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## Erosion-corrosion and wear (\*)

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**Abstract.** — The basic processes of wear, erosion and erosion-corrosion are reviewed. It is shown that oxide debris can accelerate wear when it is present as particulates, or protect and reduce friction when it is present as a glaze. Erosion-corrosion processes can be understood and organized in a series of regimes that represent a sequence of change in the relative intensities of erosive and corrosive processes. Types of mechanism expected to feature in oxide spallation and in the erosion-corrosion of alloys are described and, finally, the areas that require serious study in order to achieve further understanding of this subject are indicated.

### 1. Introduction.

Although a good understanding exists of the mechanisms of the high temperature oxidation and hot corrosion of metals, the effects of mechanical influences on high temperature attack, which usually results in enhanced degradation, are far from completely understood. Substantial progress has been made towards understanding the mechanisms of erosion-corrosion of pure metals and specific alloys, in particular the role of oxide formation and its removal. Similarly, the formation of oxide can either increase or decrease the rate of wear of metal surfaces in sliding contact.

### 2. Wear and oxidation.

Friction, due to relative motion of surfaces in contact, reflects the energy absorbed in the welding and fracture of asperities on the surfaces and in the plowing of surfaces by wear particles [1, 2]. At low temperatures, where surface oxides form slowly, metal to metal contact results in wear of the metal surface by abrasion in which metal particles are detached and may become oxide coated. As the temperature is increased, the tendency to form oxide and the fraction of oxide to oxide contact increase. Since oxide cohesion is generally less than metal cohesion, less energy is required to break the bonds between oxide asperities and the friction between the surfaces is correspondingly reduced. In fact, if oxide formation were suppressed, metal to metal wear would increase with increasing temperature, eventually leading to seizure or friction welding.

The reduction in friction due to the formation of surface oxide increases up to a critical temperature at which a complete oxide cover, or glaze, is produced by oxidation, fragmentation and consolidation under the pressure of contact.

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(\*) Keynote lecture.

Stott [3] has given a clear account of the wear mechanisms during the like on like abrasion over a range of temperatures. The results indicate a strong correlation between frictional forces and wear rates. At low temperatures, where the friction is highest, the wear rate is also high. This is explained by a mechanism involving the generation of debris, representing attrition, and the extent to which it can be oxidized and compacted to form a friction reducing glaze. The ready formation of such glazes corresponds to greatly reduced wear rates and defines the critical temperature for the material in terms of wear and friction. This observation was confirmed by Iwabuchi [4], who introduced  $\text{Fe}_2\text{O}_3$  particles between mild steel surfaces and found wear to be increased, except when the particles compacted.

At low temperatures, the debris formed is initially metallic and scars the metal surface. Such debris is comminuted between the sliding surfaces and converted to oxide particles or oxide covered metal particles. At high temperatures, more of the debris can convert to oxide and the metal surface can undergo oxidation to aid glaze formation, resulting in the relatively low wear or abrasion rates seen at higher temperatures in figure 1 [3], where Jethete (Fe-12%Cr) and Nimonic 75(Ni-20%Cr) were studied.

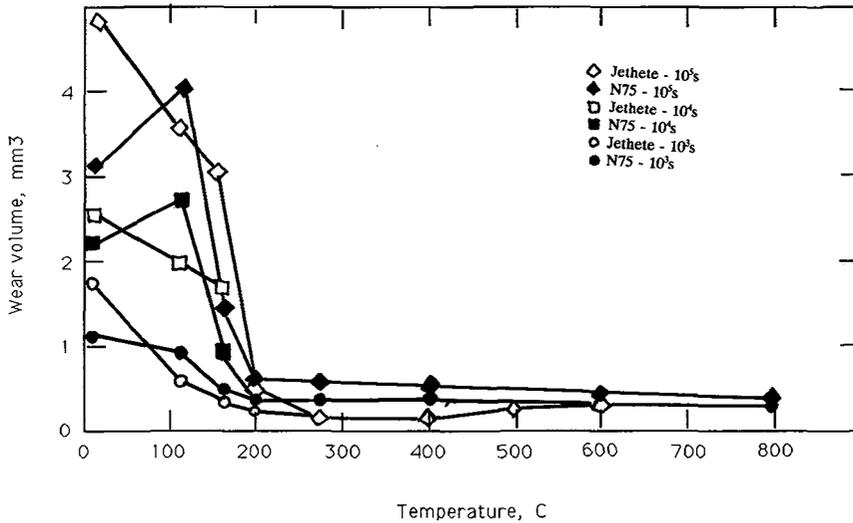


Fig. 1. — Effect of temperature on wear. Results of like on like abrasion for times indicated [3] for jethete M 152 (Fe-12%Cr) and nimonic 75(Ni-20%Cr).

