_{\text{Na}_2\text{AO}_2} = p_{\text{SO}_3} = \sqrt{K_A K}$. In this intermediate regime, $a_{\text{Na}_2\text{AO}_2}$ and p_{SO_3} are independent of the initial $p_{\text{SO}_3}^i$. Any small variation away from the equilibrium p_{SO_3} will be compensated by AO dissolution or precipitation. In other words, the AO/ Na_2AO_2 couple forms a buffer for p_{SO_3} .

For $p_{\text{SO}_3}^i \ll \frac{1}{2}\sqrt{\frac{K}{K_A}}$ (regime R3), α is approximated as $\alpha = \frac{K}{p_{\text{SO}_3}^i}$, which yields $x = \frac{K_A K}{(1+K_A)p_{\text{SO}_3}^i}$. Since for common oxides $K_A \gg 1$, this results in $a_{\text{Na}_2\text{AO}_2} = \frac{K}{p_{\text{SO}_3}^i}$. Using Eqs. (A3) and (A4), we obtain $p_{\text{SO}_3} = K_A \cdot p_{\text{SO}_3}^i$. In this basic regime, the large excess of Na_2O cannot be compensated by AO dissolution.

7.2 Independent dissolution of a basic oxide

Let BO be a basic oxide, which reacts to produce BSO_4 in solution in Na_2SO_4 . The equilibrium BSO_4 is calculated by considering the following mass balance:

	BO	+	SO ₃	=	BSO ₄	(A9)
initial	n_{BO}^i		$n_{\text{SO}_3}^i$		0	
equilibrium	$n_{\text{BO}}^i - y$		$n_{\text{SO}_3}^i - y$		y	

and the solvent dissociation equilibrium, reaction (A2). We use the same notations and assumptions adopted in Section 7.1. The equilibrium constant associated with reaction (A9) is defined as:

$$K_B = \frac{a_{\text{BSO}_4}}{p_{\text{SO}_3}} \quad (\text{A10})$$

where again the activity of the solid oxide BO is set to unity. We obtain the following system:

$$K_B = \frac{y}{p_{\text{SO}_3}^i - y + z} \quad (\text{A11})$$

$$K = (a_{\text{Na}_2\text{O}}^i + z) \cdot (p_{\text{SO}_3}^i - y + z) \quad (\text{A12})$$

which is solved to yield:

$$y = \frac{K_B}{2(1 + K_B)} \left(\beta - \frac{K}{p_{\text{SO}_3}^i} + p_{\text{SO}_3}^i \right) \quad (\text{A13})$$

$$z = \frac{1}{2} \left(\beta - \frac{K}{p_{\text{SO}_3}^i} - p_{\text{SO}_3}^i \right) \quad (\text{A14})$$

where $\beta = \sqrt{\left(\frac{K}{p_{\text{SO}_3}^i} - p_{\text{SO}_3}^i\right)^2 + 4K(1 + K_B)}$. The equilibrium activities of BSO_4 and SO_3 , obtained as $a_{\text{BSO}_4} = y$ and $p_{\text{SO}_3} = p_{\text{SO}_3}^i - y + z$, are plotted as a function of $p_{\text{SO}_3}^i$ in Figure A2.

Again three distinct regimes are identified. For $p_{\text{SO}_3}^i \ll \frac{1}{2}\sqrt{\frac{K}{K_B}}$ (regime R1), equilibrium activities can be approximated as $p_{\text{SO}_3} = p_{\text{SO}_3}^i$ and $a_{\text{BSO}_4} = K_B \cdot p_{\text{SO}_3}^i$. In this basic regime, the solubility of BO is small. Thus reaction (A9) does not proceed significantly to the right, little BSO_4 is produced and the ambient p_{SO_3} is not affected.

For $\frac{1}{2}\sqrt{\frac{K}{K_B}} \ll p_{\text{SO}_3}^i \ll 2\sqrt{K_B K}$ (regime R2), we obtain $a_{\text{BSO}_4} = \sqrt{K_B K}$ and $p_{\text{SO}_3} = \sqrt{\frac{K}{K_B}}$. In this intermediate regime, a_{BSO_4} and p_{SO_3} are independent of the initial $p_{\text{SO}_3}^i$. The BO/ BSO_4 couple forms a buffer for p_{SO_3} .

For $p_{\text{SO}_3}^i \gg 2\sqrt{K_B K}$, (regime R3), we obtain $a_{\text{BSO}_4} = p_{\text{SO}_3}^i$ and $p_{\text{SO}_3} = \frac{p_{\text{SO}_3}^i}{K_B}$. In this acidic regime, the large excess of SO_3 cannot be compensated by BO dissolution.

