The Effectiveness of Oxides in Reducing Sliding Wear of Alloys

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During like-on-like reciprocating sliding in air (amplitude 2.5 mm, load 1.5 kg, speed 500 double traversals per minute), the formation of oxides can have considerable influence on the friction and wear characteristics of high-temperature alloys, such as Jethete M152 and Rex 535. In particular, above a certain transition temperature, between 200 and 300°C for these alloys under these conditions, an adherent, smooth wear-protective oxide layer is developed on the load-bearing surfaces. At lower temperatures, oxide debris reduces the extent of metal-metal contact, thereby reducing the friction and wear rate, but does not eliminate it completely. The oxide debris is produced by two processes; one involves transient oxidation of the metal surfaces, removal of such oxide during each transversal, and reoxidation of the exposed metal; the other involves the formation, fracture, comminution, and oxidation of metal debris particles. At temperatures above the transition temperature, the oxide debris is compacted and comminuted between the sliding surfaces to develop the wear-protective oxide layer. This paper considers the reasons for the effectiveness of such oxides in terms of the influence of the hydrostatic pressures generated on plastic deformation of the very fine oxide particles or asperities in the surface. The resulting friction during sliding is less than during metal-metal contact because only limited asperity junction growth occurs before the asperities become sufficiently large and the hydrostatic pressures sufficiently reduced to allow fracture within the oxide-oxide junctions. The oxide-wear debris produced is recompacted into the surface, resulting in only very low wear rates. It has been shown that the number of asperity-asperity contacts during sliding of wear-protective oxide layers is relatively high, typically $5 \times 10^3/mm^2$ of apparent contact area, while the mean surface flash temperature rise is low, typically 2°C. Consideration is given to some of the conditions that favor development of wear-protective oxide layers.

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INTRODUCTION

The formation of oxides on metal surfaces in relative motion often results in reduced wear and friction. Hence, such oxides can play an important role in many practical situations,[1-7] particularly at high temperatures, such as during operation of gas-turbine engines.[8] For many alloys, a well-defined temperature for a particular set of test conditions exists, above which wear-protective oxide layers (sometimes known as "glazes") are effective in reducing the coefficient of friction and the wear rate, and below which these parameters are relatively high. Such oxide layers on nickel- and cobalt-base alloys are formed from very fine, crystalline particles of oxides, such as NiO, Cr_2O_3, Co_3O_4, $NiCr_2O_4$,[4,9] which are deformed plastically during sliding to produce a very smooth surface.

In addition to nickel- and cobalt-base alloys, iron-base alloys find application at elevated temperatures, particularly in the intermediate temperature range up to about 600–700°C. In the present research, a thorough investigation of the like-on-like sliding wear behavior of two typical commercial Fe–12%Cr alloys, Jethete M152 and Rex 535, over a range of temperatures in air has been carried out, with particular emphasis on the development of wear-protective oxides and the influence of such oxides on the tribological performance of the alloys. The detailed friction, wear, and contact resistance results have been presented elsewhere,[10-14] and mechanisms have been proposed for the production of oxides during sliding wear.[15] In the present paper, consideration is given to the role of those oxides in the wear processes, with emphasis on the precise development of wear-protective oxide surfaces, on the conditions that favor their development, and on the role of such surfaces in reducing friction and wear.

Experimental details are given elsewhere.[10,16] In the wear apparatus, a flat disc specimen slides in a horizontal, reciprocating mode (peak-to-peak amplitude 2.5 mm) against a hemispherical button specimen under a load of 1.5 kg at a speed of 500 double traversals/minute. Prior to sliding, the specimens were placed in contact in laboratory air and brought to temperature (±3°C) in about 15 min. Sliding was commenced when the required temperature had stabilized. The coefficients of friction and contact resistances were recorded continuously during sliding, the wear rates were determined from measurements of the wear-scar volumes after the tests, and the worn surfaces were examined using various electronoptical techniques.