When the oxide formation rate is comparable with the rate at which it is abraded, the oxide may thicken, aided by comminution and compaction of the oxide debris, under the pressure of the sliding contact, to form a glaze. Glaze formation is promoted when the debris produced has good adhesion and cohesion and is compacted rather than removed during sliding. During formation of the glaze, the oxide flows plastically rather than cracking, perhaps due to the constraint of a compressive situation [5]. At low temperatures the glaze is thought to form by the compaction of debris more than by oxide growth [6]. If the degree of oxidation during heating to the test temperature is small, the glaze formed will, initially at least, contain oxides of all of the components of the alloy [7]. If substantial selective oxidation occurs during heat-up, the glaze will initially be composed of that oxide.

The temperature of transition to low wear rates appears to be associated less with the ability to form an oxide than with its mechanical stability and, perhaps, a critical degree of plasticity [3]. In general, oxide systems with good cohesion and metal-scale adhesion will show a lower transition temperature to low wear rates, for instance nickel can form a wear-protective oxide at room temperature, whereas Ni-20Cr, which forms  $\text{Cr}_2\text{O}_3$ , cannot [8].

Wear-protective oxide glaze formation can be enhanced by the presence of certain compounds such as water vapor [9], ferric chloride, and possibly sulfides, furthermore certain oxides such as  $\text{MoO}_3$ ,  $\text{ZnO}$ ,  $\text{B}_2\text{O}_3$  etc. respond to stress *via* a ductile rather than a brittle manner and can even be used as high temperature lubricants [10, 11].

### 3. Erosion-corrosion.

Under ideal conditions, oxidation of a metal surface produces a passivating diffusion barrier [12]. In conjoint attack by erosion and corrosion simultaneously, the substrate is subjected to a second influence which is attempting to remove the passivating layer and which is influenced by variables such as particle size, shape, velocity, loading in the gas flow, angle of impingement, temperature and the composition of the gas.

The interaction between the basic processes of erosion and corrosion is complex, but can be rationalized into a series of regimes with a smooth transition from one regime to the next as the relative intensity of one process is varied with respect to the other [13]. An extreme example of erosion is provided during the combustion of coal in a fluid bed, in which heat exchanger tubes are exposed to an erosive medium of slow moving, large, particles which impact at all angles at a very high loading in an aggressive atmosphere that might be able to support the formation of sulfides as well as oxides. Another extreme situation is the case of the gas turbine in which rapidly moving smaller particles impact on the blades in an atmosphere that is primarily oxidizing.

To study such a diverse and complex phenomenon, one may simulate operational conditions, and compare the performance of different alloys, or provide an apparatus to control the primary parameters and attempt to deduce the basic mechanisms of the erosion-corrosion interactions. Both of these approaches have been used and a substantial amount of information has been compiled. Primarily, measurement of rates of degradation is combined with examination of the exposed specimens, both on the attacked surface as well as in section.

**3.1 EROSION PROCESSES.** — Most of our understanding of erosion mechanisms of brittle and ductile materials relates to room temperature. For the erosion-corrosion of metals at high temperature, the primary requirement is to understand the behavior, under erosion, of a scale on a deformable substrate. The scale may be regarded as thin or thick, depending on whether or not the deformation on impact extends to the metal.

Finnie [14], treated erosion at acute angles as cutting or machining of the specimen surface, but an understanding of the erosion rate variation in the region of  $90^\circ$  incidence required the introduction of work hardening to the model [15, 16]. A two stage mechanism for ductile erosion was proposed by Tilly [17], in which a lip of metal displaced by one particle is removed by a subsequent particle and Sundararajan [18] has recently published an extensive review and model of the erosion of ductile materials. It is also necessary to consider localized deformation and adiabatic heating [19, 20] to explain the generation of shear lips that are removed by subsequent impacts.