7.3 Coupled dissolution of an acidic and a basic oxide

We now consider the simultaneous dissolution of AO and BO in Na_2SO_4 . The equilibrium activities are calculated by considering the mass balances associated with reactions (A1), (A2) and (A9). We obtain the following system:

$$K_A = \frac{x}{a_{\text{Na}_2\text{O}}^i - x + z} \quad (\text{A15})$$

$$K_B = \frac{y}{p_{\text{SO}_3}^i - y + z} \quad (\text{A16})$$

$$K = (a_{\text{Na}_2\text{O}}^i - x + z) \cdot (p_{\text{SO}_3}^i - y + z) \quad (\text{A17})$$

which is solved to yield:

$$x = \frac{K_A}{2(1 + K_A)} \left(\gamma + \frac{K}{p_{\text{SO}_3}^i} - p_{\text{SO}_3}^i \right) \quad (\text{A18})$$

$$y = \frac{K_B}{2(1 + K_B)} \left(\gamma - \frac{K}{p_{\text{SO}_3}^i} + p_{\text{SO}_3}^i \right) \quad (\text{A19})$$

$$z = \frac{1}{2} \left(\gamma - \frac{K}{p_{\text{SO}_3}^i} - p_{\text{SO}_3}^i \right) \quad (\text{A20})$$

where $\gamma = \sqrt{\left(\frac{K}{p_{\text{SO}_3}^i} - p_{\text{SO}_3}^i\right)^2 + 4K(1 + K_A + K_B + K_A K_B)}$. The equilibrium activities of Na_2AO_2 , BSO_4 and SO_3 are plotted as a function of $p_{\text{SO}_3}^i$ in Figure A3.

Again three distinct regimes are identified. For $p_{\text{SO}_3}^i \ll \frac{1}{2}\sqrt{\frac{K}{K_A K_B}}$ (regime R1), equilibrium activities can be approximated as $a_{\text{Na}_2\text{AO}_2} = \frac{K}{p_{\text{SO}_3}^i}$, $p_{\text{SO}_3} = K_A \cdot p_{\text{SO}_3}^i$ and $a_{\text{BSO}_4} = K_A K_B \cdot p_{\text{SO}_3}^i$. In

this basic regime, little BSO_4 is produced and the large excess of Na_2O cannot be compensated by AO dissolution.

For $\frac{1}{2}\sqrt{\frac{K}{K_A K_B}} \ll p_{\text{SO}_3}^i \ll 2\sqrt{K_A K_B K}$ (regime R2), we obtain $a_{\text{Na}_2\text{AO}_2} = a_{\text{BSO}_4} = \sqrt{K_A K_B K}$ and $p_{\text{SO}_3} = \sqrt{\frac{K_A K}{K_B}}$. In this intermediate regime, all equilibrium activities are independent of the initial p_{SO_3} . The $\text{AO}/\text{Na}_2\text{AO}_2/\text{BO}/\text{BSO}_4$ quadruplet forms a buffer for p_{SO_3} . It is noted that the range of the buffered regime is larger than those of the regimes buffered by individual dissolution of AO or BO.

For $p_{\text{SO}_3}^i \gg 2\sqrt{K_A K_B K}$, (regime R3), we obtain $a_{\text{Na}_2\text{AO}_2} = \frac{K_A K_B K}{p_{\text{SO}_3}^i}$, $p_{\text{SO}_3} = \frac{p_{\text{SO}_3}^i}{K_B}$ and $a_{\text{BSO}_4} = p_{\text{SO}_3}^i$. In this acidic regime, little Na_2AO_2 is produced and the large excess of SO_3 cannot be compensated by BO dissolution.

8 References

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Figure Captions

Figure 1: Stability diagrams of the (a) Na-Al-O-S, (b) Na-Ni-O-S, and (c) Na-Cr-O-S systems at 700 °C, constructed from thermodynamic data in Refs. [10,11] and making the assumption of unit activity for all compounds. Standard states for all gases and condensed phases are states of the pure phases at 10⁵ Pa. Phase boundaries in the Na-O-S system are superimposed. The metastable γ -Al₂O₃ was identified experimentally in the present work, and was therefore chosen in (a) instead of the stable polymorph α . In (b), the mixed compounds Na₂NiO₂ and NaNiO₂ are missing, because of a lack of data (emf results by Shaiu et al [12], although used by several authors [13,14], were deemed unreliable by Shaiu et al. themselves). The vertical dotted line in (b) represents the equilibrium between NiO (s), Na₂SO₄-NiSO₄ (s) and Na₂SO₄-NiSO₄ (l) according to Misra et al. [15] (see text). The cross represents the equilibrium composition of an O₂-0.1 % SO₂ gas mixture.

