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## NASA Interdisciplinary Collaboration in Tribology

### A Review of Oxidational Wear

Terence F. J. Quinn

COOPERATIVE AGREEMENT NCC 3-14  
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## A Review of Oxidational Wear

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## SUMMARY

This in-depth review of oxidational wear starts with an attempt to clarify the terminology used by tribologists when discussing wear. It then deals with the role of oxide films in the wear of metals as it has become revealed to us over the past 50 years or so. Special emphasis is placed on the development of the Oxidational Wear Theory between 1956 and 1975. The heat flow analysis for some typical tribological situations is then described in terms of its use for calculating surface temperatures. The main impact of this part of the review, however, is to show that heat flow analysis provides an independent method for checking the surface models used in explaining oxidational wear rates. It is shown that the values of the Arrhenius Constant for oxidation during mild (i.e., oxidational) wear are not the same as for oxidation in an oxidizing atmosphere (such as in a furnace). The wear of metals at elevated temperatures is reviewed and an oxidational wear theory proposed for such conditions. The effect of partial oxygen pressures upon oxidational wear is also discussed. Finally, the likely future trends of oxidational wear in the 1980's are briefly indicated.



## NOMENCLATURE

|                    |   |  |
|--------------------|---|--|
| $A_p$              | = | Arrhenius Constant for parabolic oxidation ( $\text{kg}^2\text{m}^{-4}\text{s}^{-1}$ )                                   |
| $A$                | = | Total Real Area of Contact ( $\text{m}^2$ )  |
| $a$                | = | Radius of each of the $N$ circular areas of contact making up the real area of contact (m)                               |
| $a'$               | = | Constant relating the $K$ -factor to $P(\text{O}_2)$ ( $\text{Pa}^{1/b}$ )   |
| $B_1', B_2'$       | = | Ill-defined constants of Suh's [22] Delamination Theory [Equation (2)] for surfaces 1 and 2                              |
| $b$                | = | Power to which $P(\text{O}_2)$ must be raised for $\log(K)$ to be proportional to $\log[P(\text{O}_2)]$                  |
| $C$                | = | Heat flow rate per unit temperature gradient along the thermocouple wire ( $\text{W m K}^{-1}$ )                         |
| $c$                | = | Specific heat capacity of the substrate material ( $\text{J.kg}^{-1}\text{K}^{-1}$ )                                     |
| $c'$               | = | Power to which $P(\text{O}_2)$ must be raised for $\log(k_p)$ to be proportional to $\log[P(\text{O}_2)]$                |
| $d$                | = | Distance of sliding contact at an asperity ( $=2a$ ) (m)   |
| $d_{c1}, d_{c2}$   | = | Critical plastic displacements for each surface [Eq. (2)]  |
| $D$                | = | Diameter of pin, in pin-on-disk machine ( $=2 R_t$ ) (m)   |
| $F$                | = | Frictional force at the interface between the pin and the disk (N)   |
| $f_o$              | = | Fraction of oxide film which is oxygen   |
| $H_A$              | = | Axial heat flow rate (W)   |
| $H_R$              | = | Radial heat flow rate per unit length of element ( $\text{Wm}^{-1}$ )  |
| $H_{\text{total}}$ | = | Total heat flow rate at the pin-disk interface (W)   |
| $H_1$              | = | Heat flow rate (along the pin) at the interface between pin and disk (W)   |
| $H_2$              | = | Heat flow rate <u>entering</u> the section of the pin where the thermocouple measuring $T_A$ is conducting heat away (W) |
| $H_3$              | = | Heat flow rate <u>leaving</u> the section of the pin where the thermocouple measuring $T_A$ is conducting heat away (W)  |



|            |   |  |
|------------|---|--|
| $h$        | = | Heat transfer coefficient between cylindrical exposed surface of pin and the air ( $\text{W.m}^{-2}.\text{K}^{-1}$ ) |
| $h_1, h_2$ | = | Removed layer thickness [Eq. (2)] (m)  |
| $K$        | = | Probability of producing a wear particle at any given asperity encounter   |
| $K'$       | = | Probability of producing a wear particle per revolution of disk in a pin-on-disk wearing system                      |
| $K_d$      | = | Thermal conductivity of disk material ( $\text{W.m}^{-1}.\text{K}^{-1}$ )  |
| $K_i$      | = | Thermal conductivity of the insulator ( $\text{W.m}^{-1}.\text{K}^{-1}$ )  |
| $K_o$      | = | Thermal conductivity of the oxide ( $\text{W.m}^{-1}.\text{K}^{-1}$ )  |
| $K_s$      | = | Thermal conductivity of steel ( $\text{W.m}^{-1}.\text{K}^{-1}$ )  |
| $L$        | = | $Va/2\chi_d$ = speed parameters  |
| $L_1$      | = | Length of pin exposed to the air between the pin holder and the disk (m)   |
| $L_3$      | = | Distance between thermocouples recording temperatures $T_a$ and $T_b$ (m)  |
| $M$        | = | $\{2K_i/(K_s R_t^2 \ln(R_a/R_t))\}^{1/2}$ ( $\text{m}^{-1}$ )  |
| $N$        | = | Number of asperities <u>in contact</u> beneath the pin   |
| $N_{Nu}$   | = | Nusselt number   |
| $N_{Re}$   | = | Reynolds number  |
| $N_d$      | = | Number of contacts within annulus of width (d) upon the disk   |
| $n$        | = | Number of contacts/unit area of <u>both</u> pin and disk   |
| $P(O_2)$   | = | Partial Oxygen Pressure of the ambient atmosphere around wearing system (Pa)   |
| $P_m$      | = | Hardness of materials used for pin and disk ( $\text{N.m}^{-2}$ )  |
| $Q_p$      | = | Oxidational Activation Energy for parabolic oxidation ( $\text{J.mol}^{-1}$ )  |
| $R$        | = | Molar Gas Constant ( $\text{J.mol}^{-1} \text{K}^{-1}$ )   |