Work hardening of platelets [21], or delamination due to the coalescence of voids below the surface [22], may also feature in erosion mechanisms. Void formation and cracking have

been observed for iron [23] and copper [24] and attributed to vacancy condensation in regions of high dislocation density. Low cycle fatigue has also been cited for the erosion of ductile materials [25, 26]. It should be remembered that models of ductile erosion, that involve work hardening mechanisms, are unlikely to apply at high temperature.

Brittle materials, which usually erode most rapidly at 90° [27], are also capable of plastic deformation with very small erodent sizes [28, 29]. This is important for erosion-corrosion at high temperatures, where the mechanism of degradation depends upon response of the surface oxide to erosive impact. Such response will depend on the state of stress in the oxide arising from growth stresses [30], the erosive impacts, the plasticity of oxides [31-34] and the ductile-brittle behavior of the scale [35, 36].

The response of a brittle material to an erosive impact can involve the generation of Hertzian elastic stress fields in the case of spherical indentors, or the formation of median and lateral vents in the case of sharp indentors. The alternative, dynamic, situation must be analyzed in terms of the propagation of stress waves through the body and Rayleigh waves along the surface of the body [13]. The erosion of brittle materials has been considered by Finnie and Vaidyanathan [37] using the Hertzian analysis, and by Evans and Wilshaw [38] who introduced plasticity into the analysis and considered elastic and plastic wave formation, using a dynamic model for erosion [39].

**3.2 EROSION-CORROSION INTERACTIONS.** — The results reported on erosion-corrosion involving pure metals, alloys, simple and complex atmospheres can be coordinated into a sequence of related regimes of interactive mechanisms.

Levy *et al.* [40, 41] studied a range of steels containing 2.24%-25%Cr, 0.5%-1%Mo and 9%-20%Ni. When fluid bed combustors were simulated, using 50-100  $\mu\text{m}$  alumina, with 5  $\mu\text{m}$  coal ash flowing at 5-15 m/s, thick multilayered scales of iron and chromium oxides were formed. At higher velocities, 30-70 m/s, steels containing more than 9%Cr formed thin, smooth, adherent  $\text{Cr}_2\text{O}_3$  scales with low rates of metal loss. Steels with less than 9%Cr developed thick scales of iron and chromium oxides, with high rates of metal loss. The type of interaction between erosion and corrosion apparently depends on the oxide formed and its rate of growth, the above being an example of changing regimes of interaction by changing the conditions. In the case of alloys, a change of regime could occur with exposure time as the composition of the alloy surface and the mode of oxidation change. This may explain the observation that the scales formed on the lower Cr alloys were thicker than on the same alloy under erosion-free oxidation. It is also possible that the presence of erosion in some way enhanced the growth rate of the scale.

Wire *et al.* [42] studied the erosion-corrosion of a range of iron, nickel, and cobalt alloys, exposed to atmospheres typical of coal gasification, using alumina particles and erodents typical of coal derived particles. The results showed that the erosion-corrosion resistance increased with the chromium content and with decreasing test temperature. The erosion damage to the surface layers apparently allowed the oxidants to penetrate and produce internal attack of the metal forming iron and nickel sulfides.

Hutchings *et al.* [43] studied the erosion-corrosion of several steels at low velocity in fluid beds between 100-400 °C. They found that, whereas the metal wastage rate increased by tenfold, the mechanical properties varied only by about 20%, over the same temperature range. This confirms the important role of oxide formation in erosion-corrosion mechanisms. The formation of an oxide layer that can withstand the impact of erosion has been found to provide some protection [44, 45], in common with cases of wear.

Wright *et al.* [46] studied similar alloys to Wire [42], but under the conditions of fluid bed combustion. The alloys with the highest resistance to oxidation showed the lowest rates of

erosion-corrosion degradation. They concluded that the formation and removal of a scale is the dominant mechanism of degradation in erosion-corrosion, as opposed to the direct removal of metal. In addition, above a threshold velocity, erosion appeared to dominate the attack by achieving penetration of the scale or its complete removal.

