Effect of Environmental Sulfur on the Structure of Alumina Scales Formed on Ni-base Alloys

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Abstract

Short-term oxidation exposures of an alumina-scale forming γ' -Ni₃Al-based model alloy in air and O₂+0.1%SO₂ at 900°C revealed that the presence of sulfur can affect the kinetic competition between the θ and α structural isomorphs of Al₂O₃. After 2 hours exposure, metastable θ -Al₂O₃ growth predominated in air alone; whereas, a much larger percentage of stable α -Al₂O₃ formed during oxidation in O₂+0.1%SO₂. This promotion of α -Al₂O₃ establishment was due to sulfur enrichment on the alloy surface, which occurred even when samples were exposed to O₂+0.1%SO₂ in a low-temperature, pre-test position (~150°C), *i.e.*, prior to insertion into the hot zone. It was determined from XPS measurements that the sulfur was mainly in the S⁶⁺ valence state and, correspondingly, in the form of NiSO₄. Cross-sectional scanning transmission electron

microscopy (STEM) using energy-dispersive X-ray spectroscopy (EDS) corroborated the XPS results by detecting that a ~20 nm zone of sulfur enrichment within the surface region of a ~90 nm oxygen-rich layer formed during the pre-test exposure. A systematic explanation for this intriguing observation of sulfur promoting α -Al₂O₃ establishment is provided from the perspective of kinetics competition between θ and α . This explanation was supported by kinetic calculations and complementary tests in a low pO₂ atmosphere.

Key words: sulfur, alumina, kinetic competition, hot corrosion, surface enrichment

Introduction

Sulfur in various forms is found in the environments of a number of applications in which alloys and metallic coatings are exposed to high temperatures. Environmental sources of sulfur include the combustion of low- and high-grade fuel, sulfate deposits such as Na₂SO₄, MgSO₄, CaSO₄ or some combination of these in hot corrosion conditions, and environmental SO₂ pollution. Quite a variation in environmental SO₂ content can be detected around the world [1], with certain developing regions reporting transient levels up to about 0.1ppm [2]. Indeed, SO₂ is an important variable in salt-induced hot corrosion, which is a very aggressive mode of attack causing failures of many turbine components in the field [3]. It is well established that the extent of attack incurred during low-temperature (~700°C) hot corrosion depends significantly on the SO₂ content in the environment. Moreover, the presence of environmental SO₂ can also induce extensive internal sulfidation in conjunction with hot-corrosion attack [4].

Alloys and coatings in sulfur-bearing environments often rely on the formation of an alumina scale for protection. The establishment and growth of an alumina scale may be complicated due to alumina having a number of crystalline polymorphs, namely γ -, δ -, η -, θ -, and α -alumina [5]. Ideally, a continuous and adherent scale comprised of α -Al₂O₃ is preferred because this oxide is the most stable thermodynamically and is also the slowest growing [6]. However, during the initial stages of oxidation, particularly at temperatures below about 1050°C and for Ni-base alloys, faster-growing metastable Al₂O₃ structures (γ - and/or θ -Al₂O₃) usually predominate [7]. The metastable forms of Al₂O₃, which have a relatively open structure, grow much more rapidly than α -Al₂O₃ and will usually transform to the latter with extended exposure. Concurrent with this metastable-to- α transformation is an approximately two orders of magnitude decrease in oxidation rate [7, 8] and a ~8-10% volume reduction [6]. The latter can lead to cracking within the scale [8-10]. These changes can largely affect the protectiveness of the alumina scale to the extent that the rapid establishment of α -Al₂O₃, free of metastable-to-stable transformation(s), is preferred.

Alumina phase transformation in thermally grown scales has been the subject of extensive investigation [7, 8, 11, 12] since it was first reported [8] in the context of scaling. Most investigations have focused on the effects of alloying elements on the transformation in air or pure O₂. Alloy elements such as Cr [7], Ti [12], Fe [13] have been found to promote the θ -Al₂O₃→ α -Al₂O₃ transformation; whereas, Zr [8], La, Hf[14], Si [15], Pt[16, 17], Y[18-21] have been reported to delay this transformation. A few investigations have dealt with the environmental effects such as water vapor [22-25] and the results are not conclusive. Chevalier et al. [23] and Zhou et al. [22] reported that the

presence of water vapor promoted the $\theta \rightarrow \alpha$ on the Fe₃Al intermetallic and NiAl. By contrast, Liu et al. [24, 25] studied the oxidation of commercial FeCrAl alloys in O₂+H₂O and found that water vapor slows $\gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ transformation.

In applications related to hot corrosion, an alumina scale can form under conditions in which metastable and stable aluminas may co-exist. Recent research [26, 27] has reported that a small amount of sulfur in the atmosphere can promote metastable-to- α transformation. This observation was first reported for β -NiAl-based alloys [27]. Specifically, Ni-46Al-5Pt (in at. %) coupons were oxidized in air and O₂+0.1%SO₂ at 900°C for 100 hours. It was found that an exclusive $\theta\text{-Al}_2\text{O}_3$ scale formed on the air-exposed coupon; while, $\alpha\text{-Al}_2\text{O}_3$ predominated on the coupon exposed to the O₂+0.1%SO₂. Similar observations were subsequently observed for exposures of γ' -Ni₃Al-based systems after 20 hours of oxidation at 900°C in air, air with Na₂SO₄ deposit, and O₂+0.1%SO₂ [26]. A mechanistic understanding of the sulfur effect on alumina phase transformation is still lacking and forms the main aim of the present study.