Figure 2: XRD patterns of the NiAl and NiAlCr alloys, in as-received condition (Bragg-Brentano θ - θ configuration) and after 20 h oxidation in air at 700 °C (grazing angle, Ω = 0.5 °).

Figure 3: SEM image of bulk NiAl alloy showing the fine Ni_5Al_3 - γ' - β microstructure obtained after 20 h oxidation in air at 700 °C (cross-section).

Figure 4: TEM analysis of corrosion products formed on NiAl exposed 2 h to Na_2SO_4 in O_2 -0.1 SO_2 at 700 °C. (a) STEM image showing thin Al_2O_3 scale and thicker intrusion; (b) bright field image of an intrusion; (c) SAD pattern from the intrusion (location of SAD aperture shown in (b)) and superimposed γ - Al_2O_3 ring pattern; (d) X-ray maps of an intrusion.

Figure 5: SEM image of nodule grown on NiAl alloy after 20 h exposure to Na_2SO_4 in O_2 -0.1 SO_2 at 700 °C. The insert shows a region of intact Al_2O_3 scale and an early-stage disruption of the scale, on the same sample.

Figure 6: NiAlCr alloy after 2 h exposure to Na_2SO_4 in O_2 -0.1 SO_2 at 700 °C. (a) SEM image; (b) TEM image and X-ray maps of oxide scale and subscale region.

Figure 7: SEM images of NiAlCr after (a) 6.5 h and (b,c) 20 h exposure to Na_2SO_4 in O_2 -0.1 SO_2 at 700 °C. Image (c) shows a region where the sulfate deposit has almost entirely been consumed by reaction with the alloy.

Figure 8: SEM images of NiAl after 20 h reaction with (a) Na_2SO_4 and (b) Na_2SO_4 - MgSO_4 in air at 700 °C.

Figure 9: SEM images of (a) NiAl and (b) NiAlCr after 20 h reaction with Na_2SO_4 - MgSO_4 in O_2 -0.1 SO_2 at 700 °C.

Figure 10: Optical micrographs of NiAl surface after 20 h exposure to Na_2SO_4 in O_2 -0.1 SO_2 at 700 °C, and additional 20 h heat treatments in air with no deposit.

Figure 11: SEM image of NiAl after 20 h exposure to Na_2SO_4 - Cr_2O_3 mixed deposits in O_2 -0.1 SO_2 at 700 °C, with (a) 5×10^{-3} mol %; (b) 0.5 mol % Cr_2O_3 .

Figure A1: Equilibrium Na_2AO_2 and SO_3 activities resulting from AO dissolution in Na_2SO_4 as a function of initial p_{SO_3} (top panel), plotted for $K = 10^{-22.19}$ (obtained for $T=700$ °C from Ref. [10]) and an arbitrary $K_A = 10^5$. Standard states for all gases and condensed phases are states of pure phases at 10^5 Pa. The symbols R_i ($i=1-3$) denote the regimes identified in the text. In the intermediate regime (R2), the equilibrium $a_{\text{Na}_2\text{AO}_2}$ and p_{SO_3} are independent of the initial p_{SO_3} : the AO/ Na_2AO_2 couple acts as a buffer. In the acidic regime (R1), the solubility of AO is very low, little Na_2AO_2 is produced, and the ambient p_{SO_3} is not affected. In the bottom panel, the equilibrium $a_{\text{Na}_2\text{AO}_2}$ is plotted as a function of the equilibrium p_{SO_3} : this is equivalent to a solubility curve. The dashed lines denote four initial p_{SO_3} values shown as examples: two in the buffered regime (R2) which result in the same equilibrium composition, and two in the acidic regime (R1) which are not affected by the limited AO dissolution.

Figure A2: Equilibrium BSO_4 and SO_3 activities resulting from BO dissolution in Na_2SO_4 as a function of initial p_{SO_3} (top panel), plotted for $K = 10^{-22.19}$ (obtained for $T=700$ °C from Ref. [10]) and an arbitrary $K_B = 10^4$. Standard states for all gases and condensed phases are states of pure phases at 10^5 Pa. In the intermediate regime (R2), the equilibrium a_{BSO_4} and p_{SO_3} are independent of the initial p_{SO_3} : the BO/ BSO_4 couple acts as a buffer. In the bottom panel, the equilibrium a_{BSO_4} is plotted as a function of the equilibrium p_{SO_3} . The dashed lines denote two initial p_{SO_3} values in the buffered regime (R2) which result in the same equilibrium composition.