Results similar to those obtained using fly ash from fluid beds and pulverized coal combustion were observed using 12  $\mu\text{m}$  alumina particles [46]. This reinforces the validity of using unreactive alumina particles to study mechanisms in the laboratory, so long as conditions are avoided that would lead to liquid formation or chemical reactions in the case of ash.

In the cases of ductile alloys that normally form a thin protective oxide layer, Wright *et al.* [46] found that the impact damage is confined to the oxide film and does not deform the metal at low impact energies. They suggest that the oxide film suffers brittle erosion at the impact sites, where oxidation resumes, leading to stepped increases in oxidation rate at the individual sites and a substantially increased rate of attack. If the time between impacts at any place is less than the time required for the oxide to grow to the original thickness, then the scale will show thinning. Sethi and Wright [47] proposed that each erosive impact removed a footprint of scale by brittle fracture, up to a critical thickness, beyond which the scales did not respond in a brittle fashion but, instead, eroded at the surface. Clearly, the achievement of the critical thickness represents a boundary between regimes of interaction.

Sundararajan [48] considered erosion-corrosion in terms of the size of the zone of deformation in the oxide consequent upon impact. The erosion simply removed the oxide surface at a constant rate, for thick scales, but all of the scale was removed down to the metal at the impact site on brittle spalling which was considered to occur on reaching a critical thickness, up to which it was plastic and ductile. Both Sundararajan [49] and Kang *et al.* [50] expect oxidation affected erosion to begin when the impact causes plastic deformation of the metal surface.

Very small ( $< 5 \mu\text{m}$ ) particles were found simply to follow streamlines and to deposit on stagnant zones of the target surface instead of causing erosion [51].

Very little data exists concerning the erosion-corrosion attack of metals for the case of chemically active erodents. Stephenson *et al.* [52-54] studied the erosion-corrosion of commercial alloys using potentially reactive erodents such as sodium sulfate, sea salt and carbon particles. Apart from the effect of sea salt on oxide adhesion, no effect of chemical reaction was reported. These authors also addressed the ductile-brittle transition for oxides.

When the erosion flow is nominally at  $90^\circ$  incidence and the metal substrate is deformed plastically, the eroded surface can resemble an array of mounds and valleys distributed randomly over the specimen surface [50]. At reduced erosive intensity, the erosive impact is contained by the oxide layer, the metal is not deformed and a flat surface is produced with impact marks similar in size to the size of the particles. In order to observe this transition more readily, Kang *et al.* [50] and Chang *et al.* [55-57] studied the erosion-corrosion of nickel and cobalt at temperatures between 600-800  $^\circ\text{C}$ , using 20  $\mu\text{m}$  alumina particles impacting at speeds in the range 70-180 m/s. A pattern of hills and valleys is formed on nickel, corresponding to plastic deformation of the underlying metal, whereas cobalt developed an oxide scale with a flat surface. This illustrated by the different regimes of interaction between erosion and corrosion and the possibility of crossing from one regime to the next by changing parameters, such as particle velocity or loading rate, to affect the erosion intensity, temperature, atmosphere composition or the nature of the metal studied to control oxidation kinetics and the oxide characteristics. Kang [50], and Hogmark [58] proposed such a simple scheme of such regimes.

Kang [50] also showed, figure 2, that the degradation of nickel and cobalt by erosion, in the absence of oxidation, was very slow compared with that in the presence of oxidation. The