|       |   |   |
|-------|---|---|
| $R_a$ | = | Outer radius of the cylindrical insulating medium (m)   |
| $R_d$ | = | Mean radius of wear track on disk (m)   |
| $R_t$ | = | Radius of pin (m)   |
| $T_A$ | = | Temperature recorded by thermocouple at pin surface just as it emerges from the pin holder ( $^{\circ}\text{C}$ )   |
| $T_B$ | = | Temperature recorded by thermocouple situated at a distance ( $L_3$ ) along the cylindrical surface of pin from the thermocouple recording $T_A$ ( $^{\circ}\text{C}$ ) |
| $T_b$ | = | Bulk temperature of surface [according to Blok [40]] ( $^{\circ}\text{C}$ )   |
| $T_C$ | = | Temperature of the real area of contact between the pin and the disk ( $^{\circ}\text{C}$ )   |
| $T_D$ | = | The "fictitious" flash temperature of the interface, assuming all $H_{\text{total}}$ goes into the disk ( $^{\circ}\text{C}$ )  |
| $T_d$ | = | General Surface Temperature of the disk ( $^{\circ}\text{C}$ )  |
| $T_E$ | = | Temperature of air flowing past the pin (well away from the boundary layer on the cylindrical exposed surface of the pin) ( $^{\circ}\text{C}$ )                        |
| $T_F$ | = | Flash Temperature [according to Blok [40]] between rubbing (lubricated) surfaces ( $^{\circ}\text{C}$ )   |
| $T_O$ | = | Thermocouple reading at the inside diameter of the copper cylinder surrounding the pin and insulator ( $^{\circ}\text{C}$ )   |
| $T_P$ | = | The "fictitious" flash temperature of the interface, assuming all of $H_{\text{total}}$ goes into the pin ( $^{\circ}\text{C}$ )  |
| $T_s$ | = | The temperature of the surface of the pin outside of the real area of contact ( $^{\circ}\text{C}$ )  |
| $T_x$ | = | Temperature at a distance $x$ (m) along the pin from the conjunction ( $^{\circ}\text{C}$ )   |
| $t$   | = | Time (s)  |
| $t_c$ | = | Total time a wearing particle is at the contact temperature ( $T_c$ ) before removal as a wear particle (s)   |
| $t_o$ | = | Time of an established (equilibrium) wear rate during a wear experiment (s)   |

|                 |   |  |
|-----------------|---|--|
| $t_r$           | = | Time of oxidation at an asperity during one revolution (s)   |
| $t_{rc}$        | = | Time for which an asperity is <u>in contact</u> during one revolution (s)  |
| $t_{rs}$        | = | Time for which an asperity is <u>out of contact</u> during one revolution (s)  |
| $t_s$           | = | Total time the wearing asperity is at the general surface temperature ( $T_s$ ) before removal as a wear particle (s)      |
| $V, V_1, V_2$   | = | Speeds of sliding at the contact zone ( $m\ s^{-1}$ )  |
| $v$             | = | Volume of material removed from a wearing partner ( $m^3$ )  |
| $W$             | = | Normal Applied Load at pin (N)   |
| $\hat{W}$       | = | Load per unit width of the face of the wear track on gear surfaces ( $N.m^{-1}$ )  |
| $w$             | = | Wear Rate ( $m^3/m$ )  |
| $\hat{w}$       | = | Width of the conjunction zone between gears and other similar non-conforming contacts (m)                                  |
| $w_\ell$        | = | Wear Rate (assuming <u>linear</u> dependence of oxidational wear upon the time) ( $m^3/m$ )                                |
| $w_p$           | = | Wear Rate (assuming <u>parabolic</u> dependence of oxidational wear upon the time) ( $m^3/m$ )                             |
| $w_{expt}$      | = | Experimentally measured wear rate of the pin ( $m^3/m$ )   |
| $w_{theory}$    | = | Wear Rate predicted by oxidational wear theory ( $m^3/m$ )   |
| $Z$             | = | $(K_s/2R_t h)^{1/2}$   |
| $\alpha$        | = | Dimensionless parameter related to L   |
| $\Delta T_b$    | = | Temperature difference between the bottom of the oxide film and the general surface temperature ( $T_s$ ), ( $^{\circ}C$ ) |
| $\Delta T_{ox}$ | = | Temperature difference across the oxide film at each asperity ( $^{\circ}C$ )  |
| $\Delta m$      | = | Mass uptake of oxygen per unit area of metal surface ( $kg/m^2$ )  |

- $\Delta m_c$  = Mass uptake of oxygen per unit area at  $T_c$  ( $\text{kg}/\text{m}^2$ )  
 $\Delta m_s$  = Mass uptake of oxygen per unit area at  $T_s$  ( $\text{kg}/\text{m}^2$ )  
 $\delta_{\text{expt}}$  = Experimentally-measured division of heat at the pin-disk interface (%)  
 $\delta_{\text{theory}}$  = Theoretically-calculated division of heat at the pin-disk interface (%)  
 $\theta_m$  = The temperature at the real areas of contact in excess of surface temperature ( $= T_c - T_s$ ), known as the "flash temperature" ( $^{\circ}\text{C}$ )  
 $\xi$  = Thickness of oxide film at the real areas of contact (m)  
 $\xi'$  = Total effective oxide thickness formed on the real areas of contact during the time ( $t_o$ ) of an established equilibrium wear rate (m)  
 $\rho_o$  = Average density of the oxides formed at the real areas of contact ( $\text{kg}\cdot\text{m}^{-3}$ )  
 $\rho_s$  = Density of the substrate material ( $\text{kg}\cdot\text{m}^{-3}$ )  
 $\tau$  = Time for one single asperity encounter (s)  
 $\chi_d$  = Thermal Diffusivity of the metal of the disk =  $K_s/(\rho_s c)$ . ( $\text{m}^2/\text{s}$ )  
 $\zeta$  = Total distance of sliding in a typical wear experiment

## 1. WEAR TERMINOLOGY

### 1.1 Introduction

Tribology is a subject which has suffered from a lack of precision over the terms used to identify its various constituents. Even the word "Tribology" itself has different connotations, according to the various authorities connected with the subject. The Jost Committee [1], in its report to the British Government in 1966, was responsible for the introduction of the word into current usage, although the prefix "tribo" had been used for some time before that date, to denote properties connected with rubbing. The Jost Committee's definition for "Tribology" is the study of the interactions between surfaces in relative motion and the practices related thereto". Scott [2], in his paper presented at the Conference on The Fundamentals of Tribology in Cambridge, Massachusetts, in 1978, uses "the science and technology of lubrication, friction and wear" as his definition. The Jost committee's definition is vague (perhaps deliberately?), so as to encompass the many complex interactions and practices involved. This vagueness, however, has led to a proliferation of terms to identify the interactions involved in Friction and Wear. Only in the already well-established "related practices", namely Lubrication, has there been some measure of agreement over terminology, mainly through the use of the so-called "Stribeck Curve" [3] for delineating the various lubrication regimes.

Although some vagueness is apparent in the literature available on frictional processes (for instance, the relation between plastic deformation, elastic deformation and the frictional energy required to move one

surface relative to another), at least there is agreement amongst Tribologists regarding the terminology of Friction. This is not so for Wear. Often the words "adhesive wear" and "mild wear" are used interchangeably, even though it is clear that adhesion plays a very small role in mild wear. The differences between "severe wear", "scuffing wear", "delamination wear" and "adhesive wear" are not at all obvious, even to the experienced Tribologist. An attempt will be made, in this review, to bring some unification to the terminology of Wear, especially as regards the classifications, laws, mechanisms and theories of wear. Although some of this unification is based on the author's own views expressed in a previous publication [4], it also takes account of the views of both Tabor [5] and Ludema [6], expressed in their reviews of "Wear" and "Scuffing" respectively.