FORMATION OF OXIDE DURING SLIDING WEAR

The coefficients of friction and wear rates during like-on-like sliding were relatively similar for the two alloys under a given set of conditions.
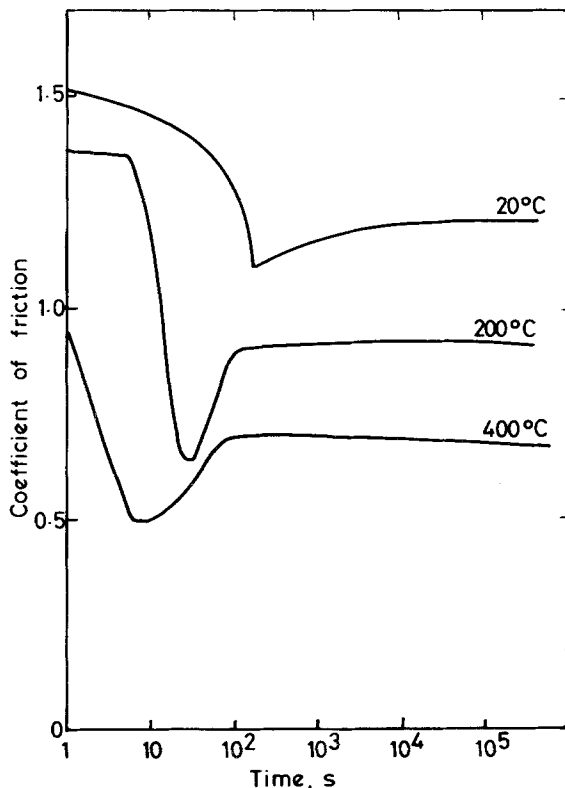
Fig. 1. Typical coefficient of friction against time plots, at
various temperatures, for Rex 535 during like-on-like sliding
in air.

The values at 300 and 400°C were considerably less than at lower tem-
peratures, as shown for Rex 535 in Figs. 1 and 2, due to the development
of smooth, adherent, wear-protective oxide layers on the load-bearing
regions after very short periods of sliding.[11] Typical wear rates after the
development of these oxides were less than 5×10^{-7} mm^3/s. At lower tem-
peratures, the presence of oxide on the load-bearing regions also reduced,
after some time, the amount of metal-metal contact and the wear rate, giving
mild wear regimes, although, unlike at 300°C and higher, metal-metal contact
was not eliminated completely, and mechanically stable, wear-protective
oxides were not fully established and maintained. Wear rates in the mild-
wear period were typically 2.0×10^{-5} mm^2/s at room temperature and
2.7×10^{-6} mm/s at 200°C.[10]

From observations of the wear scars[13] and the close correlation between
a theoretical model of expected changes in coefficient of friction with time
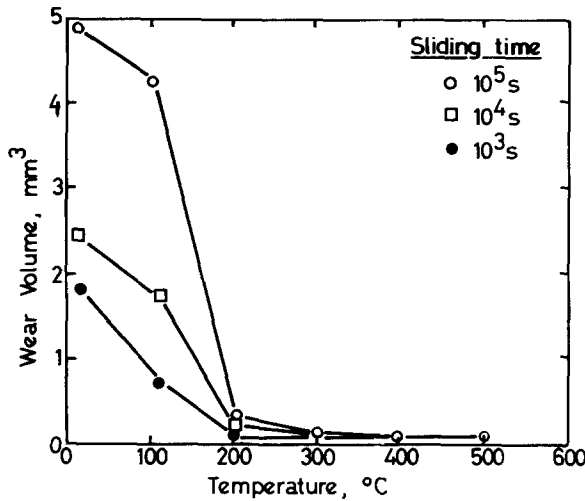
Fig. 2. Wear volume against temperature, after various sliding
times, for Rex 535 during like-on-like sliding in air.

and the measured values at 300 and 400°C,[12] it has been shown that two
processes for the production of such oxide are important during sliding at
these temperatures under the present conditions. The first consists of
transient oxidation of the entire apparent areas of sliding contact and then
removal of much of that oxide by the sliding action during each transversal,
the exposed metal surface being reoxidized after each traversal ("oxidation-
scrape-reoxidation" mechanism). The second mechanism involves forma-
tion of metal debris in the early stages of sliding and subsequent fracture
and refracture of this debris, exposing fresh areas of clean metal for further
oxidation. Comminution and oxidation of the debris produces considerable
quantities of oxide and oxide-coated metal debris ("metal-debris" mechan-
ism). In either case, at least at temperatures above the transition temperature
($\sim$200°C), the debris produced is compacted between the sliding surfaces
to develop progressively areas of wear-protective oxide (the so-called
"glaze" regions[2]). At lower temperatures (100–200°C), the "oxidation-
scrape-reoxidation" mechanism is not significant, the primary mechanism
by which oxide is produced being oxidation of comminuted metal debris.[10]
Here, oxidation is less rapid, so considerable comminution of metal debris
must occur before significant amounts of oxide are produced.