Experimental Procedures

A model alloy of nominal composition Ni-20Al-5Cr-0.05Hf-0.05Y at.% was prepared at the Ames Laboratory's Materials Preparation Center [28] by Ar-arc melting the individual powder constituents followed by drop-casting to form a ~40 g 10-mm diameter rod. The as-cast rod was then homogenized in vacuum at 1200°C for 48 h. The final structure was single-phase γ' -Ni₃Al, as determined by optical microscopy and X-ray diffraction. The heat-treated rod was then cut to produce 1-mm thick disks. Before testing, the sample disks were abraded to a P1200-grit finish using SiC paper and then ultrasonically cleaned in acetone.

Oxidation tests in air were conducted using a horizontal resistance-heated tube furnace. The furnace temperature was calibrated prior to any testing. For a given test, the furnace was initially heated to the target exposure temperature and held for about two hours. The sample, which was contained in an alumina boat, was kept outside of the hot zone during this pre-heating period. Thermal-exposure testing commenced by manually pushing the sample boat into the hot-zone using a metallic push-rod.

Oxidation tests in O_2 - SO_2 atmospheres were also conducted using a horizontal resistance-heated tube furnace that allowed for the flowing through of a controlled atmosphere (*i.e.*, a closed system was used). Figure 1 shows the schematics of sulfidation apparatus setup. Before testing, the samples were kept near the end of the furnace tube (pre-test position) while the hot-zone was heated to the test temperature of 900°C. The maximum temperature of the samples during this heating period was measured using a thermocouple to be ~150°C. The furnace tube was first flushed with pure Ar for two hours and then flushed overnight with the $O_2 + 0.1\%SO_2$ reactant gas mix. The reactant gas was passed through a platinized honeycomb ceria-based catalyst prior to reaching the hot zone. This was done to equilibrate the gas mixture. The equilibrium gas compositions were calculated using HSC chemistry software[29] and the results are shown in Table 1. After following this procedure to establish the reacting atmosphere, the samples were pushed into the hot zone of the furnace and isothermally exposed for a fixed period. During oxidation exposure, the flow rate of the reactant gas was 12.5 cm³/min, which corresponded to a linear velocity of 0.62 cm/min. At the completion of a given exposure period, the sample was removed from the hot zone and allowed to cool naturally to room temperature.

Table 1 Equilibrium gas composition at the exposure temperature of 900°C

Flowing gas	Temperature	Equilibrium gas composition*
O ₂ +1000ppm SO ₂	900°C	P _{S₂} = 3.7×10^{-16} atm; P _{O₂} = 0.999atm; P _{SO₃} = 2.5×10^{-4} atm; P _{SO₂} = 7.5×10^{-4} atm
<i>*Equilibrium calculations for catalyzed gases allow for SO₃ formation</i>		

Photo-stimulated luminescence spectroscopy (PSLS) was used to distinguish θ -Al₂O₃ from α -Al₂O₃ in the thin oxide scales that formed. The PSLS measurements were made using a LabRam™ Confocal Raman Microscope (Jobin-Yvon/Horiba, Edison, NJ) [30]. α -Al₂O₃ is known to strongly fluoresce in response to visible laser illumination if trace quantities of chromium are present, giving a peak doublet (R1-R2) at around 693 nm [31]. The θ -Al₂O₃ peak doublet (T1-T2) is blue-shifted from that of α by approximately 10 nm [32]. The origin of the abovementioned luminescence in alumina is due to the photo-stimulation and subsequent radiative decay of excited d³ electrons associated with the substitutional Cr³⁺ ions located on octahedral sites of both θ and α [9]. Fitting of the spectra was achieved using Renishaw's WiRE v3.2 software to determine the contributing intensity and positions of the R1-R2 and T1-T2 peaks.

X-ray photoelectron spectroscopy (XPS) was used to obtain surface-state information of the exposed samples, while scanning transmission electron microscopy (STEM) was used to characterize cross-sections of the surface regions. TEM cross-section samples were prepared by the conventional method of cutting, grinding and ion thinning. The alloy samples were cut into small squares and polished to a size of 0.5x0.5mm. A stack of two samples was prepared by gluing (M-Bond610 glue) the small pieces together with the region of interest, i.e., surface layer, from one sample placed on

top and facing the surface layer of the other sample. The prepared couple was then inserted into a 3 mm brass tube. A resulting 3 mm disk or slice was mechanically polished using the Allied Multiprep Polishing system on diamond lapping films of decreasing grit size (30 μm to 0.1 μm) to 40 μm thickness. Electron transparent samples were subsequently obtained by ion milling with argon ions in a Gatan Precision Ion Polishing System at 4keV to 100 eV for a total of 3 hours at -100°C. The chemical composition profiles across the interface of the sample were obtained by spatially resolved electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDS). EELS line scans were acquired using an FEI F20 UT Tecnai TEM/STEM at 200 KeV equipped with a Gatan Tridiem spectrometer. The EDS elemental mapping was done using a ChemiSTEMTM system with FEI Super X quad windowless detectors attached to an FEI Titan TEM/STEM microscope operated at 200 KeV. High angle annular dark field (HAADF) imaging was performed while simultaneously acquiring EELS line scans or EDS elemental maps.

