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PARTICULATE EROSION OF NiO SCALES

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ABSTRACT

The erosion behavior of brittle oxide scales on ductile alloy substrates is not well known. The oxidation of commercially pure nickel in an air furnace at 1000°C produces relatively thick NiO scales, providing a base for an investigation of the erosion behavior of scales of more complex alloys. The NiO scales formed consisted of two distinct layers, a columnar outer layer and a fine-grained, porous inner layer. The erosion testing was conducted at room temperature using an air blast tester. Angular silicon carbide particles were used at velocities of $V_p = 100$ mps and 30 mps, for two impingement angles, $\alpha = 20^\circ$ and 90° .

Erosion damage of the NiO scales has been observed and interpreted using simplified postulates based on fracture propagation concepts. NiO duplex scale is removed in a two-step mechanism. Plastic flow indentation and lateral crack growth in the columnar outer layer is the first step in the erosion mechanism. In the second step, pits are

produced from Hertzian cone fractures formed in the inner layer. The removal of oxide is by chipping away of the cracked scale of the outer and inner layers, enlarging the pits. At higher velocities, particle sizes, and impingement angles, the erosion of the thinner oxide scales to the bare nickel occurred in seconds. It was observed that the strength of the bond between the two scale layers and between the scale and the metal substrate directly related to the erosion behavior. NiO scales thicker than 50 μm introduced some protective action during the initial period of erosion of the outer scale. The microstructure, mechanical properties and bonding state of oxide layers are important parameters in erosion behavior of oxide scales.

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INTRODUCTION

The commercial stainless steels and superalloys have been designed to resist high temperature corrosion by a selective oxidation of chromium to form protective oxide films on external surfaces.¹ In coal gasification environments, protective oxides are not formed at the gas/metal interface because of competing oxide and sulfide forming reactions and unacceptable rates of corrosion can result. Gas compositions of coal conversion processes contain molecular species based on oxygen, hydrogen, carbon, nitrogen and sulfur. The principal corrodants are sulfur and oxygen. The combined sulfidation-oxidation of SAE 310 stainless steel produces non-protective multilayered sulfide scales.² Erosion of scales by solid particles contained in the reactive gases of coal conversion systems further inhibits the formation of protective scales on stainless steels and superalloys.

Before studying the complex behavior of combined erosion-corrosion of metallic components in coal gasification environments, it is important to have some understanding of the mechanisms of erosion of brittle scales on a ductile substrate. The objective of this program is to investigate the solid particle erosion of oxide scale at room temperature. The two-layered NiO scale on pure nickel used is similar to scale morphologies of more complex alloys; it provides a base for an extensive investigation of the erosion behavior of scales on ductile metals. The scale eroded in this investigation was formed on commercially pure nickel in an air furnace at 1000°C. It consisted of

a columnar outer layer and a fine equiaxed grained inner layer with a large quantity of pores.³

The response to multiple solid particle impacts is quite different for ductile and brittle materials. The general form of the mass removal rate as a function of the impingement angle, α , for ductile and for brittle materials is shown in Fig. 1.⁴ This curve shows that a brittle oxide formed on a metal should provide some protection as it should have a quite low erosion rate for particles impinging at angles less than about 50° . However, Fig. 1 data are for a fully dense body of brittle material. For the type of thin, duplex scale layers investigated here, some microstructural parameters will be important in erosion behavior, i.e., thickness of brittle layers, grain boundaries, porosity, impurities, stresses induced by oxide growth and interlayer adhesion properties. Moreover, a brittle material can exhibit ductile type erosion behavior at low impingement angles when the diameter of the impacting particles are small.⁴

Intuitively, it could be assumed that the fracture toughness which determines a material's resistance to fracture should be an important factor in scale erosion. However, in the case of scales formed in-situ on metal substrates, the role of microstructure and the elastic properties of the oxide layers have to be considered. The effective local toughness of the scale is reduced at layer interfaces and grain boundaries, and this reduction can result in easier material removal. Observing the fracture mechanisms which occur as the result of impact of hard SiC particles on the NiO scale will provide a better

basis for understanding the role of the microstructural parameters involved in the brittle scale erosion process than the simple application of fracture mechanics. The experimentally observed mechanisms can also be used to better understand the effects of scale morphologies and behavior on the erosion resistance of materials that form scales at high temperatures.

DESCRIPTION OF EXPERIMENTS

Nickel 200 (commercially 99.5 percent nickel) in the form of sheet specimens (50 x 19 x 1.6 mm) was oxidized in an air furnace at 1000°C for times up to 72 hours. Prior to oxidation, the specimens were ground free of oxide, using 240 grit Al_2O_3 , polishing in water.

The nickel 200 specimens develop regular scales with a tendency to spall slightly. Typical microstructure of the duplex scale on nickel 200 is shown in Fig. 2. The duplex structure consisted of a columnar coarse grained external layer with the grains oriented perpendicular to the surface and a fine-grained, porous internal layer. Scale thickness, h , was measured directly with a microscope using a calibrated optical system. The location of the metal-oxide interface is approximate in the photomicrograph because a step in plane exists between the metal surface and the oxide surface. This error is assumed to be negligible in comparison with the average values of h measured at many random sites.

Scale thickness, h , has been plotted as a function of the cube root of the time of oxidation in Fig. 3. The proportionality of scale thickness to the cube root of time has been observed by Rhines and Connell⁵ for high purity nickel (99.99 percent pure). Our experimental results for Ni-200 oxidized at 1000°C in the air furnace gives a large increase of scale thickness for $t^{1/3} \geq 2.5$ ($t \approx 16$ hr). This limit can be assumed to be the starting point of the change in the microstructural growth of the oxide scale.

The kinetics of scale formation are, in general, extremely sensitive to minor impurities; two or more orders of magnitude in scale thickness have been observed.⁶ The discrepancy between our results and the Rhines-Connell curve in Fig. 3 for 72 hours could be due to these impurities' effects.

The microstructural distinction between the two layers is mainly one of the grain shape and size. The growth of the NiO scale begins by the formation of oriented grains perpendicular to the surface of the nickel (columnar structure). At 1000°C, for an oxidation time greater than 16 hours, new fine, equiaxed grains of NiO are nucleated due to the presence of impurities in the nickel 200.