## 1.2 The Classifications of Wear

A "classification" is a means of describing a group of phenomena which have at least one feature in common, whether those phenomena be the various families of birds in Ornithology, the seven crystal systems in Crystallography, or the various classes of wear in Tribology. All the birds in the finch family have the same beak structure; all the crystals in the monoclinic system have at least one axis of rotation which leaves the crystal looking exactly the same for  $180^\circ$  rotation about that axis; and all the various manifestations of a given wear classification should have at least one observable characteristic, in common, possibly contact resistance or final surface topography. Quite

often, in scientific endeavor, classifications are made where there is insufficient experimental or theoretical knowledge to propose laws or theories respectively. Classification is the first step towards the eventual scientific description of a phenomenon.

Although there have recently appeared some new classifications of wear according to the type of wear particle (Bowden and Westcott [7]), they are strongly related to the classifications proposed by Burwell and Strang [8] and Archard and Hirst [9] in 1952 and 1956 respectively. As will be seen later, Burwell and Strang envisaged seven wear classes whilst Archard and Hirst envisaged only two. It is clear that some attempt should be made to reconcile these two classification systems, as a necessary preliminary step to formulating a definitive wear theory. Tabor [5] and the author [4] have proposed similar modifications to these systems. The following is a distillation of their ideas as regards a more viable system of classification than either Burwell and Strang [8] or Archard and Hirst [9].

Essentially, the author [4] maintains that the Archard and Hirst [9] classifications of mild and severe wear are the most basic and easy to apply to any wear situation, since they are entirely phenomenological. Because of the every day usage of the words "mild" and "severe", it is not always appreciated that these classifications are based on (i) measurements of contact resistance (severe wear is characterized by low contact resistance whereas mild wear provides surfaces that give mainly high contact resistance); (ii) analysis of the wear debris both as regards size and composition (severe wear normally consists of large,  $\approx 10^{-2}$  mm

diameter, metallic particles, whereas mild wear debris is small,  $\sim 10^{-4}$  mm diameter, and has been produced partially by reaction with the ambient atmosphere or fluid); and (iii) microscopic examination of the surfaces (severe wear leaves the surfaces deeply torn and rough whilst mild wear produces extremely smooth surfaces, often much smoother than the original surface finish). It must be emphasized that these classifications do not specify a range of wear rates for each class of wear. Under certain conditions, it is possible for mild wear processes to occur at a rate equal to severe wear processes for the same combination of materials. In general, however, the severe wear processes are often two orders of magnitude more effective at removing material from the sliding surfaces, especially close to the transition loads found to occur in the dry wear of steels [10].

The term "wear rate" is itself slightly misleading. As used by most Tribologists, it means the volume of material removed from a surface per unit sliding distance of that surface with respect to the surface against which the relative motion is occurring. Typically, wear experiments in which wear rates can readily be measured involve one of the pair presenting a much smaller area over which wear can occur than the other member (which is normally the moving surfaces). Hence although, for combinations of the same material, the wear rate of the moving surface may be the same as for the stationary surface, the removed volume comes from the whole of the wear track. Quite clearly, track wear rates are much more difficult to measure by the normal distance transducer methods favoured by most wear researchers. Molgaard [11] has pointed out that such asymmetrical sliding pairs will have very different heat flows from



the frictional sources of heat at the interface into each member. This will affect surface temperatures and possibly the wear. He suggests that all experiments should be made with symmetrical pairs, such as two annuli. Experimentally, however, this geometry has been found to be a difficult one with which to deal. Hence, the continued preference for the pin-on-disc geometry by most Tribologists researching into wear. Provided allowance is made for the different heat flows in such geometries, it is probably as relevant to practical wearing situations as the mating annuli. The volume removed per unit time is a less fundamental quantity than that removed per unit sliding distance (since it involves the speed of sliding). Any heating effects due to different speeds can be allowed for in the heat flow analysis.

Having given an account of the mild and severe wear classifications of Archard and Hirst [9], let us consider the grounds for maintaining that most of Burwell and Strang's [8] classifications are special cases of the simpler classifications of mild and severe wear. Their first class was assigned the name "Adhesive Wear". This title clearly implies a mechanism of wear, namely one involving adhesion between the surfaces, and was probably proposed with the Bowden and Tabor [12] cold-welding mechanism of friction in mind. Burwell and Strang [8] envisage parts of each surface being pulled off by adhesive forces. These fragments are then transferred to the opposite surface, where they either break away to become wear particles or they return to their original surface in a "back-transfer" mechanism. It is pertinent to ask, how does one know that a given pair of surfaces has actually worn in this way?

Optical microscopy will reveal rough surfaces have been formed, but not whether transfer or back-transfer has occurred. Radioactive tracer experiments have been used to test for transfer and back-transfer, but such experiments are difficult to perform. Recent work by Eiss and Warren [13], where they used Neutron Activation Analysis to investigate the early stages of the wear of polychlorotrifluorethylene, has shown it to be possible to follow a transfer wear process step by step, but the effort was prodigious. The expense involved in investigating the mechanisms behind the "Adhesive Wear" classification is not justified when it is clear that it is no different from the more readily assigned classification of "Severe Wear".

This is a good point at which to introduce the unification proposed by Tabor [5], since he maintains that wear can be classified as (i) Adhesive, (ii) Non-Adhesive, and (iii) A mixture of both. For the present, we will be concerned only with Adhesive Wear. Tabor [5] mainly considers clean, unlubricated surfaces in which, under normal load, the atoms at some points will be in contact and thus interatomic forces will come into operation. Some adhesion will occur at these points and the force to break the interfacial junctions so formed is primarily responsible for the frictional force. Tabor [5] discusses the nature of the atomic forces at the interface; how the interface deforms under the action of a pull-off force (for adhesion itself) or a tangential force (for sliding); and how the junction itself ruptures under shear. These factors are clearly important in establishing a quantitative model for Adhesive Wear, since they will affect the amount of surface material removed during sliding.

As yet, there has appeared no theory of Adhesive Wear expressing the wear rate in terms of these factors, but it would seem to be an approach with some promise, especially to some bright young surface analysts, with their new techniques such as Auger and X-Ray Photoelectron Spectroscopy, looking for practical applications of their instruments!

Ludema [6], in his recent review of "Scuffing" and "Run-in" and the function of surface films, particularly oxides, makes no reference to any of the previous classification schemes, although it is clear he sees "scuffing" and "run-in" as two related forms of wear in a wide spectrum of other wear forms. Ludema [6] does not accept Dyson's [14] definition of "scuffing" as "gross damage characterized by local welding between the sliding surfaces". He suggests a more general definition, namely "scuffing is a roughening of surfaces by plastic flow whether or not there is material loss or transfer". By this definition, Ludema [6] can now include the microscopic initiation of surface failure as well as the more conventional manifestation of severe damage and wear loss (such as is often seen in 4-Ball Machine experiments). Ludema [6] does not see adhesion as being the only requirement for scuffing, although he does accept that the initiation of scuffing must involve plastic flow at one asperity.