Results

1. γ' -Ni₃Al-based model alloy: 900°C oxidation in air and O₂+1000ppm SO₂

To understand how establishment of an α -Al₂O₃ scale can be promoted in the presence of sulfur [26, 27], short-term oxidation tests were conducted in air and O₂+0.1%SO₂ at 900°C. The γ' -based model alloy sample was exposed to O₂+0.1%SO₂ and air for 1, 2, 5, 10 and 20 hours. An individual sample was used for each exposure. Representative corresponding PSLS spectra are shown in Figure 2 for air oxidation and in Figure 3 for oxidation in O₂+0.1%SO₂. Overall, a luminescence spectrum for α -Al₂O₃ consisting of an R1-R2 doublet was detected at the wavelengths of 693nm and 695nm,

respectively. The relative positions of R1 and R2 were a few nanometers different from reported values [31], which may be due to some level of residual strain in the oxide scale [33]. The θ - Al_2O_3 luminescence spectrum consisting of the T1-T2 doublet was detected at 685nm and 687nm. T1 peaks were always detected while T2 peaks were detected intermittently, apparently when the oxide scale formed was thick enough to yield sufficient intensity of θ - Al_2O_3 -specific luminescence. The relative positions of the T1 and T2 peaks are in reasonable agreement with what has been reported in the literature for θ - Al_2O_3 [32].

After oxidation in air for one hour at 900°C, the R1-R2 doublet was observed, indicating the formation of α - Al_2O_3 . The doublet was not distinct due to low yield, but the two peaks of α - Al_2O_3 could be clearly identified. A broad θ -specific T1 peak was observed at a wavelength of 685nm, indicating θ - Al_2O_3 was also present. After 2 hours of exposure in air, the T1-T2 doublet of θ - Al_2O_3 was clearly discernible. The T1-T2 peak intensities and areas were much larger than those of the R2 luminescence from the α - Al_2O_3 , which clearly shows that θ - Al_2O_3 outgrows α - Al_2O_3 by this two-hour stage of the scale evolution. After 5 hours of exposure in air, the intensities and peak areas of both the θ -specific T1-T2 doublet and the α -specific R1-R2 doublet were greater than what were observed after 2 hours. The T1-T2 peak intensities and areas were much larger than those of the R2 luminescence from the α - Al_2O_3 . After 10 and 20 hours of exposure, θ - Al_2O_3 outgrows α - Al_2O_3 , as deduced from a comparison of the associated doublets. Thus, θ - Al_2O_3 growth quickly dominates during oxidation in air at 900°C.

For the case of oxidation in $\text{O}_2+0.1\%\text{SO}_2$ at 900°C, only the R1-R2 doublet was detected after one hour of exposure; there was no evidence of the θ -specific T1-T2

doublet. Such a result indicates that α -Al₂O₃ growth predominated during the initial 1 hour of exposure. After 2 hours of exposure, a T1 peak with a very weak intensity became apparent, indicating the minor formation of θ -Al₂O₃. The R1-R2 doublet increased in intensity and had a larger peak area than the T1 peak. When the exposure increased to 5, 10 and 20 hours, the luminescence spectra from both θ -Al₂O₃ and α -Al₂O₃ increased in intensity, but the α -specific R1-R2 doublet remained dominant, indicating that the scale, compared to that formed in air, consisted of a larger amount of α -Al₂O₃ during its entire early-stage growth period. In summary, during oxidation in O₂+0.1%SO₂, α -Al₂O₃ was the more predominant oxide in the scale from the very early stages of oxidation when compared with exposure in air.

The relative amounts of α -Al₂O₃ and θ -Al₂O₃ were semi-quantitatively estimated by comparing the R1-R2 (α) and T1-T2 (θ) doublet intensities. The volume fraction of α -Al₂O₃ after 1, 2, 5, 10 and 20 hours was estimated using the following approximation [34, 35].

$$f_{\alpha} = \frac{A_{R1} + A_{R2}}{A_{R1} + A_{R2} + \psi(A_{T1} + A_{T2})} \quad \text{Eqn(1)}$$

where A is the integrated area underneath peak intensity of a given characteristic doublet. The constant ψ is introduced to adjust for the relatively weaker luminescence from θ -Al₂O₃. The value of ψ was set as 12, since a previous study reported θ -Al₂O₃ luminescence can be 10-12 times weaker than α -Al₂O₃ luminescence [33]. In this analysis, ψ was assumed to be a constant, realizing that, in reality, it can vary due to dynamic effects. Although the real α -Al₂O₃ volume fraction within the oxide scale may be different from the calculated value, the estimated trend in the variation in the α -Al₂O₃

fraction should be reasonably represented, regardless of the ψ value used. The results are plotted in Figure 4.