As the oxidation process is continued with the presence of the fine grained inner layer, the texture of the external surface of the columnar outer layer varies with faceting of the oxide crystals. At this stage, it would be difficult to define the thickness of the scale. The outer layer is mainly characterized by a highly dense, textured, columnar structure. Small grains in the inner layer show several crystallographic orientations. A large quantity of pores are formed as a result of insufficient plastic flow of the NiO to maintain the contact with the substrate and void formation due to outward cation diffusion. Impurities are accumulated at the oxide grain boundaries resulting in an inherent weakness of these boundaries compared to the lattice. The same phenomenon can be assumed at the interface between the two layers.

The erosion testing was conducted at room temperature using an air blast tester shown in Figs. 4 and 5. The tester operated by feeding the eroding particles from a vibrating hopper into an air stream where they are mixed for uniform particle distribution, and then propelled down the tube by the air flow. Angular silicon carbide particles (SiC) were used as the eroding material, having a hardness of about 4500 (VHN) and a density of 3.2 gm/cm^3 . Most erosion testing was conducted using $250 \text{ }\mu\text{m}$ diameter SiC particles (-60 +65 mesh). The testing device allowed for a choice of particle velocity by changing the pressure drop and gas flow rate across a 30.5 cm long by 4.75 mm inner diameter stainless steel nozzle.

Particle velocities used in this study were 100 meters/second (mps) and 30 mps. These velocities were determined using a rotary disc velocity measurement device⁷ having a slot in the upper disc that particles from the nozzle could pass through and a soft brass plate on the lower disc that the particles impinged upon. The rotary velocity tester, as shown in Fig. 5A and B, allowed for ready calculation of velocity by measuring the distance between a reference (zero) mark and the erosion pattern formed on the lower disc at a given air pressure and angular velocity of the discs. The velocity was calculated using the parameters and equation shown in Fig. 5B.

It was found that the particle velocity was a function of the inner diameter of the nozzle, the loading factor (grams of particles/grams of air), the pressure drop across the nozzle, the internal surface roughness of the nozzle, and the size and shape of

the particles. To insure constant velocities during tests, the above parameters were kept as constant as possible. Figure 6 shows the variation of particle velocities measured at different pressures as influenced by the particle feed rates, ρ . The values recorded are compared with earlier device calibration data⁸ and show an acceptable correlation.

At any fixed setting of vibration, pressure and hopper inclination from the horizontal (see Fig. 4), the particle feed rate, ρ , is assumed to remain constant. However, an experimental measurement of the variation of the particle feed rate, ρ , as a function of the mass of impinging particles, M_p , remaining in the hopper as it is emptied shows that the feed rate, ρ , decreases as the loading, M_p , decreases (Fig. 7). This variation is important when a small amount of impinging particles are used for the study of initial erosion processes at both impingement angles used in this study, $\alpha = 90^\circ$ and $\alpha = 20^\circ$. The angle of impingement, α , was established for each test by rotating the sample under the nozzle. The sample was held in a cradle which was cantilevered from the front port door.

The multiple particle impact experiments were conducted by impacting five, 60-gram hopper charges of SiC on the sample surface with weight loss measurements of the sample taken after each 60-gram amount. A total of 300 grams (five charges) of SiC were used to erode each sample. Other tests were conducted using a very small quantity of particles to determine erosion initiation behavior and to obtain separate impacts in the field of the eroding flow. An experimental

measure gives a number of SiC particles ($d = 250 \mu\text{m}$) equal to

$N_p \approx 1500 \pm 100$ particles for a loading mass of 0.1 gm.

DAMAGE OBSERVATIONS IN NiO SCALE

Before proposing an analytical erosion model for NiO scales, it is necessary to know what the relative probabilities of occurrence are of one or more of several possible mechanisms involving nucleation and growth of damage in the NiO scale. This information has been obtained through microscopic observations of the sequence of events leading to material removal and verified by a series of controlled tests.

A flow of 0.1 gm of 250 μm diameter SiC impacting particles ($N_p \approx 1500$ particles) at velocity $V_p = 100$ mps was used to determine the distribution and morphology of isolated impacts. Figure 8 shows multiple single particle impact pits on the surface of $h = 80$ μm thick NiO scale caused by impacting flow ($\Delta M_p = 0.1$ gm) at $\alpha = 90^\circ$. Each pit was made by an individual particle and they are randomly distributed with different orientations. The diverse shapes of the pits formed depend on the sharpness and orientation of the angular particles at the moment of contact with the target surface. The detail of a single impact pit in Fig. 9 shows a characteristic plastic zone induced with some observable radial crack formation in the pit side walls.

A mechanical polishing of the NiO scale surface which removed a thin layer ($\Delta h = 10 - 10$ μm) has shown an increase in the size of the area affected by the impact (the dark areas) below the surface as shown in Fig. 10 by optical microscopy (OM). This observation can be attributed to the formation of lateral cracks under the impact pit. In some cases, cracks are formed around the pits as well (Fig. 11).

However, this phenomenon is not frequent and can be attributed to other mechanisms than erosion such as the cracks being induced by thermal stresses around a fault during oxide scale growth.

Continuing the polishing of the NiO scale surface until a zone close to the outer, columnar-inner, fine grain interface is reached, shows circumferential cracks symmetric about the load axis (Fig. 12). The diameter of these circumferential cracks increases inside the inner layer after progressive removal of scale layers. Figure 13 shows the larger cracks at a smaller magnification than Fig. 12 in the inner layer and involves cone crack propagations of Hertzian type cracks. This cone crack configuration in the inner layer is an indirect effect of the impact deformation in the outer scale layer. The single particle impact appears to induce a constant size, flat contact area at the interface of the layers.

A schematic representation showing a proposed sequence of crack initiation events as the result of single particle impacts is illustrated in Fig. 14. At impact loading, subsurface lateral cracks can be assumed to form beneath the plastically deformed indentation pit and to propagate practically parallel to the surface in the columnar outer layer. Lateral crack propagation can also be induced at the interface between the scale layers resulting in a loss of scale by exfoliation of the outer layer. Ring cracks also form at the interface between the two layers. As a result of multiple particle impacts, downward propagation of these ring cracks proceeds along

trajectories to form a Hertzian type truncated cone (frustrum cone) fracture.