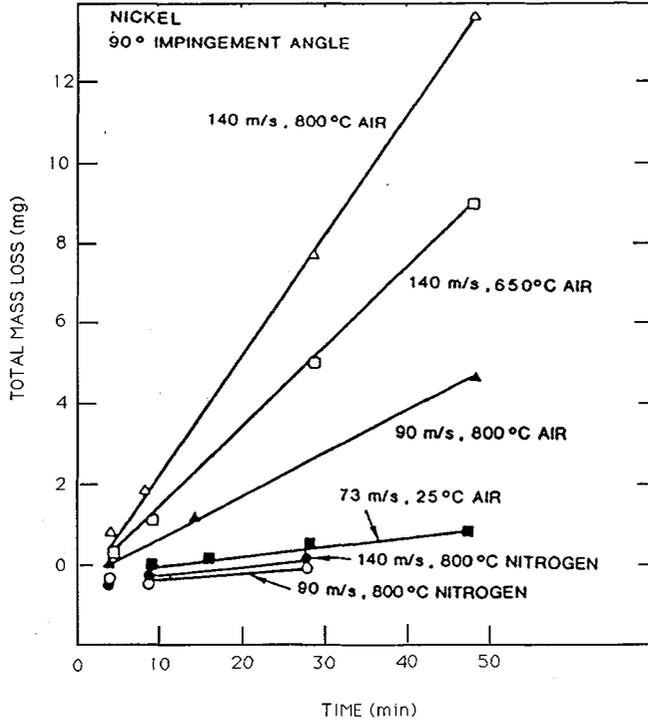


Fig. 2. — Erosive loss kinetics for nickel at 90° impact [50].

formation of oxide and its removal by erosion was thus demonstrated [50] to be an important aspect of erosion-corrosion interaction.

Rishel *et al.* [59] presented, figure 3, a logical scheme of interaction between erosion and corrosion, based on the proposals of Kang [50] and Hogmark [58] but extended to incorporate regimes where spalling and enhancement of oxidation by erosive impact occur. The regimes are basically pure erosion, erosion enhanced oxidation and oxidation affected erosion.

Pure erosion refers to the erosion of the metal only or to the erosion of the oxide only, as in the case of very thick scales.

Erosion enhanced oxidation is one of the primary erosion-corrosion interactions and refers to situations where a scale provides complete cover of the surface, but is being degraded on its outer surface by an erosive stream, whose impacts are contained by the oxide layer and do not directly affect the metal substrate mechanically. If the corrosion rate exceeds the erosion rate, then the scale will grow up to a limiting thickness where the erosion rate is equal to the scale growth rate. This has been confirmed for the case of cobalt by Chang *et al.* [55], as shown in figure 4. Rishel [13] produced an interesting result by exposing nickel in atmospheres containing  $\text{SO}_2$  at various flow velocities and loading rates, using  $20\ \mu\text{m}$  alumina particles. Where thick duplex scales of nickel sulfide and oxide were formed, the erosive impacts apparently suppressed the formation of voids and improved the scale-metal contact enhancing the corrosion rate, as reflected in the thicker scale formed in the presence of erosion than for corrosion alone, in spite of the removal of scale by erosion.

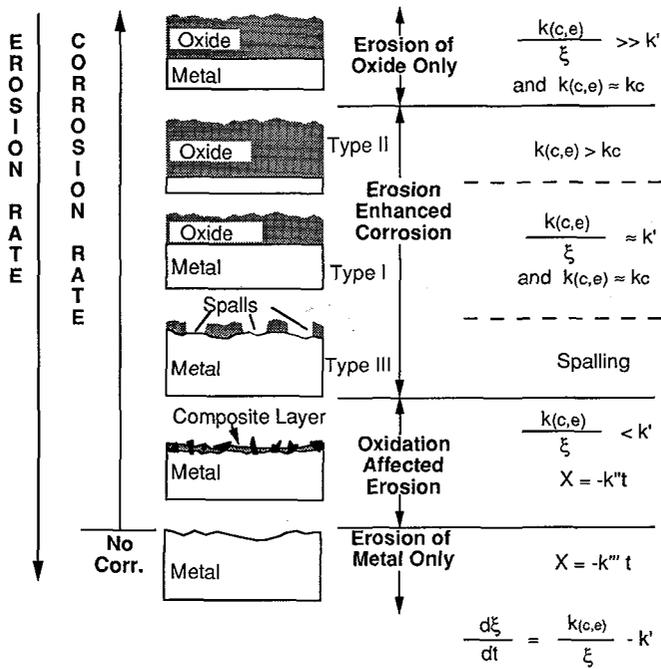


Fig. 3. — Erosion-corrosion interaction regimes [59].