A larger percentage of α -Al₂O₃ was observed after one hour of oxidation in both environments, indicating predominantly α -Al₂O₃ growth during this very early stage of scale evolution. With increasing exposure time, the fraction of α -Al₂O₃ first decreased at 2 hours and then increased at 5 hours. The extents of these changes depended on the atmosphere. Specifically, the volume fraction of α -Al₂O₃ formed in the SO₂-containing atmosphere is ~43% greater than what formed in air after 5 hours. The fraction of α -Al₂O₃ was very small during oxidation in air from 5 to 20 hours, increasing only slightly. By contrast, it is seen in Figure 4 that the comparatively higher fraction of α -Al₂O₃ in the O₂+1%SO₂ atmosphere increased with exposure time, suggesting that there was a continual establishment of α -Al₂O₃ during the scale growth during this period.

2. Sample condition before exposure to an O₂+0.1%SO₂ atmosphere at 900°C

To understand the sulfur effect in promoting the α -Al₂O₃ establishment, the sample surface condition immediately prior to high-temperature exposure to the O₂+0.1%SO₂ atmosphere was investigated. Based on the experimental procedure used, the samples sat outside the hot zone at around 150°C for at least 12 hours in an O₂+0.1%(SO₂+SO₃) environment prior to being inserted to the hot zone.

XPS was used to identify the chemical state of the sulfur enriched on the sample surface after the low temperature exposure and the resulting spectra are shown in Figure 5. The sample was exposed to O₂+0.1% SO₂ at ~150°C for 12 hours. From the broad region scan (Figure 5a), main peaks are from Ni, O and S, with a very minor Cr peak. The Sp2 peak (Figure 5c) located at 168.9 eV corresponds to sulfur in the S⁶⁺ state [36].

Figure 5 also shows the results from de-convoluting the spectrum to individual contributing peaks from S^{6+} and elemental sulfur. It was determined from this de-convolution that 98% of the sulfur exists in the S^{6+} state. The main Ni $2p^{3/2}$ peak (Figure 5b) is located at 857 eV, which corresponds to $NiSO_4$ [37-39]. As the sample contains >70at.% Ni and the majority of cation spectra are from elemental Ni, it was deduced that the surface-enriched sulfur exists primarily in the form $NiSO_4$. Järnäs et al. [40] similarly reported sulfate formation on the oxide surface of a 304L stainless steel exposed to $O_2+40\%H_2O+100ppmSO_2$ at 600°C.

Cross-sectional TEM samples were prepared from this “pre-test” sample. Figure 6 is an HAADF-STEM image and corresponding EDS elemental maps of the surface of the alloy. The presence of two distinct layers was observed. The alloy surface layer was oxygen-rich with a total thickness of ~90 nm (Figure 6b), while an outermost sulfur-rich layer ~20 nm thick (Figure 6c) was also present. This sulfur-rich layer is in agreement with the XPS results, which identified sulfur-enrichment at the surface in the form of $NiSO_4$. The formation of an outermost $NiSO_4$ layer at the low temperature of 150°C was calculated to be thermodynamically stable, as will be discussed in the next sections. It should be noted that during STEM characterization, only certain areas were found to have a sulfur-rich surface layer. This may be attributed to the TEM sample preparation, wherein the 20 nm thin sulfur layer may have been removed from some regions during the ion milling step. It may also be due to the layer being discontinuous. Regardless of the continuity of this layer, it will be reasoned in the following sections that sulfur (in some form) was retained at the surface during subsequent sample heating and served to kinetically poison the oxidation processes.

The chemical identities of the sulfur-rich and oxygen-rich layers detected by EDS (cf. Figure 6b and c) on the pre-test sample were further explored through analysis of the EELS O K edge signal. The presence of pre-peak α in the O K edge from the O-rich layer spectrum in comparison to no pre-peak in the S-rich layer (cf. Figure S1 in the Supplemental Information section) indicated that the oxygen bonding is different in these two layers, possibly NiO and/or Cr₂O₃ versus sulfate. However, confirmation of the oxygen bonding within the oxygen-rich and sulfur-rich layers was not possible due to the lack of reference spectra to compare the O K edges against for near-edge fine structure analysis, as is further discussed in the Supplemental Information section, S1.

3. Verification of the effect of surface-enriched sulfur

It is conjectured that the promoted α -Al₂O₃ establishment is related to the surface enrichment of sulfur that occurred prior to high-temperature exposure. To test this, samples of the model alloy were given the pre-test exposure (O₂+0.1%SO₂ at 150°C) and then oxidized in air at 900°C for 10 and 20 hours. The specific testing procedure involved: (1) laying the sample in the pre-heat zone of the furnace (maximum temperature~150°C) and exposing it to flowing Ar gas for two hours followed by O₂+0.1%SO₂ for 12 hours and then (2) removal of the sample from the pre-test position followed immediately by exposure to air at 900°C for 20 hours.