Figures 15 and 16 show multiple single impact pits for the same eroding conditions as the preceding figures but for a thinner NiO scale of thickness, $h = 50 \mu\text{m}$. In general, the pits formed in the thinner scale are not single plastic indentations as occurred in the $h = 80 \mu\text{m}$ scale. Around the impacting zone, an exfoliation of the columnar outer layer occurs. This may be seen especially well in the detail shown in Fig. 16. This behavior is more evident for the still thinner NiO scale thickness, $h = 20 \mu\text{m}$, which is composed mainly of the columnar outer layer morphology and where the underlying ductile matrix nickel has an even greater effect on the deformation of the scale.

The sequence of the erosion process of NiO scale, $h = 80 \mu\text{m}$, can be further defined by increasing the number of impacting particles. Figures 17 and 18 show the pits formed after impact of a flow of 0.2 gm of SiC, $250 \mu\text{m}$ diameter particles ($N_p \approx 3000$ particles) at a velocity, $V_p = 100$ mps and angle, $\alpha = 90^\circ$. Additional impacts continue to nucleate pits and remove small chips of the cracked outer layer resulting in a mechanism of erosion by pit growth in the outer layer. The inner layer, no longer protected, is in turn, subjected to multiple particle impacts which initiate chipping of material from the surface in the vicinity of the conical fractures. This chipping appears to be a preferential fine scale fragmentation of the material surrounding initial conical fractures, resulting in the formation of

frustrums (Fig. 18). This process has an analogy in the particulate erosion of fused silica by glass beads observed by Adler.⁹

Figure 19 shows the side view of a frustrum formation in the inner layer of NiO scale. A progressive increasing of the amount of impacting particles for the same impacting conditions confirms the postulated erosion mechanisms.

Figure 20 shows the crater formed by the total removal of the NiO scale (both layers) for a mass of 0.3 gm, 250 μm diameter SiC particles ($N_p \approx 4500$ particles) at $V_p = 100$ mps and $\alpha = 90^\circ$. The edge of the pit shown in Fig. 21 at a higher magnification shows the three stages in NiO scale erosion: multiple single particle pits, frustrum formation and impact pits on the nickel substrate. Figure 21 also shows the transition areas where the eroded nickel substrate is observable on the left of the picture. The ghost lines in the nickel substrate conform to the periphery of the Hertzian cone cracks at their intersection with the substrate nickel.

POSTULATED MECHANISM OF SOLID PARTICLE IMPACT FRACTURE IN BRITTLE NiO SCALE

This section discusses the erosion mechanism described in the section on Damage Observations in NiO Scale in terms of the postulated active stress fields and the observed target material deformation and cracking.

Solid particle erosion damage of brittle materials has been studied by Sheldon and Finnie.¹⁰ These authors studied the erosive regime where the contact between the particle and the body is exclusively elastic, usually referred to as Hertzian fracture. Their analysis considers dynamic forces between the surface and the particle resulting in a prediction of the volume removed for a material with specific properties. The fracture at the surface is a function of the volume of material constrained in the primary erosion zone in relation to the surface and volume flows. Their theory assumes the applicability of Hertzian fracture, elastic response, and predicts reasonable velocity and site exponents. Their analysis for solid body brittle material is not based on a material removal mechanism that is consistent with the experimental observations of NiO scales discussed in the previous section.

Erosion tests on NiO scales involve permanent plastic deformation within the contact zone and the inducement of cracks. The character of the damage created by the impact of the solid particles onto a brittle material is not only dependent on the dynamic conditions of the impacting flow, but is equally a function of the elastic-plastic

response of the target. This response is determined, in turn, by the relative plastic deformation properties, acoustic impedance, etc., of the projectile and the target. The behavior of the target is an integration of the properties of the brittle scale and the underlying ductile base metal. The thinner the scale is, the greater the effect of the ductile metal.

FRACTURE INITIATION ANALYSIS

Outer Layer NiO Scale

The damage studies of erosion of the outer layer NiO scale show that the particle impacts induce both elastic and elastic-plastic target response. The dynamic erosion phenomenon cannot be assumed to be a simple extension of the quasi-static processes proposed by Wilshaw.^{11,12} Evans and Wilshaw¹³ suggest a semi-empirical approach based on quasi-static indentation fracture for establishing the relative importance of the target properties on the impact damage of brittle materials. Some inelastic deformation will tend to occur about any high stress concentration in an otherwise elastic indentation field.¹¹ Such a situation poses complex problems in stress analysis. It is not easy to establish which of the two active plastic deformation processes, shear induced plastic flow or localized hydrostatic pressure induced densification, dominates within the small contact zone in a given target material. However, through the introduction of simple modes, basic concepts for elastic-plastic behavior can be expressed.

Directly below the erosive particle indenter in Fig. 22 a hydrostatic compression region occurs (shaded areas on either side of indenter) surrounded by an ideally plastic region within an elastic matrix, all in the outer scale layer. A symmetry of the elastic-plastic boundary conditions is assumed for simplification. This symmetry should be modified for an angular indenter. After one complete loading cycle caused by a single particle impact, a number of

radial cracks have been initiated (see cracks in the side wall of the plastic indentation in Fig. 9). The stress distribution after unloading has resulted in a tensile stress field beneath the indentation and a compressive stress field around it as shown in Fig. 22. The tensile stresses initiate lateral cracks beneath the plastically deformed indentation that are practically parallel to the surface (see Fig. 10). These lateral cracks are the basis for the initial scale loss, which generally occurs upon subsequent particle impacts that extend them to form free chips.

Inner Layer NiO Scale

The fracture initiation by ring and cone cracks in the inner layer NiO scale can be well defined using the Hertzian elastic field response.¹⁵ In the case of the fine grained, porous inner layer, this type of crack initiation is due to the propagation of stress patterns from the impact of particles on the outer layer (Fig. 23). The brittle, porous inner layer is not capable of undergoing plastic deformation and, instead, cracks will be generated. In the absence of deformation-induced nucleation centers in the inner layer, the fracture will initiate at a preexisting flaw in the inner layer surface just outside the impact zone where the principal tensile component reaches its maximum. The fracture begins its growth by running around the contact zone along the circular stress trajectories of the ideal Hertzian field. Parallel to this inner layer surface ring crack, a downward propagation of the surface ring occurs along

the maximum stress trajectories to form the fully-developed Hertzian truncated cone cracks.