      This paper is concerned mainly with the reasons for the beneficial
effects of the wear-protective oxide layer in reducing friction and wear. One
factor which is apparent from this and other work is that such layers may
form from a variety of inorganic materials. In the present work, α-Fe_2O_3

was the main constituent, while other research has identified NiO, $NiCr_2O_4$, FeO, Cr_2O_3 as major constituents on other materials.[6,9] Indeed, it has even been shown that similar wear-protective layers can be developed from ferric-chloride crystals introduced between sliding metal surfaces.[16]

THE EFFECT OF TEMPERATURE ON THE DEVELOPMENT OF WEAR-PROTECTIVE OXIDE LAYERS

Now, we consider the influence of temperature on the development of the wear-protective oxide layer. Such layers develop on Jethete and Rex 535 at temperatures of 300°C and above. At lower temperatures (room temperature to 150°C) extensive oxide debris is produced, which reduces metal-metal contact and hence the extent of wear, but the shiny, adherent, compacted wear-protective oxide layer is not developed.[10] Even at 200°C where some regions of such oxide layers are observed, these do not eliminate completely metal-metal contact.[10] In general, the sliding time to develop the compact, adherent wear-protective oxide layers decreases with increasing temperature above the transition temperature, presumably associated mainly with the faster rate of oxide production at the higher temperatures. However, even after very long periods, such oxide layers do not appear to develop at temperatures below the transition temperature. It is clear that this transition is not necessarily associated with any change in the type of oxide generated during sliding since it was found that α-Fe_2O_3 facilitated the formation of an adherent, shiny wear-protective surface at 300°C but not at room temperature. Furthermore, experimental evidence has confirmed that the transition temperature is not that temperature below which such oxide layers cannot develop but is that temperature below which a wear-protective oxide layer is mechanically unstable during normal sliding.[13,16] For instance, it was found that preoxidation of Jethete at 600°C to develop a steady-state oxide scale resulted in the development of a wear-protective oxide surface during subsequent normal sliding at 300°C but not at room temperature, the layer in this case being broken down by the sliding action. However, at room temperature, a single transversal of the preoxidized specimens did produce a degree of compaction and agglomeration of the surface-oxide particles and the characteristic shiny, load-bearing oxide surface. Hence, the process of forming the wear-protective oxide layer does not require a minimum ambient temperature, although an increase in temperature may be beneficial; but low ambient temperatures favor detachment and breakup of the oxide during sliding.

A decrease in adhesion at the oxide/metal interface, perhaps caused by differential thermal contraction of the metal and oxide constituents, or in cohesion within the oxide, could be responsible for this effect. However,

although this may explain the breakup of the wear-protective oxide layer formed at a high temperature on cooling to a low temperature, it does not explain why a wear-protective oxide layer does not reform from the oxide debris so produced, or from the masses of individual oxide particles produced during sliding even at low temperatures.