The present author considers that both Tabor [5] and Ludema [6] have brought about some clarification of the mechanisms and initiation of what he (the author) considers to be "Severe Wear". It is maintained that there would be no contradiction in terminology if the terms "Adhesive Wear", as used by Burwell and Strang [8] and Tabor [5], and "Scuffing", as used by Dyson [14] and Ludema [6], were considered to be slightly

different forms of "Severe Wear", as defined by Archard and Hirst [9]. The differences could possibly lie in the relative amount of adhesive and non-adhesive contact, which could be interpreted as being equivalent to saying that the differences lie in the relative amounts of plastic and elastic deformation which occurs between contacting surfaces. If one assumes that "severe wear" involves plastic deformation and "mild wear" elastic deformation, then one can see how all the various forms of wear described by Burwell and Strang [8] and Tabor [5] as well as "Scuffing" and "Run-in", as proposed by Ludema [6], should in principal, be describable in terms of relative dominance of either severe or mild wear in any given situation.

Unfortunately, it is difficult to specify the effect of relative proportions of mild and severe wear upon the observable characteristics of contact resistance, composition and size of wear debris, and the topography of the worn surfaces (although this could be the subject of future research!). Another, and perhaps more important, problem is that all the classification systems other than Archard and Hirst's [9] involve the classifier knowing the mechanisms of wear [4]. A full discussion of how the various classifications can be reconciled can be found in reference 4. For the sake of brevity, an attempt is made in Table 1 to summarize the main conclusions of that discussion, and also include the recent classification systems proposed by Tabor [5] and Ludema [6].

Table 1: Comparison of the Various Classifications of Wear

| Burwell & Strang [8]      | Tabor [5]                                  | Ludema [6]                         | Quinn [4]  |
|---------------------------|--|------------------------------------|--|
| Adhesive Wear             | Adhesive Wear                              | Scuffing                           | Severe Wear  |
| Corrosive Wear            |  | "Run-in"                           | Mild Wear  |
| Surface Fatigue (Pitting) | Non-Adhesive Wear                          | Mechanisms of Scuffing or "Run-In" | Mechanisms of mild and severe wear (See Section 1.4) |
| Abrasion                  |  |                                    |  |
| Fretting                  |  | Not Covered in Ludema's Review     |  |
| Cavitation                | Mixtures of Adhesive and Non-Adhesive Wear |                                    |  |
| Erosion                   |  |                                    |  |

It is possibly unfair to Ludema to include his "run-in" classification as being equivalent to corrosive or mild wear alone. Clearly, he envisages some surface fatigue and abrasion being involved in obtaining run-in surfaces, as well as chemical interaction to form protective films. Nevertheless, it would seem that "Scuffing" is one form of adhesive or severe wear and "run-in" is essentially corrosive or mild wear. It is interesting to note that Tabor sees no difference between Adhesive and Corrosive Wear. Obviously, controversy still exists over Wear Classification, especially over Quinn's [4] placing all other types of wear under

the category 'Mechanisms of Wear', and this will be discussed in Section 1.4. It does seem, however, that it is generally agreed that there should be a simpler classification than that proposed by Burwell and Strang [8].

### 1.3 The Laws of Wear

The laws of wear are a comparatively recent [1950] description of the general wear behavior of surfaces which interact during relative motion. They should be compared with the well-established Laws of Friction, which were first discovered by Leonardo da Vinci in the 15th Century. In fact, they are very similar, since both the wear rate and the force of friction are proportional to the normal applied load and both are independent of the apparent area of contact. However, the proportionality of wear rate with load is only true provided the nature of the surfaces does not change, i.e., provided the composition and topography of the surfaces remain essentially unaltered. Apart from this, the similarity is most striking, leading one to believe that, since the friction laws have been "explained" in terms of plastic deformation [12] and elastic deformation [15] of surfaces, it will only be a matter of time before the wear laws are also explained in these terms. It is almost certain that in the experiments undertaken to validate the plastic deformation hypothesis of friction, oxide films or other surface contaminants were not present, i.e., the plastic deformation hypothesis of friction is only applicable to surfaces exhibiting 100% severe wear. The proof of Archard's [15] elastic theory of friction is most unsatisfactory, being based on a model polymer surface sliding at very low speeds on a tool steel flat surface. Hence the "explanations"

of frictional force so far produced may be less universally valid than the supporters of these explanations realize.

#### 1.4 The Mechanisms of Wear

The "explanations" of frictional forces during sliding, mentioned in the last section, must clearly have some relevance to the "explanation" of wear. In other words, both friction and wear must occur by related "mechanisms". We have seen how plastic deformation seems to be strongly involved in the Bowden and Tabor [12] theory of friction, whereas elastic deformation was the basic mechanism of Archard's [15] theory of friction. It is reasonable, therefore, to expect plastic deformation to be a dominant factor in Severe Wear (in what follows, we will use this classification to stand for what Burwell & Strang [8] and Ludema [6] call "Adhesive Wear" and "Scuffing" respectively). Similarly, elastic deformation should be dominant in Mild Wear [or Corrosive Wear [8] or "run-in" wear [6]]. Because of this, it is difficult to see how adhesion can be involved in mild wear [as proposed by Tabor [5]]. Let us consider, in more detail, what are the mechanisms of, firstly, mild wear and, secondly, severe wear.

Mild Wear clearly involves reaction with the environment, in particular with the oxygen in that environment. It is not always appreciated that mild wear can occur even under wet lubricated conditions due to the large amounts of air absorbed and entrained in all typical lubricants. If the lubricants contain "extreme-pressure" or "anti-wear" additives, it is likely that the dominant reaction will be between the metal

(or its oxide) and the additive. Most typically, however, mild wear involves reactions between the surface and any ambient oxygen, that is, mild wear occurs through an Oxidational Wear Mechanism. This mechanism has evolved gradually over the past 20 years [16,17,18,19,20] and can best be summarized as follows:

In the initial (severe wear or scuffing) stages, the surfaces achieve a measure of conformity, so that the real area of contact consists of several comparatively large areas, each of which is about the size to be expected from the Bowden and Tabor [12] plastic deformation theory, namely, of the order of  $(W/p_m)$ , where  $W$  is the normal applied load and  $p_m$  is the Brinnell Hardness (expressed in units of stress). At any given instant one of these areas bears most of the load. It then expands (in a manner similar to that proposed by Barber [21]) so as to become a plateau of contact and remain the only region of contact until it is removed by wear. If the sliding speed is comparatively slow, or the loads are so light, that frictional heating is negligible, then the expansion of the contacting plateau will not be sufficiently large for it to be the preferred contact region. Furthermore, the rate of oxidation of the contacting plateau will not be very different from that of the remainder of the surface for the very low "hot-spot" temperatures (i.e., excess over general surface temperature) under these conditions. This is, of course, essentially describing a mechanism for severe wear and we will return to this aspect again in a later paragraph.