An analytical model for this fracture initiation and propagation in the inner layer is very complex. A quantified value will depend on the dynamic elastic analysis of contact. Moreover, the crack formation is determined by the size and distribution of precursor micro-cracks (porosity), the grain size and the strength of the adhesion of the inner layer to the substrate nickel. This interface is not easy to analyze.

Figure 24 shows the preferential adhesion of the inner layer along the grain boundaries of the nickel. This figure also gives an illustration of the high density of porosity near the interface between the nickel and the inner layer.

EXPERIMENTAL MEASURES OF EROSION RATE OF NiO SCALES

The crack formation and growth mechanisms in NiO scale eroded by SiC particles, $d = 250 \mu\text{m}$, described in Section 3, indicate that erosion mass loss by removing scale chips should be dependent on the thickness and microstructure of the scales. For a particle velocity, $V_p = 100 \text{ mps}$, and an impingement angle, $\alpha = 90^\circ$, the variation of the mass loss, M_E , compared to the mass of impacting particles, M_p , shows three different erosion periods; first an incubation period, then an acceleration and finally, a steady state period. These periods vary for the different NiO scale thicknesses investigated as shown in Fig. 25. For the same mass of impacting particles, M_p , the erosion mass loss, M_E , decreases proportionately with a decrease in the NiO scale thickness. This erosion mass loss can be related to time, M_p being proportional to the time (Fig. 7).

By comparison with the erosion behavior of the nickel substrate, the erosion mass loss of NiO scales involves a shorter incubation period followed by a relatively high acceleration period. This behavior is more apparent in Fig. 26 showing the initial period in the NiO scale erosion ($M_p = 0$ to 1 g). The incubation period (absence of any erosion mass loss) is more pronounced for the thicker scales ($h \geq 50 \mu\text{m}$). The amount of erosion in the initiation period decreases with increasing thickness. The nickel substrate is initially exposed (arrows for each curve in Fig. 26) after an amount of impacting particles which increases with the increase of the NiO scale thickness.

An instantaneous erosion rate, E_i , has been plotted against the mass of impacting particles in Fig. 27. The erosion rate, E_i , is the instantaneous slope at each point of the curves in Fig. 26. At the limit, E_i is the differential coefficient of the curves.

$$E_i = \frac{\Delta M_E}{\Delta M_p} \rightarrow 0 \frac{\Delta M_E}{\Delta M_p} = \frac{dM_E}{dM_p} \quad [1]$$

The erosion rate shows a peak value for each NiO scale thickness that increases with scale thickness. The values of the maximum erosion rate occur prior to the transition between NiO and NiO/Ni exposure (black signs in Fig. 27). The values decrease from $E_{i \text{ max}}$ = 120 mg/g, for $h = 100 \text{ } \mu\text{m}$ to $E_{i \text{ max}} = 35 \text{ mg/g}$ for $h = 20 \text{ } \mu\text{m}$. This peak erosion rates for all scale thicknesses except $h = 20 \text{ } \mu\text{m}$, which has essentially no inner scale, occur at the same quantity of impacting particles.

The erosion rate at 1 gm of impacting particles in Fig. 27 appears to have leveled off to a steady state value, but the steady state erosion rate for the NiO plus nickel substrate was measured at 0.3 mg/gm and, so, the curves gently slope toward this value with more weight of impacting particles. The nickel substrate incubation period extends to between 3 and 5 gm of particles, so the erosion shown in Fig. 27 is primarily the widening of the eroded area in the NiO scale. Since the thickness of the inner scale is greatest for the thickest scale, 100 μm , its rate is highest for the entire period plotted in Fig. 27.

Test results for NiO scales, $H = 80 \mu\text{m}$ and $h = 50 \mu\text{m}$, eroded at the same impacting conditions, but at an impingement angle, $\alpha = 20^\circ$, are shown in Figs. 28, 29 and 30. Figure 28 shows that for the 20° impingement angle, the general erosion behavior of NiO scales has the same characteristics that were observed for the 90° impingement angle over the longer erosion period but differs markedly in degree during the initiation period, the erosion being 20 times slower at 1 gm of impacting particles at $\alpha = 20^\circ$ than at $\alpha = 90^\circ$. It has been generally observed in the erosion of brittle materials that the erosion rate increases with increasing impingement angle (Fig. 1). The incubation period is longer than that measured for $\alpha = 90^\circ$ and the slope for the acceleration period is less (see Fig. 29). A greater mass of impacting particles is necessary to reach the transition point between NiO and NiO/Ni exposure at $\alpha = 20^\circ$ compared to $\alpha = 90^\circ$. For the two thicknesses of scale studied at $\alpha = 20^\circ$, the maximum erosion rate, E_i , occurred at the transition point between NiO and NiO/Ni exposure rather than prior to it as occurred at 90° (Fig. 20). The maximum erosion rate has a value of $E_{i \text{ max}} = 4 \text{ mg/g}$ for $h = 80 \mu\text{m}$ and $E_{i \text{ max}} = 2 \text{ mg/g}$ for $h = 50 \mu\text{m}$, which is an order of magnitude less than the peaks observed at $\alpha = 90^\circ$.

The curves measured for $\alpha = 90^\circ$ have been plotted in Fig. 30 (dashed lines) to show the effect of the change in impingement angle on the erosion rate of the NiO scales.

At steady state erosion, the erosion rate at $\alpha = 20^\circ$ for the $80 \mu\text{m}$ scale was $E_i = 0.6 \text{ mg/g}$ and for the $50 \mu\text{m}$ scale was $E_i = 0.5 \text{ mg/g}$.

The steady state erosion rate measured for the NiO plus nickel substrate at $\alpha = 90^\circ$ was $E_i = 0.3 \text{ mg/g}$. The erosion rates measured for unoxidized nickel were $E_i = 0.3 \text{ mg/g}$ at $\alpha = 20^\circ$ and $E_i = 0.15 \text{ mg/g}$ at $\alpha = 90^\circ$. This indicates that the NiO scale loss was contributing to the steady state erosion of the combined NiO/Ni target material.