A second factor that may account for the existence of a transition temperature under given sliding conditions is a change in mechanical properties of the oxide with temperature, resulting in the observed increase in coefficient of friction with decrease in ambient temperature during sliding between wear-protective oxide surfaces. In particular, as the temperature is decreased, the appropriate properties change in such a way that the shearing forces acting at the sliding interface increase, favoring detachment of the wear-protective oxide. Of course, it is difficult to compare exactly coefficients of friction for comparable situations at different temperatures as the oxides are usually more adherent/coherent at the higher temperatures but are less so during sliding at lower temperatures. However, for Jethete and Rex 535, the increase in steady-state coefficient of friction, μ, with decrease in ambient temperature is significant, with $d\mu/dT$ being about −0.05 per 100°C in the range 800–300°C.[11,16] As the temperature is decreased further, the modulus of the negative slope increases, a typical coefficient of friction value, for the mild wear regime, being 0.75 at 300°C and 1.1 at 100°C. Furthermore, if this effect is important, it may be expected that those oxides which show particularly good adhesion and cohesion would exhibit lower transition temperatures. The ability of a preformed NiO scale on nickel to form adherent and coherent wear-protective oxide layers during sliding at room temperature[9] is consistent with this hypothesis since the Ni–NiO combination is known to show strong adhesion/cohesion. Correspondingly, a preformed Cr_2O_3 scale on Ni–Cr alloys breaks down rapidly during sliding at room temperature, probably due to poor adhesion characteristics.

A further and potentially important effect which may be thought to have relevance to the process of wear-protective oxide layer formation is the extent of frictional heating during sliding. It was originally postulated that the frictionally generated, surface flash temperature rises, and the consequent increase in temperature in the vicinity of the contacting oxide asperities was significant and important in the development of wear-protective oxide layers.[4] However, the results from the present research do not support this requirement. Contact resistance measurements indicate a mean surface flash temperature rise between contacting oxide asperities of only about 6°C during sliding under the present conditions.[14] As discussed later, this value is similar to that calculated by another method. Other experimental evidence is in agreement with these calculated low values. For instance, the

dependence of the exhibited coefficient of friction on the value of ambient temperature, yet the relative independence of this quantity upon either the value of normal load or sliding speed,[10,13] is hard to reconcile if the flash temperature or more general surface temperature rise is appreciable. It would be expected that the coefficient of friction would be relatively insensitive to small changes in ambient temperature. Also, since the shiny wear-protective layer can be developed on one low-speed, low-load traversal of preoxidized specimens at room temperature, it is clear that such surfaces can form under conditions of a near zero flash temperature rise, and hence such a temperature rise is not a prerequisite for them to be established.

PLASTIC FLOW OF OXIDES UNDER SLIDING CONDITIONS

The wear-protective oxide layers consist of compacted debris, upon which surface oxide is postulated to deform plastically to produce the smooth, shiny appearance. The reason why oxides may undergo plastic deformation rather than brittle fracture is not immediately obvious since, in common with other inorganic solids, oxides are regarded as being brittle from the way in which they behave in normal tensile tests. However, in compression, or in tension with a superimposed hydrostatic pressure, oxides, like other brittle materials, may behave in a plastic manner and exhibit large plastic strains, as demonstrated for glass, alumina, and rock salt.[17] This behavior is not anomalous and is readily explained by the modified Griffith crack theory. Under normal tensile conditions, minute cracks or flaws in brittle materials act as stress enhancers and cause an increase in the effective tensile stress at these flaws. The presence of a large hydrostatic pressure does not in itself promote plastic flow of the material per se,[18] but simply promotes healing of the flaws and postpones the onset of crack growth and brittle fracture. In the presence of a hydrostatic pressure, Hp, if the value of $Y + Hp$ (where Y is the stress required to cause failure of the material in the absence of a hydrostatic pressure) is greater than the plastic yield strength of the material, then, under stress, the material should flow plastically and not fail prematurely by brittle fracture.

It has been shown[19] that, within the stress field associated with a nondeformable, normally loaded spherical indenter upon a softer, flat surface, there exists a hydrostatic pressure equal to about 66% of the mean contact pressure. Hence, it may be expected that brittle solids could exhibit plastic deformation under normal loading or sliding conditions. Indeed, "brittle" oxides have been observed to deform plastically under compressive loading, with regularly shaped, crack-free, permanent indentations being produced.[20] Furthermore, if the value of the yield pressure exhibited during such microhardness measurements is compared with the value of the shear

strength of the material at the same hydrostatic pressure, it is found that the ratio of the two parameters is about 0.17 for a number of oxides of different structures (MoO_3, Cu_2O, ZnO, MnO, NiO, TiO_2, ZrO_2),[16] a value expected for perfectly plastic materials. Since the asperities of sliding surfaces may be viewed as microindenters, it is expected that oxides and other inorganic materials should exhibit plastic deformation during sliding. This has been found to be the case for lithium fluoride,[21] magnesium oxide,[21] and rock salt.[22]