PSLS was conducted on the exposed surfaces and the resulting luminescence spectra are shown in Figure 7. The α -specific R1-R2 doublet was detected with very strong intensity while the θ -specific T1-T2 doublet intensity was weak. The fraction of α -Al₂O₃ was quantified to be around 50% at 10 hours when sulfur is enriched on the sample surface, even though the high-temperature exposure was done in air. The same alloy

exposed directly to air and without exposing to the pre-test condition formed predominantly θ - Al_2O_3 . The volume fraction of α - Al_2O_3 was estimated to be less than 4% within 20 hours (c.f. Figure 2 and Figure 4). Thus a small amount of sulfur on the alloy surface, present prior to high-temperature exposure, can promote α - Al_2O_3 establishment.

Discussion

1. The kinetic competition of alpha and transient aluminas

A key finding in this study is that the presence of trace sulfur in the atmosphere can promote the establishment of α - Al_2O_3 . Such a finding has only been recently reported [26, 27]. The nature of the $\theta \rightarrow \alpha$ transformation is diffusion controlled [11] and generally involves the heterogeneous nucleation of α - Al_2O_3 followed by lateral growth and associated conversion of the initially-grown θ to α . Nucleation is a thermally activated process [11], in which nuclei have to overcome a certain free energy barrier and elements migrate to nuclei by diffusion. Once α - Al_2O_3 nucleates, it grows laterally more rapidly than vertically [9, 41-43], with the α - Al_2O_3 nuclei eventually impinging and developing into a complete layer on the alloy. This layer significantly slows the outward flow of Al cations and thus stifles further θ -phase growth [44].

The α - Al_2O_3 nucleation rate and the relative growth rates of α - Al_2O_3 and θ - Al_2O_3 are important factors in determining their proportions in the initially-established oxide. The nucleation rate of α - Al_2O_3 is important because a larger density of nuclei will make it easier for this stable oxide to coalesce and form a continuous layer. The growth rates of the different alumina phases are important because before α - Al_2O_3 eventually establishes to a complete layer, there is a competitive growth of θ - Al_2O_3 and α - Al_2O_3 [42, 45]. This competitive growth can be particularly pronounced due to the significantly different

growth rates of θ -Al₂O₃ and α -Al₂O₃. Usually at low temperature in air, the much faster growth of θ -Al₂O₃ is favored to predominate initially, which in turn slows the rate of α -Al₂O₃ to establish as a layer at the alloy/oxide interface. Based on this, any effects that change the relative growth rate of θ -Al₂O₃ can affect its proportion in the scale. Stated differently, any effect that facilitates α -Al₂O₃ nucleation and lateral growth would serve to promote its establishment.

The observations in this study clearly revealed the kinetic competition between θ -Al₂O₃ and α -Al₂O₃. As shown in Figure 2, the relative peak intensities of the θ -specific T1-T2 doublet and the α -specific R1-R2 doublet change in quite different manners as a function of oxidation time. In particular, there is a dramatic difference in the intensities when going from 1 hour to 2 hours of oxidation. These intensities reflect the relative amounts of θ - and α -Al₂O₃ formed within the scale, which in turn can be ascribed to a kinetic competition between the metastable and stable polymorphs of alumina during the early stages of reaction. During early-stage oxidation in air, θ -Al₂O₃ eventually overtakes the growth of α -Al₂O₃ and is therefore the predominant phase (Figure 2), whereas, a larger percentage of α -Al₂O₃ was formed (Figure 3) throughout all stages of oxidation in O₂+1%SO₂. Interestingly, α was apparently the predominant phase in the scale at the very early stage of reaction in both air and O₂+1%SO₂ (*i.e.*, at one hour). Thus, sulfur clearly affected the kinetic competition between θ -Al₂O₃ and α -Al₂O₃ during scale establishment.

After 20 hours of oxidation in O₂+0.1%SO₂, the volume fraction of α -Al₂O₃ was around 51% (Figure 4). Without cross-sectional TEM characterization of the formed oxide scale, accurate determination of the volumetric distribution of α -Al₂O₃ is not

possible. As reported elsewhere[46], kinetic measurement of the oxidation rate of the model alloy with pre-test exposure ($O_2+0.1\%SO_2$ at $150^\circ C$) during oxidation in air at $900^\circ C$ showed a progressive decrease in k_p from $3.0 \times 10^{-13} \text{ g}^2/\text{cm}^4\text{s}$ at 2.5 hour to $1.6 \times 10^{-13} \text{ g}^2/\text{cm}^4\text{s}$ at 20 hour. By contrast, the k_p remained relatively constant at $3.5 \times 10^{-13} \text{ g}^2/\text{cm}^4\text{s}$ when the model alloy was directly oxidized in air at $900^\circ C$. These k_p values compare well with reported rate constants for $\theta\text{-Al}_2\text{O}_3$ scale growth [7]. The gradual decrease in k_p when sulfur is present is inferred to be due to sulfur promoting $\alpha\text{-Al}_2\text{O}_3$ establishment. Thus, given the measured kinetics, there is clearly a mixed mode of oxide growth during oxidation in $O_2+0.1\%SO_2$, with the volume fraction of $\alpha\text{-Al}_2\text{O}_3$ steadily increasing.