Figure A3: Equilibrium Na_2AO_2 , BSO_4 and SO_3 activities resulting from simultaneous AO and BO dissolution in Na_2SO_4 as a function of initial p_{SO_3} (top panel), plotted for $K = 10^{-22.19}$ (obtained for $T=700$ °C from Ref. [10]) and arbitrary $K_A = 10^5$ and $K_B = 10^4$. Standard states for all gases and condensed phases are states of pure phases at 10^5 Pa. In the intermediate regime (R2), the equilibrium $a_{\text{Na}_2\text{AO}_2}$, a_{BSO_4} and p_{SO_3} are independent of the initial p_{SO_3} : the AO/ Na_2AO_2 /BO/ BSO_4 quadruplet acts as a buffer. In the bottom panel, the equilibrium $a_{\text{Na}_2\text{AO}_2}$ and a_{BSO_4} are plotted as a function of the equilibrium p_{SO_3} . The dashed lines denote two initial p_{SO_3} values in the buffered regime (R2) which result in the same equilibrium composition.

Tables

Table 1: Phase constitution of the model alloys before and after 20 h oxidation in dry air at 700 °C. gb: grain boundaries; β' : L1_0 martensite.

Alloy	Experimental (XRD, EPMA)				Literature		
	As-received		After oxidation		1150 °C	700 °C	Ref
	bulk	gb	bulk	gb			
NiAl	$\beta' + \beta$	γ'	$\beta + \text{Ni}_5\text{Al}_3 + \gamma'$	γ'	β	$\beta + \gamma'$	[30]
NiAlCr	β		β	γ'	β	$\beta + \gamma' + \alpha$	[30]

a $\log (p\text{O}_2, \text{bar})$

b

C $\log (p\text{O}_2, \text{bar})$

Relative intensity (arb. unit)

NiAlCr

* Ni_5Al_3

×: $\alpha\text{-Cr}$

10 μm

a

Na_2SO_4

resin

Al_2O_3 scale

Al_2O_3 intrusion

500 nm

b

500 nm

c

(311)
(222)
(400)
(440)

8 nm⁻¹

d

$\text{NiO} + \text{NiAl}_2\text{O}_4$

$\gamma\text{-Al}_2\text{O}_3$

20 μm

2 μm

a

mixed sulfate

5 μm

γ' + mixed
sulfide

Ni-rich
sulfide

Al-rich
oxide

b

a

mixed sulfate

Na_2SO_4
(~1 Ni, <1 Al)

Ni-rich
oxide

10 μm

$\gamma' + (\text{Al,Cr})_3\text{S}_4$

Ni-rich
sulfide

Al-rich
oxide

b

Ni-rich oxide

mixed sulfate

10 μm

$\gamma' + (\text{Al,Cr})_3\text{S}_4$

Ni-rich
sulfide

Al-rich
oxide

C

Ni-rich oxide

20 μm

$\gamma' + (\text{Al,Cr})_3\text{S}_4$

Ni-rich
sulfide

Al-rich oxide

a

Na_2SO_4

mixed sulfate

thin Al_2O_3
scale

Al_2O_3
intrusions

10 μm

b

MgO

MgAl₂O₄

mixed
oxide-
sulfate

10 μm

γ' + sulfides

a

mixed oxides-sulfates

50 μm

$\gamma' + \text{Al}_2\text{O}_3$

b

Ni-rich oxide

Al-rich oxide

mixed oxide-
sulfate

10 μm

γ' + mixed sulfide

20 h in O_2 -0.1 SO_2
with Na_2SO_4

deposit washed off,
+ 20 h in air

+ 40 h in air

+ 60 h in air

a

$\text{NiO} + \text{NiAl}_2\text{O}_4$

NiO

Al_2O_3

20 μm

b

NiO + NiAl₂O₄

NiO

20 μm

sulfides

This scanning electron micrograph (SEM) shows a cross-section of a material with distinct layers. The top layer is dark and labeled 'NiO + NiAl₂O₄'. Below it is a lighter, textured layer labeled 'NiO'. A small rectangular box in the lower-left portion of the NiO layer is magnified in an inset. The inset shows a detailed view of the material's microstructure, with dark, irregularly shaped regions labeled 'sulfides'.

**log activity,
equilibrium**

**log $a_{\text{Na}_2\text{AO}_2}$,
equilibrium**

log activity,
equilibrium

log a_{BSO_4} ,
equilibrium

log activity,
equilibrium

log a_{BSO_4} ,
equilibrium