An important concept associated with the ability of oxides to deform under microindentation or under sliding conditions is associated with the size of the microindentors or contacting asperities (the so-called Auerbach effect). If a nondeformable hemispherical indenter is normally loaded on the flat surface of a brittle material such that the deformation is elastic then, associated with the elastic stress field beneath the region of contact, is a tensile stress in the surface. This tensile stress is directed radically, and its maximum value occurs at the edge of the circle of contact. Upon increasing the load, the maximum tensile stress increases and, in a brittle material, a ring crack may be produced before the mean contact pressure reaches the material yield pressure, even in the presence of the hydrostatic pressures. However, experimental observations suggest[23] that there is a size effect (the Auerbach effect) since, for indenters of small radius of curvature, the critical load for cracking is proportional to the indenter radius. The radius of the circle of contact, a, is given by

$$a \propto (WR)^{1/3}$$

where R is the indenter radius and W is the applied load. Hence, the maximum tensile stress before cracking, σ_{max}, is given by

$$\sigma_{max} \propto \frac{load}{area} \propto \frac{W}{(WR)^{2/3}} \propto \frac{W^{1/3}}{R^{2/3}}$$

In the regime where the critical load for cracking is proportional to the indenter radius, then,

$$\text{maximum tensile stress before cracking} \propto \frac{R^{1/3}}{R^{2/3}} \propto \frac{1}{R^{1/3}}$$

Hence, as R decreases, the maximum tensile stress in the surface below which cracking does not occur increases, and so, for a small enough indenter radius, the tensile stress necessary for crack formation may not be exceeded before the yield strength of the material is attained. Hence, the material would flow plastically before the crack developed.

However, a theoretical study of this phenomenon[24] has indicated that, on the normal loading of a brittle material, a minute ring crack forms before

the main cone crack, and it is the load dependence of the initiation of this second larger crack which is responsible for the Auerbach effect. Nonetheless, it was noted that, since for small indenters, the initial smaller crack occurs so soon before the larger cone crack, the smaller crack may partially heal as a result of the stress field beneath the indenter. Thus, although this study[24] shows that asperities of small radius do not undergo plastic flow before brittle cracks develop, it indicates that further loading does not lead to catastrophic failure but, instead, allows the extending region of hydrostatic pressure to promote healing of the crack and eventually cause plastic deformation. Thus during sliding, it is postulated that plastic deformation of the oxide and development of a wear-protective oxide layer occurs when the oxide–oxide asperity contacts are sufficiently small for the hydrostatic pressure developed to become effective in preventing crack propagation.

It is concluded that the hydrostatic pressure field in the region of an asperity–asperity junction of contacting oxides may influence significantly their surface deformation, such that the frictional behavior is largely dependent on their plastic properties. Although plastic deformation of the oxide asperities results in development of a smooth, shiny surface, the extent of junction growth that follows the formation of adhesive contacts between the oxide asperities is relatively small before junction failure occurs and the asperities separate. This is the reason for the relatively low coefficient of friction and wear rate for such oxide surfaces. Junction growth during sliding causes an increase in the size of the asperity–asperity junctions. Since it also leads to a reduced contact pressure at any particular junction, it naturally leads to a decrease in the magnitude of the hydrostatic pressure. Hence, the effects of hydrostatic pressure in preventing brittle failure decrease as microsliding occurs. It is difficult to predict at what point junction growth terminates (and thereby predict the coefficient of friction) since this requires a knowledge of the hydrostatic pressure distribution in the regions of contact for all stages of microsliding, together with a quantitative description of its ability to prevent brittle failure. Nonetheless, much can be learned from a qualitative study of this problem, especially with regard to those material parameters which may be conducive to formation of wear-protective oxide layers.