Given a sufficient amount of frictional heating, however, the contacting plateau will oxidize preferentially to the other plateaux and the remainder of the surface. It will oxidize, during contact with



the opposing surface, at a temperature ( $T_c$ ) normally well in excess of the general surface temperature ( $T_s$ ). The existence of these plateaux has been proved by many investigators (for example, see references [18, 22, 23]). They are extremely smooth with fine wear tracks parallel to the direction of sliding, typically with an area of about  $10^{-2} \text{ mm}^2$  and heights of about 2-3  $\mu\text{m}$ . The plateaux often show surface cracks perpendicular to the sliding direction, somewhat similar to the fatigue crack systems found in fracture mechanics. Clearly, one sees a possible reason for wear through fatigue due to intermittent heat and stress cycles as the plateaux comes into contact with similar plateaux on the opposing surface. The surfaces surrounding each plateau are rough and strewn with debris fragments, although there are no visible wear marks. It would seem that these fragments were once part of a previously existing contact plateau which, upon reaching its critical height became unstable, cracked, and eventually became the source of all the debris fragments in the non-contacting rough areas.

The contacting plateau is the site for all the asperity/asperity interactions between two opposing surfaces. According to the oxidational wear mechanism, these asperities are the sites for oxidation at the temperature  $T_c$ . Since oxidation occurs by diffusion of oxygen ions inwards and (sometimes) by metal ions outwards, one would expect the plateau to grow in height from the interface between the oxide and the metal beneath each asperity contact. In the course of many passes, one would find that the increases in height were spread over the whole contact area of the plateau. When the plateau reaches a critical oxide

film thickness ( $\xi$ ), the film becomes unstable and breaks up to form flakes and, eventually, wear debris. The electron microscope evidence [18,22] indicates a fatigue mechanism could be operating. Certainly, the cellular sections discovered by Rigney, et al. [24] and, more recently, found in some debris analyses by Allen [25], would seem to be consistent with the fatigue cracks and their regular spacings at right angles to the direction of sliding.

The oxidational wear mechanism, possibly to its own disadvantage, does not attempt to explain why the plateau breaks up at a thickness ( $\xi$ ). It merely states that, when the contacting plateau finally breaks up completely, then another plateau elsewhere on the surface becomes the operative one. The virgin surface beneath the original plateau is now free to oxidize at the general temperature of the surface ( $T_s$ ). Without externally-induced heating, the amount of oxidation at  $T_s = 80^\circ\text{C}$  (say) is orders of magnitude less than the oxide growth at  $T_c = 400^\circ\text{C}$  (say). Hence, the original plateau sub-surface region will not oxidize significantly until it becomes the operative area of contact once again. This mechanism is based on actual experimental as well as microscopic evidence. For instance, it has been shown [26] that the height of a cylindrical pin wearing its smallest dimension against a flat rotating disc exhibits periodic, sharp decreases in height about every five minutes. Taking into account the speed and the decrease in height, it is very likely that these periodic variations relate to sudden removal of a plateau of thickness about 1 or 2  $\mu\text{m}$ .

We have seen that, before mild wear (or "run-in" wear) starts, there is always a period of severe wear (i.e., adhesive or scuffing wear). Clearly, this is when the surfaces are being made to conform to each other, through some abrasion or plowing process. If the deformation of the surface is so severe that conformity cannot occur, then we have seen there is no opportunity for an area to dominate any other area of the surface. Obviously, for an unreactive material, such as a polymer, there is no opportunity for mild wear to occur unless, of course, the other counterface is a metal which readily oxidizes or reacts in some way with the ambient. In effect, we are saying that, if one has microscopically non-conforming surfaces, or if one has unreactive material, then severe wear must ensue by plastic deformation and subsequent removal, perhaps in the manner described in the "Delamination Mechanism" proposed by Suh and his co-workers [22]. It would seem that most of their work relates to severe wear, although this is never explicitly stated in their publications.

### 1.5 The Theories of Wear

Most of the current theories of wear accept Archard's [27] interpretation of the K-factor in the expression relating wear rate ( $w$ ) to the real area of contact ( $A$ ), namely

$$w = K A$$

(1)

Archard [27] suggests that, since the units of wear rate (volume/distance)

are the units of area, then  $K$  is dimensionless and can be interpreted as the probability of producing (on the average) a wear particle at each asperity encounter. Hence, on the average,  $(1/K)$  encounters are needed to produce a wear particle. It is astonishing how much ' $K$ ' can vary for the same operating conditions but different material conditions (for example, for mild steel sliding on mild steel, without any lubricant, we have  $K = 10^{-2}$  whereas for Stellite on tool steel, we have  $K = 10^{-5}$ ). It can also alter by two orders of magnitude for the same material combination but just a slight change in load (or speed), as shown by Welsh [10] in his paper on severe/mild and mild/severe wear transition loads. Most Tribologists would agree that the  $K$ -factor is what we need to concentrate our fundamental research on, if we are to understand the complexities of wear. A full discussion of the oxidational theory of mild wear, which is mainly based on Archard's probabilistic interpretation of the  $K$ -factor, is given in Section 2.

For severe wear, it would seem that the Delamination theory is the most relevant one. It is possible [Engel [28]] to recast Suh's [22] expression into the same form as Equation (1), namely:

$$w = \left[ \frac{B_1' h_1}{d_{c_1}} + \frac{B_2' h_2}{d_{c_2}} \right] \cdot A \quad (2)$$

where the expression within the brackets is the  $K$ -factor;  $h_1$  is the removed layer thickness from one surface and  $h_2$  is the thickness removed from the other surface of the sliding pair;  $d_{c_1}$  and  $d_{c_2}$  are the critical plastic displacements for each surface;  $B_1'$  and  $B_2'$  depend mainly on topography and are not very well-defined.

These theories of wear have received a considerable amount of support from experimental research over the past few years, more so than for any of the other wear theories which have appeared from time to time. The problem with all wear theories is that it is difficult to reduce the number of ill-defined variables to a manageable few. As can be seen, from Equation (2), the Delamination Theory requires knowledge of two ill-defined parameters,  $B_1'$  and  $B_2'$ . The present situation as regards the oxidational theory of mild wear, under conditions where insignificant oxidation occurs at the real areas of contact when they are not in contact, is most encouraging, namely there is only one parameter which has to be obtained by calibration against experimental results. However, as soon as one introduces external heating or different partial oxygen pressures from atmospheric, one again is forced to introduce more parameters. There are ways of overcoming this problem through the use of direct measurement of oxide film thicknesses by scanning electron microscopy and these will be discussed in Sections 5 and 6.