Some tests have been performed to check the effect of the faceted NiO scale surface on erosion behavior. After a light mechanical polishing of the facets, the erosion data showed no change compared to the as-grown columnar grain outer scale surface conditions.

A change of impacting conditions by decreasing the relative particle diameters ($d = 30 \text{ }\mu\text{m}$) and the particle velocity ($V_p = 30 \text{ mps}$) resulted in a significant decreasing of the erosion rate during the NiO scale eroding period.

DISCUSSION

This study of erosion of oxide scales has been oriented to correlate the thickness and the microstructure of NiO scales with the fracture mechanisms induced by multiple impacts of hard particles of SiC.

Material Removal Sequence

The sequence of cracking and material removal for NiO scale erosion is illustrated by the schematic in Fig. 31. At the sites of initial, discrete impacts, the first cracks to form in the two-layered NiO scale are the radial cracks and the lateral cracks that form just under the impact pits and, subsequently, at the interface between the columnar and fine-grained NiO layers. Chips of scale begin to be removed when the radial and, especially, lateral cracks interact (E_1). Also at this time the ring cracks form and the conical fractures are initiated. The removal of material occurs in the outer layer by chipping and pit growth (E_2). When the erosion extends into the porous inner layer, the rate of erosion rapidly accelerates (E_3). It reaches a peak when the maximum effective impingement angle along the pit wall occurs. After this point, the increasingly steep pit wall angle results in an effective shallower angle of impingement between the incoming particles and the eroding pit wall and the erosion rate decreases. At point E_4 , the bare nickel substrate begins to be exposed, but, because of its threshold period for erosion, does not erode, resulting in a further fall-off in the erosion rate curve. The NiO crater continues to widen and the

initiation of Ni substrate erosion occurs at 3 - 5 gm of erodant. The combined rate of erosion is somewhat greater than that of the nickel substrate only, but is heavily influenced by it.

Figure 32 plots the area of the crater formed by the impacting particles, A , starting at test time = 0 against the amount of erosion, M_E , that has occurred. The curves can be interpreted using the sketches in Fig. 31 even though Fig. 31 describes the behavior of individual pits and Fig. 32 describes the whole crater being formed under the particle flow from the test nozzle. The incubation period, E_1 , when the outer, columnar scale is being plastically deformed and then cracked laterally and the initial loss of outer scale to condition E_2 show no material loss at the ordinate scale used in Fig. 32. The initial removal of inner layer scale, which is easier to remove, causes a high mass loss of target material without much growth in the crater diameter. As condition E_3 is reached, the impacting particles can more easily break off outer layer chips because the outer layer of scale has been somewhat undermined by the conical cracks and the rapid rate of removal of inner scale and the crater grows in diameter with less material removal. When the base metal nickel is exposed, condition E_4 , only the scale crater walls are being eroded, presenting a much smaller target to the impacting particles and the crater grows slowly with respect to the amount of material removal.

Crack Analysis

An elementary calculation of lateral crack length, C_e , based on the experimental erosion results gives some information for

determining the erosion mechanism in the columnar outer layer NiO. For a determined increment of mass of impacting particles, ΔM_p , the erosion rate, E_i , can be expressed in first approximation by

$$E_i = \frac{\Delta M_E}{\Delta M_p} \quad [2]$$

where ΔM_E is the erosion mass loss.

$$\Delta M_E = \Delta V \cdot \delta_{IS} \quad [3]$$

with δ_{IS} the density of the outerlayer scale and ΔV the volume removed by the impacting particles (ΔM_p)

$$\Delta V = N_u V_i \quad [4]$$

where N_u is the number of impacting particles and V_i the volume of scale removed by each particle. This volume V_i is assumed to be limited by the length of the interacting lateral cracks, C_e

$$V_i = \pi C_e^2 h_i \quad [5]$$

where h_i is the depth of the lateral crack below the surface. It is assumed that h_i is equal to the radius, a , of the indentation crater. Experimental measures of impact craters from SiC 250 μm particles at velocity, $V_p = 100$ mps and impinging angle, $\alpha = 90^\circ$, give the following relationship when $a \cong h_i \cong h_I$, where h_I is

the thickness of the outer layer. Finally, we obtain a relation for the lateral crack length, C_e , combining Equations [2] and [5]:

$$C_e = \left(\frac{E_i \Delta M_p}{\pi N h_I \delta_s} \right)^{1/2} \quad [6]$$

A calculation of C_e values is presented in Table I. The transition value of the erosion rate, E_i , between erosion of the outer and inner oxide layer where the faster eroding inner layer being eroded occurs between E_w and E_3 conditions in Fig. 31. The total number of impacting particles, N , is a function of the mass of impacting particles, M_p . Experimental measures give $N \approx 1500$ particles for $\Delta M_p = 0.1$ g. The density of the columnar outer layer is assumed to be $\delta_s = 6.8 \text{ cm}^3$, the density of dense NiO. Assuming a regular distribution between the impacts, it was possible to measure the distance between impact pits, λ , on the impacting surface area, A (the total crater area), measured experimentally (Fig. 32). An erosion efficiency factor is used for the actual number of particles inducing a pit, $N_u = 0.7 N$.

The empirical analysis summarized in Table I shows that when the diameter of the lateral crack zone is large enough to span between individual impact pits, $\lambda < 2C_e$, for the NiO scale, $h = 20 \text{ } \mu\text{m}$, which only has a columnar outer layer, the erosion mechanism can be attributed to the formation of interacting lateral cracks at the depth $h_I = h$, the scale thickness, causing a decohesion of the weak bond between the NiO scale and the nickel substrate. This is seen in

Table I

Scale thickness h (μm)	100	80	50	20
Outer layer thickness h_I (μm)	30	30	25	20
Erosion rate at transition between outer and inner scale erosion	4	6	15	20
E_i (10^{-3}g/g)				
Mass of impacting particles M_p (g)	0.15	0.10	0.10	0.25
Quantity of particles N	2250	1500	1500	3750
Quantity of pits created N_u	1575	1050	1050	2625
Eroded crater area $A(10^{-6}\text{m}^2)$	30	20	20	35
Distance between impact pits λ (μm)	138	138	138	115
Diameter of lateral crack zone $2C_e$ (μm)	40	50	86	118

Fig. 31 for the $h = 20 \mu\text{m}$ scale. For the double-layered NiO scales ($h > 20 \mu\text{m}$), the lateral cracks cannot span the distance between individual impact pits and an incubation is required to propagate the lateral cracks before chip removal of the outer scale is possible.