DEVELOPMENT OF A WEAR-PROTECTIVE OXIDE SURFACE LAYER

Consideration may now be given to the process by which the wear-protective oxide surface can develop from the oxide asperities or oxide particles produced at the contacting sliding surfaces. During sliding of Jethete, Rex 535 (or any other wear-protective oxide layer-forming alloy),

oxide and oxide-coated metal debris is produced by the "oxidation-scrape-reoxidation" mechanism or the "metal-debris" mechanism, as discussed earlier. If the adhesive and cohesive forces binding the debris together and to the substrate alloy are of sufficient magnitude to overcome the frictional forces tending to remove it from the wearing surfaces, it remains in the wear track and compacts under the loading forces. At junctions between larger asperities, or particles, cracking and fragmentation occur. This causes both a redistribution of the load on other junctions and the production of smaller debris particles. As this fracture process leads eventually to the generation of many smaller particles, it ultimately aids compaction. After some time, the particle size at the surface of the compacted debris is reduced to such an extent that plastic flow of the oxide is able to occur without further cracking, as discussed in the previous section.

Evidence of plastic deformation at the oxide–oxide asperity junctions during sliding is clearly apparent by examination in the electron microscope.[11] The oxides are very smooth and often show evidence of "smearing," with the occasional presence of abrasion grooves. In addition, close examination of the surfaces fails to reveal any surface chevron cracks, usually produced during normal loading of brittle materials by the tensile forces developed within the surface, as discussed earlier.

The observed thickness of the compacted surface of the wear-protective oxide is also consistent with it being deformed plastically. The surface oxide originates from many individual oxide particles, and plastic flow of such an agglomerated array during sliding wear would cause them to merge into a solid mass, each particle losing its individual identity; the visual appearance of the oxide surfaces is entirely consistent with the concept. Hence, the thickness of the agglomerated surface layer of oxide is the depth to which plastic flow has occurred. Detailed measurements have indicated that the thickness of this layer was typically in the region of 0.25 to 1.0 μm, depending on temperature and sliding conditions.

It has been shown[25] that, for plastic deformation of a solid by a loaded, spherical indenter, the material initially becomes plastic at a point $0.6a$ beneath the surface, where a is the radius of the contact region. Further loading causes the plastic region to extend slightly but, even at full plasticity, the depth of the plastic region is little greater.[18] Also, it has been shown[26] that the depth to which plastic deformation occurs is relatively unaffected by the presence of an accompanying shear traction force. Thus, the thickness of the surface layer of the wear-protective oxide is approximately equal to $0.6a$, indicating that the typical oxide junction radius is 0.5–1.6 μm. It is pertinent that, where abrasion grooves are exhibited in the oxide surfaces, their widths (0.5–2 μm) are consistent with these values of junction radii.

ESTIMATION OF THE NUMBER OF LOAD-BEARING JUNCTIONS

If the mean junction radius is assumed to be 1 μm, it is possible to calculate a typical value for the number of load-bearing junctions between plastically deformed, wear-protective oxide layers. Now,

$$A = J_0 \frac{W}{P_0} = n\pi a^2$$

and

$$\mu = \frac{S_0}{P_0} (J_0^2 - 1)^{1/2}$$

where μ is the coefficient of friction, S_o is the shear strength of the oxide, P_o is the yield pressure of the oxide, and J_o is the junction growth factor for the oxide. Thus, for a typical value of μ during oxide-on-oxide sliding (i.e., 0.7) and if S_o/P_o is 0.2,[12] the junction growth factor is about 3.5. For an applied load of 1.5 kg and a reasonable oxide yield pressure[20] of 600 kg/mm^2, this gives n a value of approximately 2500. As the apparent area of contact during sliding is typically 0.5 mm^2, the number of load-bearing contacts is approximately 5×10^3/mm^2. Of course, there is some uncertainty in the values of a and P_o, which may be quite dependent on ambient temperature as well as on oxide composition.[28]

ESTIMATION OF THE MEAN FLASH-TEMPERATURE RISE DURING SLIDING

As the number of contacting junctions for oxide-oxide sliding is relatively high, the load supported by any one junction is quite small (typically less than 1 g). Hence, the mean, surface, flash-temperature rise during sliding would be expected to be relatively low, as indicated earlier. From a knowledge of the mean surface rise for metal-metal contacts under the same sliding conditions (approximately 5°C[16]), it is possible to estimate the corresponding temperature rise for oxide–oxide contacts. The flash-temperature rise developed in a heated contact, for the low-speed sliding case, is[29]

$$T_f = \frac{\mu g P v w}{8 B a \lambda}$$

where w is the load carried by an asperity-asperity junction, B is the mechanical equivalent of heat, λ is the thermal conductivity, g is the acceleration due to gravity, and v is the sliding speed.