#### 1.6 Summary

Much of the slow progress in the development of our knowledge of tribological situations can be attributed to the complex nature of the interactions which occur between surfaces in relative motion. Some can be attributed, however, to the lack of precision in the terminology used in Tribology, especially in the study of Wear. In this section, an attempt has been made to clarify, and possibly simplify, the existing situation as regards the various types or classifications of wear. If it is accepted that all wear can be considered to be severe, mild or a mixture of both,

then the laws, mechanisms and theories of wear need concern themselves only with these two phenomena, instead of the multitude of situations currently described as scoring, scuffing, gouging, abrasion, pitting, cutting, fretting, erosion, adhesion and corrosion! The next few sections are concerned with the oxidational mechanisms which have been proposed to explain the laws of mild, dry wear and with the oxidational wear theory which has emerged from these explanations. It is possible that similar mechanisms are involved when extreme-pressure additives interact with the wearing surfaces in lubricated wear, but this possibility will have to be investigated in a later review.

It is hoped that the current review will encourage a more "global" view of wear, instead of the current attitude that wear is so complex that all we can do is to study specific situations and make limited predictions based on the experimental evidence. Complexity has not deterred investigators in other fields of research -- why should Tribologists not search for a universal theory of wear? Furthermore, why should they not also try to include friction in this theory, since both depend on surface topography and surface interactions. Although this review makes no attempt to discuss severe wear, it is clear that severe wear is what happens when mild wear is prevented from occurring after run-in, regardless of whether or not the sliding surfaces are lubricated. Perhaps severe wear can be explained (and quantified) in terms of competition between plastic removal and the chemical formation of new surface through an interaction with the ambient fluid? These questions will not be pursued in this review, but it is hoped that merely by posing them as we read the following, we may glimpse the beginnings of a universal theory of friction and wear.

## 2. THE ROLE OF OXIDE FILMS IN THE WEAR OF METALS

### 2.1 Introduction

This section concentrates very much upon the role of oxide films in the unlubricated wear of steels, since this is where most of the definitive research has taken place. Nevertheless, there is nothing very special about steels (apart from their wide use in engineering structures) nor about the fact that no deliberate lubrication was used. Oxidation can occur at the real areas of contact at extremely low partial pressures. There is enough oxygen in most oils (and even in water) to produce a significant reaction with the surface at the high temperatures normally obtained in rotating machinery. Oxide films are readily formed on most metallic surfaces and these will prevent intermetallic contact and adhesion, which is, of course, the usual role of a lubricant. An oxide film is just one (all-pervading) form of boundary lubricant, and it is suggested that all the analyses to be reviewed in the remainder of this review could, in principle, be applied to any metal/metal combination being slid under load in any fluid, provided that the fluid contains active molecules which can react with the real areas of contact to form a boundary film.

It is true, however, that reciprocating machinery often has to be used under high loads, low linear speeds and, frequently, in an ambient atmosphere at a temperature well above room temperature. Under these conditions of externally-induced heating (rather than frictional heating), the whole of the surface oxidizes. Under frictionally-heated conditions, however, it is generally only at the

real areas of contact that one gets significant oxidation. In this section, we will only be concerned with such conditions.

## 2.2 The Origins of Oxidational Wear

In 1930, Fink [29] published the first paper in which oxidation was identified as a new component in the wear of metals. As a result of his experiments with rail-tire steel, both under normal and inert atmospheres, he proposed that oxygen access was essential for this type of wear to take place.

Rosenberg and Jordan [30] in 1935, actually analyzed the wear debris formed when two disks were rolled against each other with 600N load and ten percent slip, under normal atmospheric conditions. Using eutectoid (0.81 percent) carbon steel which had been tempered at 320°C, the wear rate in hydrogen was found to be 50 times that in air. Only highly distorted iron could be detected by their x-ray diffraction analyses of the debris formed under hydrogen atmospheres. Under air, the debris was found to be  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ .

Thum and Wunderlich [31], also in 1935, described the "frictional oxidation" which occurred at solid joints between two metals clamped together and then subjected to small amplitude vibrations. In all cases, the red or black "rust" which appeared was always found (by x-ray diffraction analysis) to be  $\alpha\text{-Fe}_2\text{O}_3$ .

In 1943, two important papers appeared in the German scientific literature which, because of the war, did not make the impact which they deserved. One was related to the unidirectional sliding of soft



iron upon chromium-steel (Mailander and Dies [32]), whilst the other related to the reciprocated sliding of these two materials (Dies [33]). In the unidirectional sliding experiments, loads were used from 30N up to 600N and speeds from 1 to 3 ms<sup>-1</sup>. Mailander and Dies [32] describe how the wear rate versus load curve had a maximum at about 150N for 1 ms<sup>-1</sup>; this maximum became less pronounced and moved towards lower values of load as the speed increased. Examination of the wear debris indicated that there was a maximum amount of metallic iron and FeO at this "critical" load and a minimum amount of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. In the reciprocated sliding experiments, Dies [33] showed that "fretting corrosion" (as this type of wear is often called) rarely occurred under lubricated conditions, unless oxygen was also present in the lubricant. At a load of 750N, a frequency of vibration of 48Hz and an amplitude of oscillation of 250  $\mu$ m, Dies obtained dark brown debris (under unlubricated conditions) which proved to consist of 69%  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, 24% FeO and 2.5% metallic Fe (according to proportional analysis by x-ray diffraction). Chemical analysis also showed that the debris contained nitrogen, presumably in the form of iron or chromium nitride. Dies [33] showed that these proportions depended upon both load and frequency of oscillations. For instance, by decreasing the load to 130N and increasing the frequency to 200 Hz, the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> content decreased to 0.5% whereas the Fe and FeO contents increased to 24.5% and 75.6% respectively.

It is interesting to note that the origins of oxidational friction and wear occurred either contemporaneously, or even before, the origins of the adhesive mechanism of friction, first proposed by

Bowden and Tabor and described in their book in 1954 [12]. Their elegant and extremely simple hypothesis relates the force of friction to the force required to break the adhesive junctions formed at the real areas of contact between sliding solids (in the absence of oxide films), together with the force required for one set of surface asperities to plough through the asperities on the opposing surface. Their ideas were so successful in giving a qualitative and physical "picture" of what happens during sliding that, for the period 1945-1955, there was a tendency to use this "picture" beyond its ranges of validity and apply it to all tribological situations, even in those situations where plastic deformation could not possibly be the only (or even the dominant) mechanism.

In 1956, however, Archard and Hirst [9] produced their definitive paper on the wear of metals under unlubricated conditions, in which mild and severe wear were first defined in terms of observable characteristics. Researchers were now able to isolate mild (oxidational) wear from severe (adhesive and ploughing) wear and, as a result, progress began towards a better understanding of wear, in particular, mild wear. The next sub-section highlights the more important contributions to the subject over the 20 years following the publication of Archard and Hirst's 1956 paper.