Relation of Scale Morphology to Erosion Rate

The effect of the scale morphology of the two-layered NiO scale on its erosion behavior is significant. The dense, columnar, outer scale appears to be able to absorb the initial kinetic energy transfer from the impacting particles by a combination of plastic flow and sub-critical size, lateral crack propagation. After the nucleation period for material removal is over, the outer scale begins to erode by chip formation along lateral cracks tying together impact pits. The rate of this erosion increases as the outer scale is penetrated and reaches a peak rate when the inner, more porous and friable scale is eroding. As the erosion gets near the inner scale-metal interface, it decreases. This sequence, which was discussed above and is shown in Fig. 31, can be directly related to the changes in the integrity of the scale microstructure.

The morphology of the duplex NiO scale on nickel is very similar to the formation of duplex sulfide scales on an austenitic stainless steel.² Thus, the behavior of the NiO scale observed in this investigation has direct applicability to the sulfidation scales that occur on commercial alloys used in coal conversion systems. Furthermore, the results of the morphological study of the sulfide scales in Reference 2 can be used to gain a better understanding of the role of

scale morphology in the erosion process. Figures 33, 34 and 35 taken from Reference 2 show the change in the microstructure of the duplex sulfide scale going from the outside columnar scale to the scale interface with the base metal. The sulfide scales, having weaker bonds between the scale layers than the NiO scales, could be separated and the upper and lower surface of each of the two layers could be observed on the SEM. The sequence and rate of erosion of the NiO scales will be discussed, using the sulfide scale micrographs as models.

Figure 33 shows that the outer surface of the outer scale consists of closely packed columnar grains, some of the grains rising above the general plane of the scale surface. It is this material that undergoes the plastic deformation to form impact pits. Figures 8 and 9 show this type of scale surface in the NiO. It is this dense scale with the columnar grains oriented to provide the greatest strength that resists the initial impacting particles during the nucleation period. As the outer scale's surface is cracked so that the lateral cracks span the distance between the impact pits, chipping removal of the scale begins. As the scale is penetrated, the morphology approaches that shown in Fig. 34, the underside of the outer scale. This portion of the outer scale is more equiaxed and is porous. The porous scale is less resistant to erosion and, thus, the erosion rate increases, as denoted by E_2 in Fig. 31.

The outer surface of the inner scale is shown in Fig. 35, upper photo. It is equiaxed and is quite porous. The low strength of this

porous material makes it vulnerable to the eroding force of the impacting particles. The Hertzian cone fractures serve to further decrease the integrity of the inner scale, making it still more susceptible to erosion by chipping. The erosion of this microstructure is fast, resulting in an increasing erosion rate to the peak rate at E_3 in Fig. 31. As the inner scale erosion surface approaches the scale-metal interface, the porosity begins to decrease, eventually achieving the morphology shown in Fig. 35, lower micrograph at the scale-metal interface. The increasing density of the fine grained scale has an ever-increasing resistance to erosion and the erosion rate decreases from the peak rate shown in Fig. 31. The change in effective angle of impingement as the eroded crater grows, discussed in the Material Removal Sequence above, also contributes to the shape of the curves in Fig. 31.

Analysis of Erosion Rates

The plots of erosion presented in Section 6 above give several insights into the erosion behavior of the duplex NiO scale. The increase in the amount of erosion for the same weight of impacting particles as the thickness of the scale increases, shown in Fig. 25, coupled with the measurement of the thickness of the outer and inner scales shown in Table I indicates that the thicker the more porous inner scale is, the easier it is to erode. The outer scale has a relatively constant thickness over the range of scale thicknesses tested. The inner scale thickness ranges from 70 μm for the 100 μm scale to 25 μm for the 50 μm scale. The 20 μm scale consists primarily

of outer scale. Once the dense outer surface of the outer scale is penetrated and porous material is reached by the impacting particles, the thicker the inner scale is, the less transfer of the kinetic energy of the impacting particles through the scale to the ductile metal occurs and, hence, the scale removal efficiency of a given number of impacting particles is greater. Figure 27 shows that the erosion rate of the scales at the peak and after it varies directly as the thickness, additional evidence of the fact that the thicker the inner scale is, the easier it is to erode.

While the outer scale grows to approximately the same thickness for the three thicker scales tested, its integrity and erosion resistance increases with increasing time at the oxidizing temperature. Figure 26 shows that the incubation period is more pronounced for the thicker scales. Also, the amount of erosion that occurs in the initiation period decreases with increasing total scale thickness.

The thicker scales provide some increment of protection to the base metal from the erosion process. Figure 26 shows that the incidence of combined NiO/Ni erosion is increasingly delayed as the total scale thickness increases. However, the amount of this delay is very small and has no practical importance.

The 20 μm scale, which consists primarily of outer scale structure, has a greater erosion resistance than the thicker scales, as seen in Figs. 25, 26 and 27. The increased erosion resistance of the outer, columnar scale can have a practical significance in elevated temperature combined erosion-corrosion behavior. Since the

outer scale forms first, in cases where it is being removed by erosive forces as it forms, the less erosion-resistant inner scale will never have a chance to form. Thus the most resistance scale morphology will be present.

Comparing Fig. 29 for $\alpha = 20^\circ$ erosion and Fig. 26 for $\alpha = 90^\circ$ erosion shows the effect of the dense, more erosion-resistant outer scale at the beginning of the erosion period. The $\alpha = 20^\circ$ scale specimens have lost 1 mg of scale after 1 gm of eroding particles have impacted, while the $\alpha = 90^\circ$ specimens have lost on the order of 20 mg. This difference can be considered more than a straight impingement angle effect on a homogeneous brittle material. Rather, it is the protective shield of high erosion resistant outer scale acting at $\alpha = 20^\circ$ to protect the less erosion-resistant inner scale.