The initial predominance of $\alpha\text{-Al}_2\text{O}_3$ was unexpected, given the widely reported results that the first-formed scale is usually comprised of metastable aluminas [41, 42], with stable $\alpha\text{-Al}_2\text{O}_3$ taking over at a later stage [42]. The underlying reason for this observed sequence is still not clear, but it is apparently not limited to a Ni-based system. A recent study by Chegroune et al. [45] on the Fe-based alloy “Aluchrom YHfAl” exposed for various times at $925^\circ C$ in $Ar+15\%O_2$ also showed an initial growth of $\alpha\text{-Al}_2\text{O}_3$, followed by transient alumina growth and later transformation back to $\alpha\text{-Al}_2\text{O}_3$. After 30 minutes of exposure, those authors could detect only $\alpha\text{-Al}_2\text{O}_3$ using glancing-angle XRD. $\theta\text{-Al}_2\text{O}_3$ was detected later and its percentage increased with time up to a maximum at 14 hours, after which $\alpha\text{-Al}_2\text{O}_3$ again predominated.

2. The surface blocking effect induced by the surface enrichment of sulfur

One key finding in this study is that a 20 nm-thick layer enriched with sulfur (Figure 6c) formed on the sample surface when exposed for 12 hours to $O_2+0.1\%SO_2$ in

the pre-test position ($\sim 150^\circ\text{C}$). Based on XPS analysis, which has a $\sim 10\text{nm}$ depth of penetration limit[47], the sulfur was mainly in the form of NiSO_4 (i.e. S^{6+} state) at least in large part if it is not exclusive. Another key finding is that $\sim 50\%$ of $\alpha\text{-Al}_2\text{O}_3$ was formed during subsequent oxidation when sulfur is enriched on the sample surface, even though the high-temperature exposure was done in air (Figure 7). Thus, the low-temperature surface enrichment of sulfur can promote $\alpha\text{-Al}_2\text{O}_3$ establishment during subsequent thermal exposure. These findings are novel and a proposed mechanism is presented in the following.

To seek a mechanistic understanding of the observed sulfur effect, the formation path of NiSO_4 at low temperature was analyzed. NiSO_4 can be formed by the following reaction[48]:

Though NiSO_4 had formed at the surface, an analysis based on bulk materials thermodynamics can still provide guidance on stabilities. As can be seen in the NiO/NiSO_4 stability diagram (Figure 8), reaction (1) is only stable to proceed to the right at temperatures below about 675°C in an equilibrated $\text{O}_2+0.1\%\text{SO}_2$ atmosphere. Thus, the NiSO_4 is stable to form at low temperature ($\sim 150^\circ\text{C}$) in the pre-test position but it is apt to dissociate during heating to 900°C .

An important question would be: How is the alumina scale establishment affected at high temperature if NiSO_4 dissociates? One possibility is that after NiSO_4 dissociation, sulfur is still retained (i.e., chemisorbed) on the sample surface and has a poisoning effect on the subsequent oxidation reaction. It has been reported that sulfur can chemisorb on an alloy surface and block the surface sites required for the decomposition of the gas

molecules responsible for corrosion [49, 50]. Further, recent study on 9-12%Cr steels by Quadakkers et al. [51] showed greater adsorbing strength of SO_2 compared to O_2 . Thus, it is possible that once the available reactive adsorption sites are occupied by SO_2 or sulfur in general, O_2 adsorption, and hence oxidation reaction is impeded. Regardless of whether sulfur or a sulfur-containing species inhibits the O_2 adsorption or the O_2 decomposition on the sample surface, the oxygen supply for the scale growth will be effectively hindered. Accordingly, the following hypothesis is proposed to explain how sulfur promotes the $\alpha\text{-Al}_2\text{O}_3$ establishment: the enrichment of sulfur blocks surface sites for oxygen reaction, thus, effectively leading to a decreased oxygen supply to the extent that $\theta\text{-Al}_2\text{O}_3$ growth is hindered more than $\alpha\text{-Al}_2\text{O}_3$ growth, favoring establishment of the latter. It is assumed that such a process caused the experimental observation of sulfur apparently promoting the $\theta \rightarrow \alpha\text{-Al}_2\text{O}_3$ transformation. Regardless of the form of sulfur on the sample surface at high temperature, the sulfur-inhibited oxygen supply for oxidation will be generally referred to in this paper as a “the blocking effect” by surface-enriched sulfur.

3. Evaluation of the surface blocking effect hypothesis

The hypothesis outlined in the previous section assumes that the blocking by sulfur at the surface results in an effective decrease in the oxygen supply such that the growth rates of $\theta\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ are affected to different extents; that establishment of thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$ becomes kinetically facilitated. To evaluate this hypothesis, the oxygen supply required for maximum $\theta\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ parabolic growth rates shall be calculated.