### 2.3 Oxidation of the Real Areas of Contact and its Influence upon Wear

We have already seen that the production of oxidized debris is one of the characteristics of mild wear. Leaving aside the often-posed

question about whether the oxidation occurs after removal (in which case we would not have an oxidational wear mechanism), it is possible to make three alternative assumptions about the temperatures at which the surfaces oxidize before removal as wear debris. These are (i) the oxides are produced at the "hot-spot" temperature ( $T_c$ ) at the real areas of contact, (ii) the oxides are formed at the general surface temperature ( $T_s$ ), or (iii) the oxides are formed at some intermediate temperature. With these three alternative mechanisms in mind, the author [16], in 1962, made a comparison of the structures of the wear debris obtained in several published accounts of the mild wear of steel with those to be expected from the results of static oxidation experiments. He showed a good correlation for the first possible mechanism.

Having shown the importance of oxidation at the "hot-spot" temperatures at the real areas of contact in the mild wear of steels, the present author [16] proposed two possible mechanisms of wear particle formation. These were (i) the bulk of the oxidation occurs at the instant the virgin metal is exposed; this is followed by further contacts which merely cause the oxide to shear at the oxide metal interface, or (ii) an equal amount of oxidation occurs at each contact until a critical oxide thickness is reached, beyond which shearing occurs at the oxide-metal interface. As implied in Section 1.4 of this review, the second alternative is the one currently favoured. The work of Tao [34], which deals with oxidational wear under lubricated conditions, considers both mechanisms to be possible. In what follows,

we will consider the second alternative mechanism to be more likely than the instantaneous oxidation mechanism. We should remember, however, that this could be a point of weakness in the "structure" of the oxidational wear theory in the event of that theory failing to adequately describe any particular mild wear situation other than for steels.

In 1967, the author [17] produced an expression for the wear rate under mild wear conditions, based on Equation (1). He modified Archard's [27] interpretation somewhat by assuming that  $(1/K)$  encounters are necessary to produce a critical oxide thickness  $(\xi)$  at the real area of contact  $(A)$  and obtained the following expression:

$$w_{\text{theory}} = \left[ \frac{d A_p \{ \exp - Q_p / RT_c \}}{\xi^2 \rho_o^2 f_o^2 v} \right] \cdot A \quad (3)$$

The expression within the brackets is the K-factor for mild oxidational wear assuming no appreciable oxidation occurs when the wearing area is out of contact with the opposing surface. It should be noted that the contact temperature  $(T_c)$  is the operative temperature, as far as oxidational wear without external heating is concerned, where  $T_c$  is related to the "hot-spot" temperature  $(\theta_m)$  by the relation:

$$T_c = T_s + \theta_m \dots \quad (4)$$

Since we assumed that an equal amount of oxidation occurs at each contact, we must therefore invoke a parabolic dependence of mass uptake of oxygen per unit area (i.e.,  $\xi \rho_o f_o$ ) upon the time of oxidation (i.e. the time required for  $(1/K)$  contacts to occur at a given asperity).

Hence  $A_p$  and  $Q_p$  are respectively the Arrhenius Constant and Activation Energy for parabolic oxidation. In Equation (3),  $\rho$  is the mean density of the oxide in the contact zone,  $f_o$  is the mass fraction of oxide which is oxygen,  $V$  is the speed of sliding,  $R$  is the Molar Gas Constant and  $d$  is the distance of a sliding contact.

To test the validity of Equation (3), the present author [17] rearranged the equation so that  $(\xi^2/d)$  was on the LHS, leaving only those terms on the RHS which were thought to be readily measured or available from the literature. For instance, it was assumed (following Bowden and Tabor [12]), that  $A = W/p_m$  where  $W$  is the load and  $p_m$  is the room-temperature hardness of the material below the oxide film. In particular, (we will return to this later), it was assumed that the bulk static oxidation characteristics of iron would be relevant to the mild wear of low-alloy, medium-carbon steels. In fact, the Kubaschewski and Hopkins [35] values of  $Q_p = 193$  kJ/mole and  $A_p = 1.2 \times 10^4 \text{ kg}^2 \text{ m}^{-4} \text{ s}^{-1}$  were used. Although  $T_s$  was not measured, it was considered that it was so small that one could assume  $\epsilon_m \approx T_c$  and hence use Archard's [36] Figure 3 for these experiments. By plotting  $\log(\xi^2/d)$  versus  $\theta_m$ , it was shown [17] that, provided  $\theta_m$  was greater than about  $800^\circ\text{C}$ ,  $(\xi^2/d)$  was constant at about  $10^{-8} \text{ m}$ . Since Archard's [36] analysis assumes only one contact area, we can assume that  $\pi d^2/4 = A = W/p_m$ , so that  $d \approx 4 \times 10^{-5} \text{ m}$ , which in turn leads to a value of about  $0.6 \times 10^{-6} \text{ m}$  for  $\xi$ , the critical oxide thickness.

Unfortunately, below  $\theta_m \sim 80^\circ\text{C}$ , the value of  $(\xi^2/d)$  fell rapidly to about  $10^{-15} \text{ m}$  for  $\theta_m \sim 400^\circ\text{C}$ . We now know that this was probably due to the fact that the appropriate values of  $Q_p$  and  $A_p$  were not used. Also

the value of  $\theta_m$  was based on calculations which did not take into account the effect of oxide films upon the division of heat between sliding surfaces.

The period 1967 to 1975 saw the emergence of much work designed to confirm the validity of the oxidational wear theory. For instance, the present author [18] showed, by transmission electron microscopy of replicas of worn steel surfaces, that during a mild wear process, large flat and extremely smooth plateaux were formed on both surfaces, the height of these plateaux being about  $3$  or  $4 \times 10^{-6}$  m above the general surface. The plateaux also revealed crack systems reminiscent of fatigue cracks and some micrographs showed large areas about to flake away from the surface, leaving the rough non-contacting areas beneath. Later work [23], using scanning electron microscopy, showed similar features which could only be interpreted as oxide plateaux of contact about to break up at a critical oxide thickness.

In another paper, the author [26] used x-ray diffraction analysis of the wear debris formed in the unlubricated sliding wear of steel to provide evidence that the temperatures at these plateaux were considerably less than would be expected from an application of Archard's [35] analysis to the system. It was shown that the contact temperature ( $T_c$ ) was approximately  $200^\circ\text{C}$  above the general surface temperature ( $T_s$ ) for several high-speed experiments, which meant that  $T_c$  varied from  $300^\circ\text{C}$  to  $450^\circ\text{C}$ , in direct contrast to the temperatures predicted by applying Archard's [36] Figure 3, namely,  $T_c$  should be around  $1000^\circ\text{C}$ .