The protective effect of the outer scale can also be seen in Fig. 30 which plots erosion rates at both impingement angles. The peak rates for the 80 and 50 μm thick scales at $\alpha = 90^\circ$ are 60 mg/gm and 45 mg/gm, respectively (from Fig. 27) compared to the peak rates at $\alpha = 20^\circ$ of 4 mg/gm and 2 mg/gm, respectively. The peaks have also moved, from 0.25 gm of particles at $\alpha = 90^\circ$ up to 5 mg of particles for $\alpha = 20^\circ$.

The behavior of the ductile substrate nickel is consistent with the pattern of erosion of ductile metals as the impingement angle is varied, see Fig. 1. In Fig. 28, the erosion rate of the nickel at $\alpha = 20^\circ$ is 0.3 mg/gm while at $\alpha = 90^\circ$ (Fig. 25) it is only 0.15 mg/gm. Since the peak erosion rate of ductile materials occurs around $\alpha = 20^\circ$ and the rate subsequently decreases with increasing impingement angle, the data in Figs. 28 and 25 for base nickel is

consistent. Steady state erosion tests that were simultaneously eroding both scale and substrate metal also show the impingement angle effect on ductile metals. At the steady state conditions of NiO/Ni combined erosion where much of the eroding surface is metal, the erosion rates at $\alpha = 20^\circ$ for the 80 μm thick scale was 0.6 mg/gm and for the 50 μm thick scale was 0.5 mg/gm. At $\alpha = 90^\circ$, the steady state erosion rate for all thicknesses of scale was 0.3 mg/gm. The lower rate at $\alpha = 90^\circ$ is due to the lower rate of erosion of the nickel because of the impingement angle.

Halo Effect

The erosion tests by multiple particle impacts are characterized by some specific conditions of the particle flow from the test nozzle. The particle velocity, V_p , the true impingement angle, α , decrease at the boundaries of the eroded crater, creating a "halo" effect.¹⁶ It has been determined on metals that at 60° impingement angle, the amount of material loss in the "halo" zone is less than 3 percent of the total material loss. At 90° this percentage should be even less. Since the primary test condition, α , in this NiO scale erosion investigation was 90° , the halo effect can be considered a minor one.

CONCLUSIONS

The two different scale morphologies in the duplex NiO scale formed on commercially pure nickel each have a different mechanism and rate of erosion. The actual loss of material from both the layers, however, have essentially the same mechanism, i.e., chipping away of cracked scale material.

The outer scale layer has a columnar microstructure and fails by a sequence of: plastic deformation of the surface forming individual impact pits; formation of lateral cracks beneath the impact pits, especially at the interface between the outer and inner scale layers; and eventual connection of the impact pits through crack propagation causing chips of scale to be removed.

The inner scale layer has a porous, equiaxed microstructure and fails by a sequence of: ring cracking at the interface between the outer and inner scale layer; downward propagation of the ring cracks as the result of multiple particle impacts along trajectories to form Hertzian type truncated cone fracture; and chipping away of the porous, cracked scale material.

The erosion susceptibility of each layer of the NiO scale can be related to the strength, integrity and orientation of its microstructure. The dense, columnar grain, outer layer has a greater erosion resistance than the porous, equiaxed grain, inner layer. The morphology of the layers is very similar to those of sulfides formed on austenitic stainless steel and the easier to separate and microscopically observe sulfide layers can be used as models for the

NiO scales. The changing rates of erosion through the scale layers can be related to the changes in microstructure.

The role of the ductile nickel substrate in the erosion of the brittle NiO scale can be deduced by comparing the erosion rates of the scales as a function of scale thickness. The thinner scales transfer more of the kinetic energy of the impacting particles to the ductile nickel and, hence, erode at lower rates than the thicker scales. As the thicker scales are removed, their rates of erosion decrease to a rate that becomes nearly the same for all scale thicknesses.

The outer scale resists erosion more at an impingement angle of 20° rather than at 90° , which is typical for brittle materials. At low impingement angles, the outer scale protects the inner scale until it is removed, resulting in an erosion rate $1/20$ of that which occurs at $\alpha = 90^\circ$ after the first gm of particles has impacted the surface.

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- Figure 1. Erosion as a function of angle of impingement for aluminum (ductile) and high density aluminum oxide (brittle). Results adapted from Reference 1.
- Figure 2. Morphology of duplex NiO scale formed during oxidation of nickel 200 at 1000°C for 72 hours. Optical microscopy by polarized light.
- Figure 3. NiO scale growth as a function of the cube root of exposure time in air at 1000°C.
- Figure 4. Schematic diagram of the room temperature erosion tester.
- Figure 5. A) Schematic diagram of erosion tester with rotary particle velocity testing device installed.
B) Calculation of particle velocity.
- Figure 6. Variation of particle velocity, V_p , with differential pressure ΔP across nozzle for SiC particles.
- Figure 7. Variation of particle feed rate, ρ , as a function of the mass of impinging particles, M_p , for SiC particles at a particle velocity, $V_p = 100$ mps.
- Figure 8. Scanning electron micrograph (SEM) of multiple single impact pits on surface of $h = 80 \mu\text{m}$ thick NiO scale, using 0.1 gm of 250 diameter SiC, $V_p = 100$ mps, $\alpha = 90^\circ$.
- Figure 9. Scanning electron micrograph of a single impact pit on NiO surface.
- Figure 10. Optical micrography (OM) of multiple single impact pits after surface polishing to a depth $\approx 10 \mu\text{m}$ for same impacting conditions as in Figure 8.

- Figure 11. Crack formation in the NiO scale induced by thermal stresses.
- Figure 12. Optical micrograph of ring cracks formed at the interface between outer and inner scale layers as the result of multiple single impacts. Impacting conditions same as those for Figure 8.
- Figure 13. Optical micrograph of ring cracks formed by conical, Hertzian type cracks in the inner layer of NiO scale. Impacting conditions same as for Figure 8.
- Figure 14. Schematic illustrating the types of cracking events that occur during loading by single particles.
- Figure 15. Scanning electron micrograph of multiple single impact pits on NiO scale ($h = 50 \text{ } \mu\text{m}$) using 0.1 gm of 250 μm diameter SiC particles at $V_p = 100 \text{ mps}$, $\alpha = 90^\circ$.
- Figure 16. Scanning electron micrograph of a single impact pit of NiO surface ($h = 50 \text{ } \mu\text{m}$). Impacting conditions same as for Figure 15.
- Figure 17. Scanning electron micrograph of multiple single impact pits on NiO surface ($h = 80 \text{ } \mu\text{m}$) using 0.2 gm at 250 μm diameter SiC, $V_p = 100 \text{ mps}$, $\alpha = 90^\circ$.
- Figure 18. Scanning electron micrograph of frustrum formation in inner layer of NiO scale, by multiple impacts. Impacting conditions same as for Figure 17.
- Figure 19. Optical micrograph showing the side view of a frustrum formation inside the inner layer of the NiO scale.