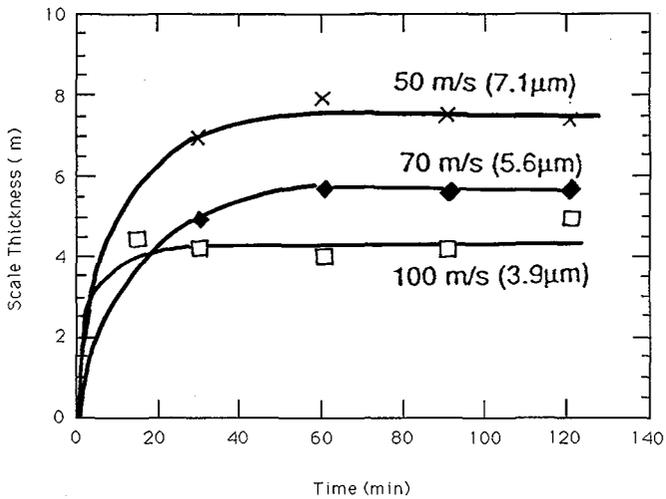


Fig. 4. — Development of constant thickness scales on cobalt under erosion-corrosion at 780 °C and 90° impact [55].

A further subdivision of the erosion enhanced oxidation regime concerns the failure of the scale by spalling at a critical thickness. Although it is easy to visualize the cutting, chipping and deformation of the oxide surface, it is difficult to see what causes this method of scale removal to be replaced by spalling under certain conditions.

Spalling, which has been observed [13, 40, 62] to be responsible, at least partly, for scale loss apparently occurs at an interface. This may be the metal-scale interface in the case of nickel, or that between  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  in the case of iron [13]. Spalling can also occur where the scale has blistered or risen locally from the metal surface. Rishel [13] has shown that the scale can be induced to buckle and separate from the metal surface under certain conditions of particle loading rate. This requires compressive stresses consequent upon erosive impact to reach a level necessary for initiation of buckling at sites where voids already exist. Rishel [13] also observed circular spalled defects in the scale cover that were not connected with prior buckling. These may be ascribed to conical brittle fracture or, perhaps, to the effects of Rayleigh waves inducing a circumferential crack in the scale around the site of a particle impact. It was not possible to relate any special conditions to any particular particle impact and the subject of the initiation of spalling requires substantial further consideration.

The oxidation affected erosion regime is entered when the erosive impacts begin to affect the metal substrate and to deform it plastically. The erosive particles penetrating the scale impinge directly into the metal causing heavy plastic deformation. Such a surface is difficult to define, being a composite of metal, scale and erodent particles. The metal surface is, therefore, exposed to the atmosphere with little or no protection and the oxide, being removed quickly as it is formed, may not be seen on the eroded surface. Degradation of the metal is maximized in the oxidation affected erosion regime, which is the least understood, in terms of mechanism. The intense plastic deformation of the metal surface under these conditions is estimated to occur at about  $10^6 \text{ s}^{-1}$  [61] and is likely to occur adiabatically producing local temperature increases. The metal, laid bare by the erosive impacts, oxidizes rapidly and supplies heat of reaction at a considerable rate. It is difficult to deduce precisely how oxidation affected erosion occurs, although the following steps are involved:

- 1) Erosive particles impinge and penetrate the surface to cause plastic deformation of the metal at a high strain rate. A composite surface of metal, oxide and erodent develops.
- 2) Where the deformation rate is high compared with the thermal conductivity of the alloy, the process becomes adiabatic and leads to an increase in surface temperature that can be considerable.
- 3) The metal surface, exposed to the atmosphere and overheated by the impacts, proceeds to oxidize rapidly, which adds heat of reaction to the surface thus further encouraging the surface temperature excursion.
- 4) The erosive impacts are likely to cause some of the metal of the surface to extrude rapidly, liquefy and to be ejected into the atmosphere, some metal oxidation may therefore take place away from the metal surface.
- 5) The high degradation rates indicate that oxide formation and removal is occurring, although oxide may not be seen on the surface in some cases.