The thermal properties of typical wear-protective oxide layers are not readily assessed because the oxide layer may be a composite of several species, and its density and ability to absorb and conduct heat would depend on the degree to which it has been compacted. However, for this order-of-magnitude calculation, it is assumed that the thermal properties of the oxide are similar to those of alumina, for which data are available. Also, the average number of metal–metal contacts during sliding of metal surfaces under the present conditions is approximately 50 (i.e., $100/mm^2$)[16], giving a typical junction radius after junction growth of 13 μm. For both the situation of oxide-on-oxide sliding and that of metal-on-metal sliding, the low-speed case[29] is satisfied (i.e., $Va/2M$, where M is the thermal diffusivity, < 0.1).

Thus the mean flash-temperature rise at a typical oxide–oxide junction during sliding may be written as

$$T_f(\text{oxide}) \cong T_f(\text{metal}) \cdot \frac{W_o \mu_o a_m \lambda_m}{W_m \mu_m a_o \lambda_o}$$

where subscripts o and m refer to oxide and metal, respectively. Inserting appropriate values for the metal and oxide gives a value for T_f (oxide) of approximately 2°C. Although this calculation is not very precise, it does give reasonable agreement with the corresponding value determined from contact-resistance measurements (6°C),[14] indicating that the assumed values for n and a are realistic.

CONDITIONS FAVORING DEVELOPMENT OF WEAR-PROTECTIVE OXIDE LAYERS

If a wear-protective oxide is deformed plastically and its tribological chracteristics stem from its ability to exhibit plastic flow rather than brittle fracture, it is possible to speculate about which material properties and environmental conditions should favor its formation. Clearly, relatively more ductile rather than very brittle oxides should be more amenable to plastic deformation, which suggests that Co_3O_4 or NiO should more readily form wear-protective oxide surfaces than Cr_2O_3, as is found at low ambient temperatures.[6] Also, although it is not generally possible to control the nature of wear-formed oxides, it would be advantageous to adjust the oxidation conditions to favor growth of relatively more ductile oxides during any preoxidation treatment. Thus, provided the oxide adhesion and cohesion are equal in both cases, the growth of NiO rather than Cr_2O_3 on a given Ni–Cr alloy or of FeO or Fe_3O_4 rather than Cr_2O_3 on an Fe–Cr alloy would be expected to be more conducive to formation of a wear-protective oxide surface during wear of the specimens. However, it should be borne in mind

that such oxides are not so protective in normal oxidation situations in the absence of wear.

Since the hardness of oxides may decrease appreciably and ductility increase with increase in ambient temperature,[28] then, for any particular oxide, the formation of a wear-protective surface layer should occur more readily at higher ambient temperatures. This is supported by various experimental observations. In addition, it has been reported[30] that surface coatings of mixtures of relatively soft oxides, PbO, B_2O_3, MoO_3, BaO, and CoO, behave as effective lubricants and exhibit low friction and wear over a wide temperature range. Also, it has been found[31] that materials which possess adequate adhesion to the substrate and low hardness exhibit favorable sliding characteristics, with PbO, MoO_3, and ZnO (hardnesses 40, 80, and 184 kg/mm^2, respectively) being more effective than the much harder Cr_2O_3 and SiO_2. Finally, a study of the effect of oxide additions (15 wt.%, particle size 0.5–10 μm) to lubricating greases showed that the wear rate decreased linearly with decrease in oxide hardness.[32]

In addition to increasing the possibility of plastic flow by facilitating formation of relatively soft or ductile oxide, other effects which reduce the possibility of brittle fracture are likely to be important. The work of Gupta[33] suggests that two-phase ceramics should be tougher and more crack-resistant than single-phase systems, the presence of particles of a harder phase causing a significant increase in the energy required for crack growth. Thus, if a wear-protective oxide is to be both tough (to resist surface and subsurface cracking) and yet amenable to plastic flow, a two-phase system may be more effective than a single-phase system, although this concept has not yet been tested in practice.