The instantaneous amount of oxygen needed to grow α - or θ -Al₂O₃ at a maximum, diffusion-controlled rate is dictated by the oxidation kinetics. From the Arrhenius plots for Al₂O₃ scale growth [7], the 900°C parabolic rate constant is $2.2 \times 10^{-13} \text{ g}^2/\text{cm}^4 \cdot \text{s}$ for θ -Al₂O₃ scale and $6.8 \times 10^{-16} \text{ g}^2/\text{cm}^4 \cdot \text{s}$ for α -Al₂O₃ scale. The oxygen supply needed for α or θ growth, J_o , is given by.

$$J_o = \frac{d(\Delta m_o)}{dt} = \frac{1}{2} \sqrt{\frac{k_p}{t}} \quad \text{Eqn(2)}$$

where k_p is the parabolic rate constant and t is time. The calculated J_o is plotted as a function of reaction time in Figure 9. The oxygen needed for θ growth is much more than that for α due to the three-orders of magnitude difference in the respective k_p values. As time increases, the instantaneous growth rate decreases, and so the oxygen supply needed correspondingly decreases.

Based on a treatment of mass transfer in the viscous gas flow regime [52], which is presented in the Supplemental Materials section, S2, the oxygen supply in the air is calculated to be $J_{o,air} = 3.1 \times 10^{-6} \text{ (g/cm}^2\text{s)}$, which is above the scale used in Figure 9. Thus, the amount of oxygen supply in air is abundantly sufficient for both θ and α -Al₂O₃ to grow at their maximum parabolic rates. In such a case, the θ is able to kinetically displace, at least initially, the α -Al₂O₃. When sulfur is present, it is postulated that there is a surface blocking effect that essentially reduces oxygen supply in O₂+0.1%SO₂. If the oxygen supply is decreased to the level indicated by the black arrow in Figure 9, there would not be enough oxygen for θ -Al₂O₃ to grow at its maximum rate, but sufficient for the maximum growth rate of α -Al₂O₃. In this case, $k_{p,\theta}$ would decrease

relative to $k_{p,\alpha}$. When θ -Al₂O₃ formation is significantly hindered, the stable α -Al₂O₃ can more easily establish itself as a complete scale by having less kinetic competition.

To support this inference, samples of the model alloy were oxidized in 99.999% high-purity Ar (O₂<1.4ppm). As outlined in the Supplemental Materials section, S3, the oxygen supply in Ar is approximated to be $J_{O,Ar} = 4.6 \times 10^{-11}$ g/cm²s. (assuming $P_{O_2}=1.01 \times 10^{-6}$ atm). This $J_{O,Ar}$ value is indicated by the dot dash line in Figure 9. The value is below that for un-inhibited θ growth, but close to the oxygen supply needed for α growth at its reported rate. Thus, if the hypothesis that limited oxygen supply favors α -Al₂O₃ formation is valid, then one should expect to see the promoted establishment of α -Al₂O₃ in Ar. Figure 10 shows PSLS spectra from the scales formed on model alloy during isothermal oxidation in Ar at 900°C. Very strong α -Al₂O₃ peaks were clearly observed after 10 and 20 hours of oxidation. The α -Al₂O₃ fraction was estimated to be 51% after 20 hours of oxidation in high-purity Ar. The same alloy, when oxidized in air for 10 and 20 hours, formed primarily θ -Al₂O₃ (α -Al₂O₃ fraction was estimated to less than 4% within 20 hours), as shown in Figure 2 and 4. Thus, the establishment of α -Al₂O₃ was favored when exposure was done in high-purity Ar. In other words, low P_{O_2} or, in turn, low J_o , favors α -Al₂O₃ establishment. A similar result was observed on an EBPVD NiCoCrAlY coating during oxidation at 1100°C [53, 54]. Specifically, it was found in those studies that after 1 hour oxidation in 0.1Pa oxygen atmosphere, an exclusive α -Al₂O₃ scale was formed; whereas θ -Al₂O₃ scale formed when oxidized at 100Pa oxygen.

For a complete analysis of the α -Al₂O₃ establishment, nucleation rates must also be considered. For heterogeneous nucleation, there is a substrate structure effect such that any orientation that provides compatibility with α -Al₂O₃ will facilitate its nucleation [55-

57]. The same is true for θ -Al₂O₃. For example, due to an epitaxial orientation relationship between β -NiAl and θ -Al₂O₃, β -NiAl substrate prefers θ -Al₂O₃ nucleation [14, 58, 59]. For β -NiAl, low P_{O_2} might not necessarily promote α -Al₂O₃ scale establishment. However, in this study, the alloy substrate is γ' -Ni₃Al and there is no known orientation preference for either θ -Al₂O₃ or α -Al₂O₃ nucleation. Thus, it is inferred that the significantly reduced growth rate of θ -Al₂O₃ relative to that of α -Al₂O₃ in a low P_{O_2} environment promotes α -Al₂O₃ scale establishment on γ' -Ni₃Al.