- Figure 20. Scanning electron micrograph of multiple impact pits on NiO Surface ($h = 80 \mu\text{m}$) using 0.3 gm of $250 \mu\text{m}$ diameter SiC, $V_p = 100 \text{ mps}$, $\alpha = 90^\circ$.
- Figure 21. Scanning electron micrograph showing three states on NiO scale erosion: multiple single impact pits at the surface of outer layer, frustrums formation inside the inner layer and pits in nickle substrate, from right to left.
- Figure 22. Schematic showing the stress-strain fields caused by the impact of a single particle on the outer NiO scale.
- Figure 23. Schematic view showing the sequence of crack formation and growth events during single particle impact on the outer and inner NiO scale.
- Figure 24. Optical micrograph of the transition zone between the inner layer and the nickel substrate showing the preferential oxidation growth along the grain boundaries and the porosity.
- Figure 25. Plot of erosion mass loss, M_E (mg), versus mass of impacting particles, M_p (gm), for Ni and NiO scales of thickness, $h = 100, 80, 50, 20 \mu\text{m}$, using $250 \mu\text{m}$ diameter SiC, $V_p = 100 \text{ mps}$, $\alpha = 90^\circ$.
- Figure 26. Initial period of eroded NiO scales showing erosion mass loss, M_E (gm), versus mass of impacting particles, M_p (gm). Impacting conditions same as for Figure 25.

- Figure 27. Initial period erosion rate versus mass of impacting particles, M_p . Impacting conditions same as for Figure 25.
- Figure 28. Plot of erosion mass loss, M_E , versus mass of impacting particles, M_p , for Ni and NiO scales, $h = 80, 50 \mu\text{m}$, using $250 \mu\text{m}$ diameter SiC, $V_p = 100 \text{ mps}$, $\alpha = 20^\circ$.
- Figure 29. Initial period of eroded NiO scale showing erosion mass loss, M_E , versus mass of impacting particles, M_p . Impacting conditions same as for Figure 28.
- Figure 30. Initial period erosion rate value, E_i , versus mass of impacting particles, M_p . Impacting conditions same as for Figure 28.
- Figure 31. Schematic view illustrating the sequence of crack formation and growth events during multiple particle impacts on the duplex NiO scale.
- Figure 32. Plot of erosion mass loss, M_E , versus the area, A , of the eroded crater for Ni and NiO scales.
- Figure 33. Microstructure and composition of the top surface of the outer layer (gas-scale interface) of a sulfide scale formed on 310 stainless steel formed at a sulfur potential of 10^{-2} atm ; $t = 5 \text{ hr}$. a), b), and d) show the morphological variations, and c) gives the composition of the columnar crystal at the spot indicated in a).

Figure 34. Microstructure and composition of the bottom side of the outer layer of a sulfide scale formed on 310 stainless steel: a) scanning electron micrograph of the surface; b) same as in (a) but higher magnification; c) EDAX analysis of the overall surface shown in (a); d) EDAX analysis of grain indicated by arrow in (b).

Figure 35. Microstructure and composition of the top and bottom surfaces of the inner layer of a sulfide scale formed on 310 stainless steel:

- a) Scanning electron micrograph of the top surface;
- b) EDAX analysis of overall area shown in (a);
- c) EDAX analysis of crystallite indicated by arrow in (a);
- d) Scanning electron micrograph of the bottom surface;
- e) EDAX analysis of the overall area shown in (d).

FIGURE 1.

XBL 793-974

FIGURE 2.

FIGURE 3.

XBL 793-975

XBL775-5525

FIGURE 4.

L = DISK SEPARATION
 S = ARC LENGTH BETWEEN EROSION MARKS
 R = RADIUS TO ARC LENGTH
 ω = ANGULAR VELOCITY - REV/SEC
 V_p = PARTICLE VELOCITY
 $= 2\pi R\omega L/S$

XBL 775-5524

FIGURE 5.

FIGURE 6.

XBL 793-976

FIGURE 7.

XBL 793-981

XBB 784-4664

FIGURE 8.

XBB 784-4663

FIGURE 9.

XBB 784-4644

FIGURE 10.

XBB 791-410A

OM

FIGURE 11.

XBB 784-4642

FIGURE 12.

XBB 784-4641

FIGURE 13.

XBL 786-9271

FIGURE 14.

XBB 784-4661

FIGURE 15.

XBB 784-4657

FIGURE 16.

XBB 784-4656

FIGURE 17.

XBB 784-4654

FIGURE 18.

XBB 784-4645

FIGURE 19.

XBB 784-4653

FIGURE 20.

XBB 784-4652

FIGURE 21.

FIGURE 22.

XBL 793 - 982

XBL 793 - 983

FIGURE 23.

FIGURE 24.

XBL 786-9270

FIGURE 25.

XBL 786-9269

FIGURE 26.

XBL 793-977

FIGURE 27.

XBL 79I-7824

FIGURE 28.

XBL 793-980

FIGURE 29.

XBL 793-978

FIGURE 30.

XBL 793-991

FIGURE 31.

XBL 793 - 979

FIGURE 32.

OUTER SCALE MORPHOLOGY

(GAS SCALE INTERFACE)
 T 1070 K REACTION TIME 5 HRS

FIGURE 33.

OUTER SCALE MORPHOLOGY

(BOTTOM SIDE OF THE TOP SCALE)
T = 1070 K REACTION TIME = 5 HRS

XBB 763-2063

FIGURE 34.

INNER SCALE MORPHOLOGY

T = 1070° K REACTION TIME = 5 HRS
A) TOP SIDE OF THE LOWER SCALE
B) SCALE-ALLOY INTERFACE

XBB 763-2065

FIGURE 35.

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