It is also likely that a low coefficient of friction is desirable in maintaining an effective oxide layer because the surface tensile stresses in the region of asperity–asperity junctions increase quite rapidly with increases in friction force.[26] Brittle fracture and an increased wear rate would be expected if the coefficient of friction increased appreciably. It has been observed that the coefficient of friction for sliding oxide surfaces increases with decrease in temperature.[11] It is probable that this effect, together with the influence of temperature on oxide cohesion and oxide/substrate adhesion, determines the transition temperature below which wear-protective oxide layers cease to be fully effective. Unfortunately, it is not possible to test directly the suggestion that a low coefficient of friction is essential for a wear-protective oxide layer to remain effective since friction is an intrinsic, not an extrinsic variable. However, no effective wear-protective oxide layer is known to exhibit a coefficient of friction greater than 0.8 during like-on-like sliding, this value being exhibited by NiO during sliding at room temperature.[9] It is significantly less than those typical of metal–metal contact during sliding.

Hence, for rapid formation of an effective wear-protective oxide layer, the oxide debris should be relatively amenable to compaction and should be reasonably amenable to plastic flow, leading to development of the smooth, flat oxide surfaces. However, for friction and wear between such surfaces to remain low, the contacting oxide asperity junctions should fail fairly easily during sliding without excessive junction growth and with failure occurring near the points of asperity contact.

If the surfaces are very plastic and form very good adhesive bonds at the contacting asperities, high friction and severe wear would result, as occurs for clean metallic surfaces. Thus, the most effective oxides would be expected to have an optimum degree of plasticity. For instance, a deformed layer forms relatively easily for NiO even at low temperatures, but the adhesive bonds between the contacting oxide asperities do not break easily, and the friction is relatively high. Conversely, Cr_2O_3 and Al_2O_3 do not even develop a coherent/adherent deformed layer easily, particularly at low temperatures, because of their very low plasticity. The most effective wear-protective oxide layer would consist of oxide that would deform sufficiently to develop the smooth surface, but the resulting oxide–oxide contacts would break relatively easily to maintain low friction and wear. An additional requirement is that the metal substrate upon which the oxide develops should be sufficiently strong to support the load at the operating temperature. In practice, an effective system over a wide temperature range is a layer of Co_3O_4 oxide developed on a cobalt composite substrate.[34]

CONCLUSIONS

During like-on-like reciprocating sliding (amplitude 2.5 mm, load 1.5 kg, speed 500 double traversals/minute) in air at 300 to 600°C, alloys such as Jethete M152 and Rex 535 develop smooth, adherent wear-protective oxide layers, resulting in relatively low coefficients of friction and very low wear rates. These wear-protective oxide layers develop from and on oxide and oxide-coated metal debris, which is produced either by transient oxidation of the metal surface and removal of that oxide on each traversal, or by the fracture and refracture of metal debris particles, which exposes clean metal for further oxidation. The oxide debris is comminuted and compacted to form a layer, with oxide particles at the surface being relatively very small. The presence of a large hydrostatic pressure during sliding promotes healing of cracks in the very fine oxide particles, facilitating subsequent plastic flow of the asperities in the oxide surface. Junction growth of the oxide asperities is relatively small as the conditions for plastic flow soon break down.

Wear-protective oxide layers can develop during sliding at temperatures below 300°C, but are unstable and break down rapidly under the normal sliding conditions compared with the more resilient layers formed above 300°C. The wear-protective oxide surfaces are very smooth, typically with approximately 5×10^3 asperity contacts over an apparent contact area of 1 mm².

High asperity temperature increases are not required for development of the wear-protective surfaces. In fact, it is estimated that the mean flash-temperature rise at the oxide asperity contacts during sliding is only approximately 2°C.

Relatively soft and deformable oxides would facilitate development of a wear-protective oxide surface, while good oxide cohesion and oxide/substrate adhesion facilitate retention of such a surface. However, low friction and wear necessitate reasonably easy fracture of oxide–oxide asperity junctions between the surface oxide layers, resulting in an optimum ductility for an effective wear-protective oxide.

ACKNOWLEDGMENTS

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