Conclusions

A γ' -Ni₃Al-based metal alloy was oxidized at 900°C in air and O₂+0.1%SO₂ for 1, 2, 5, 10 and 20 hours. A kinetic competition between θ -Al₂O₃ and α -Al₂O₃ was observed during the scale growth. θ -Al₂O₃ predominates during oxidation in air after a short time, while a comparatively larger percentage of stable α -Al₂O₃ formed throughout all stages of oxidation in O₂+0.1%SO₂. Thus, the presence of sulfur is inferred to affect this kinetic competition of θ -Al₂O₃ and α -Al₂O₃ in such a way that α -Al₂O₃ establishment is promoted.

The observed promotion of α -Al₂O₃ establishment in the SO₂-bearing atmosphere was due to sulfur enrichment on the alloy surface. The enrichment occurred when samples were exposed to O₂+1%SO₂ in the pre-tested position (~150°C), outside the hot zone. It was found by XPS measurement that the sulfur was mainly in the S⁶⁺ state, which was deduced to be associated with NiSO₄. Cross-sectional STEM in conjunction with EDS confirmed a ~20 nm sulfur-rich outermost layer and a ~90nm oxygen-rich inner layer, thus providing direct evidence of sulfur enrichment at the alloy surface. At elevated temperature, this NiSO₄ is apt to dissociate, but sulfur is inferred to still be

retained on surface. The surface enrichment of sulfur, whether continuous or not, was deduced to block the surface sites for oxygen reaction and consequently have the effect of decreasing oxygen supply for the scale growth. It is assumed that with limited oxygen supply, the faster growing θ -Al₂O₃ is less favored, thus facilitating α -Al₂O₃ establishment to a continuous layer during its kinetic competition with θ -Al₂O₃. This hypothesis was supported by kinetic calculations and complementary tests in a low p_{O₂} atmosphere. The establishment of an α -Al₂O₃ scale was promoted on a model NiCrAlY alloy when oxidation took place in high purity Ar (O₂<1.4ppm) at 900°C. When oxygen supply is limited, the lateral growth rate of θ -Al₂O₃ decreases more dramatically than that of α -Al₂O₃. This inhibition of θ -Al₂O₃ growth will allow α -Al₂O₃ to gain advantage in establishing a continuous layer underneath. Therefore, the sulfur-promoted α -Al₂O₃ establishment is due to sulfur preferentially adsorbing, acting as an O₂ adsorption poison, and effectively limiting the supply of oxygen.

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Figures

Figure 1 Sulfidation apparatus setup

Figure 2 PLS spectra from the scales formed on model alloy during isothermal oxidation in air at 900°C for various times (the characteristic spectrum of $\alpha\text{-Al}_2\text{O}_3$ is R1-R2 doublet, the characteristic spectrum of $\theta\text{-Al}_2\text{O}_3$ is T1-T2)

doublet)

Figure 3 PLS spectra from the scales formed on model alloy during isothermal oxidation in $\text{O}_2 + 0.1\% \text{SO}_2$ at 900°C for various times

Figure 4 Estimated volume fraction of $\alpha\text{-Al}_2\text{O}_3$ within the oxide scale formed on model alloy exposed to air and $\text{O}_2+0.1\%\text{SO}_2$ at 900°C for 1, 2, 5, 10 and 20 hours.

Figure 5 XPS binding-energy spectra on model alloy exposed to O₂+0.1%SO₂ at pre-test position (~150°C) for 12 hours (a) broad region, (b) Ni²⁺ 2p^{3/2} region, (c) deconvoluted spectra in the S⁶⁺ 2p region

Figure 6 Cross-sectional STEM images from the alloy sample exposed to $O_2+0.1\%SO_2$ at $\sim 150^\circ C$ for 12 hours, with the alloy and alloy surface layers identified in the HAADF image (a). EDS elemental maps for oxygen (b) and sulfur (c), simultaneously acquired using the ChemiSTEMTM system, show the alloy surface to be composed of a 90 nm O-rich layer with the top-most 20 nm layer being S-rich. The circles 1 and 2 correspond to where EEL spectra were acquired from the S-rich and O-rich regions, respectively (See supplemental information, S1).

Figure 7 PSLS spectrum from the scales formed on model alloy during isothermal oxidation in air at 900°C after 150°C pre-exposure to $O_2 + 0.1\% (SO_2 + SO_3)$

Figure 8 Stability diagrams of NiO and $NiSO_4$

Figure 9 Comparison of J_o vs. t curves for α -Al₂O₃ and Θ -Al₂O₃ growth at 900°C. The oxygen supply available in the air at 900°C and the proposed decreased oxygen supply in O₂+0.1%SO₂ atmosphere due to surface blocking effect (schematically shown by grey arrow). The oxygen supply available in 99.999% high purity Ar (represented by the dash-dot line)

Figure 7 PLS spectra from the scales formed on model alloy during isothermal oxidation in high purity Ar (O₂<1.4ppm) at 900°C.