In the oxidation affected erosion regime when the erosive particles impinge at an angle to the specimen, the random hills and valleys become aligned into ripples, reflecting the directional deformation of the substrate. The parallel vector of the erosive energy is responsible for the directionality of the ripples and for their tendency to move over the specimen surface [56]. Chang [56] also found the crest of a ripple to be hammered into a thin sliver and cut off as it oxidized and lost ductility. This is shown in the time sequence of figure 5. This phenomenon was estimated to be responsible for about 20% of the degradation rate in the case of nickel at an impingement angle of  $60^\circ$ . The formation of such thin lips at the wave crest

is aided by the formation of a buttress of oxide in the lee of the wave against which the lip is hammered out; this is shown in figure 6.

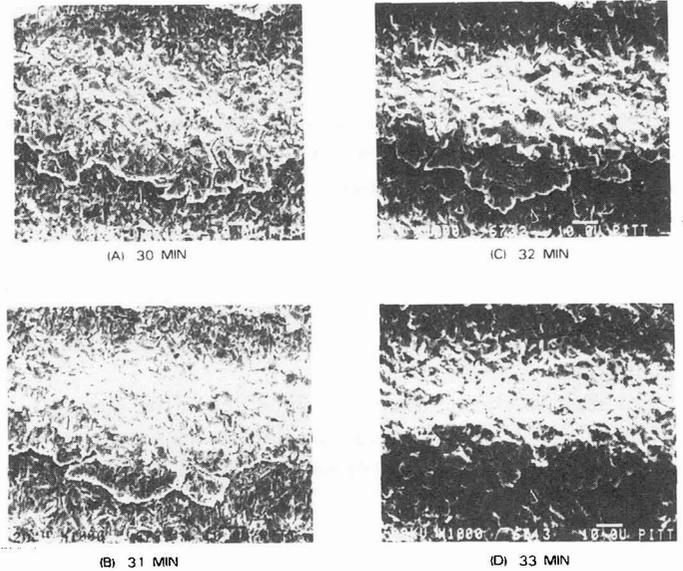


Fig. 5. — Development and removal of deformation slivers and wavecrests during the erosion-corrosion of nickel at 780 °C by 20 μm alumina flowing at 140 m/s and 30° incidence (56).

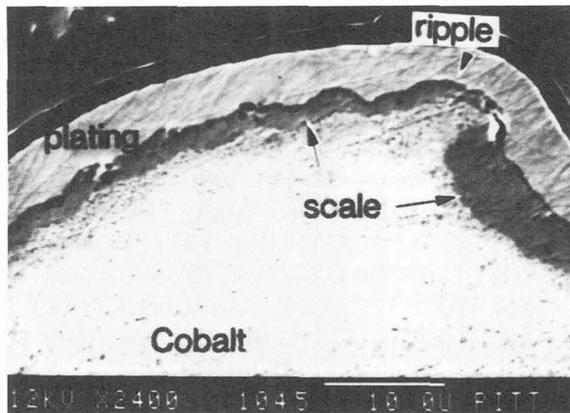


Fig. 6. — Section of a cobalt wave crest showing scale build up in the lee with sliver development at the wavecrest [56].

#### 4. Summary.

Although fundamental understanding of erosion-corrosion interactions has advanced, much remains to be clarified, particularly where alloys are involved and where oxidation enhanced erosion is involved. In many cases, where the alloys tend to form thin slow growing oxides, the two areas converge.

In the case of alloys, erosion may extend the duration of transient oxidation, during which little selective oxidation can occur. Alternatively, where selective oxidation is achieved, the constant removal and reforming of the protective scale can cause denudation of the protective element in the alloy eventually leading to the formation of scales based on the more noble parent metals and changing regimes as a result.

The least understood regime, oxidation affected erosion, also gives rise to the highest degradation rates. Unfortunately, the attack of many heat resistant alloys lies in this regime. In order to understand the fundamental processes involved, it is necessary to address the following: -deformation of oxides and metals at very high strain rates under impact, the adiabatic nature of the deformation, temperatures that can be generated and the depth of the deformed zone in the metal.

It is also necessary to address the nature and intensities of the stress and strain fields that are induced on erosive impact in order to explain the features such as mounds and valleys, ripples and an apparent brittle fracture that gives rise to spalling of thin scales.

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