This conflict with Archard's calculated "hot-spot" temperature was originally thought to be due to possible flaws in the oxidational

wear theory rather than in the temperature calculations. In the same paper as the x-ray diffraction evidence [26], a new theoretical derivation of the wear rate (in oxidational mild wear) was given. This derivation did not depend on the Archard "Wear Law" (Equation 1). In fact, it equates the total volume of oxide formed on the real area of contact ( $A \xi'$ ) to the total volume of wear occurring during the time ( $t_o$ ) of an established equilibrium wear rate ( $w$ ), namely:

$$A \xi' = w V t_o \quad . \quad (5)$$

In Equation (5),  $\xi'$  is total effective thickness of oxide formed at the real areas of contact and  $V$  is the speed of sliding. But we know that  $\xi'$  is also related to the time of oxidation through the expressions:

$$f_o \rho_o \xi' = k_p^{1/2} \cdot t^{1/2} \quad (6a)$$

or

$$f_o \rho_o \xi' = k_l \cdot t \quad (6b)$$

according to whether one assumes parabolic [6(a)] or linear [6(b)] oxidation kinetics prevail during wear.

The author [26] then proposed two possible equations for the mild wear rate, namely:

$$w_p = \frac{A k_p^{1/2}}{f_o \rho_o V t^{1/2}} ; \quad w_l = \frac{A k_l}{f_o \rho_o} \quad . \quad (7)$$

In these equations the 'p' subscript stands for parabolic and the 'l'

stands for linear oxidation. We shall discard the linear oxidation model for the present, since linear oxidation is normally concerned with the initial stages of oxidation when the oxide film is still very thin. However, this could be yet another assumption to be investigated more fully, should the parabolic model fail. From oxidation kinetics, we know that  $k_p$  is related to the temperature ( $T$ ) through the relation:

$$k_p = A_p \exp - \{ Q_p / R T \} \quad . \quad (8)$$

The author [26] applied the parabolic wear rate equation to those experiments in which the contact temperature ( $T_c$ ) was found to be approximately 200°C above the general surface temperature ( $T_s$ ) for various applied loads but with a constant sliding speed of 6.25 m/s. He also applied it to some experiments carried out over the same range of loads as above, but at a much slower speed (0.05 m/s). In these slow speed experiments, however, the sliding specimens (i.e., the pin and the disc) were externally heated so as to give the same readings on all the measuring thermocouples as had been obtained (at the appropriate load) in the high speed experiments through internal (frictional) heating. By comparing the wear rates for frictional ( $w_f$ ) and external ( $w_e$ ) heating, it was possible to use Equations (7) and (8) to obtain an independent value for  $Q_p$ , the oxidational activation energy relevant to mild wear processes, namely  $26 \pm 4$  kJ/mole for  $100^\circ\text{C} < T_c < 300^\circ\text{C}$  and about 76 kJ/mole for  $300^\circ\text{C} < T_c < 450^\circ\text{C}$ .

These  $Q_p$  values were, of course, different from the 193 kJ/mole given by Kubaschewski and Hopkins [35] in their book on the oxidation



of metals. This discrepancy could be due to many factors. At the present time, it seems likely that it was due to an implicit assumption made in comparing the high and low speed experiments, namely, that the Arrhenius constant ( $A_p$ ) was the same in both sets of experiments. However, we also must not overlook the possibility that our (implicit) assumption that the Activation Energy ( $Q_p$ ) is the same, no matter how the oxidation temperature is achieved, could, in fact, be wrong! We will return to the question of constancy of  $A_p$  and  $Q_p$  later in the review.

#### 2.4. Disadvantages of the Original Oxidational Theory of Mild Wear

As with most of the theories of wear, the oxidational theory of mild wear, as originally proposed (see Equation (3)) and as modified (see Equation (7)), contained several ill-determined parameters. These were 'd' (the distance of sliding contact at an asperity), ' $\xi$ ' (the critical oxide film thickness), and ' $T_c$ ' (the temperature at the real areas of contact) in the original theory. The modified theory was an improvement in this respect, since it only contained the temperature of oxidation, which is assumed to be the same as the contact temperature,  $T_c$ . However, as was mentioned at the end of the last sub-section, both  $A_p$  and  $Q_p$  were somewhat suspect. Also, both the original and the modified theories included the real area of contact ( $A$ ), which was assumed to be given by the Bowden and Tabor [12] relationship, namely  $A = W/p_m$ . Now  $p_m$  will be the hardness of the substrate metal immediately below the contact, which will be affected by the general surface

temperature ( $T_s$ ). In fact, Earles and Powell [37], have shown that, if one takes into account the variation of hardness with surface temperature ( $T_s$ ), then one can obtain a consistent relation between wear rate ( $w$ ) and the product ( $W^{\frac{1}{2}}V$ ).

In order to deduce 'd' and ' $\xi$ ', it is necessary to use microscopic techniques on worn surfaces. To deduce  $T_c$ , one can use an indirect method, namely the detection of oxide or metallic phases which can only exist over certain temperature ranges. One can use the static values of  $A_p$  and  $Q_p$ , but one should be prepared to find differences between static and tribological values of these oxidation constants. Following Earles and Powell [37], one can use the values of  $p_m$  appropriate to  $T_s$ , since it must be the hardness of the substrate immediately below the contact areas which determines the real areas of contact and not the hardness of the oxide which lies on top of that metal. However, even here one should be prepared to consider, as did Stott, Lin and Wood [38], that the plastic properties of the oxide might play an important role in the mechanisms of oxidational wear.

Clearly, there are too many parameters to be deduced from supplementary sources (with the consequent uncertainties involved in such deductions) for the original oxidational wear theory to be given more serious consideration as a predictive practical model. A surface model was, in fact, implied by that theory, namely that there were  $N$  asperities on each of the opposing surfaces and that there was an oxide film of thickness ( $\xi$ ) at the time each asperity broke off to form a

wear particle. The assumption was hidden by following the Bowden and Tabor [12] convention that  $(W/p_m)$  was equal to the sum of all the individual areas of contact making up the real area of contact.

Another method for confirming this surface model was needed.

Measurement of the frictional force and its relation to the surface model was not considered very relevant, since friction forces depend on all contacts and not just on those contributing to the wear [39].

Measurement of the division of heat at the wearing interfaces is a much more reliable way to confirm the model. Hence, the next section of this review describes the application of heat flow analysis to oxidative wear.

### 3. HEAT FLOW ANALYSIS AND THE OXIDATIONAL WEAR THEORY

#### 3.1 Heat Flow Analysis for some Typical Tribological Situations

Probably Blok [40] was one of the first researchers to realize the importance of temperature in the failure of tribological systems. Blok was dissatisfied with the limitations inherent in the empirical criteria then available for design calculations for the "scoring" (or "scuffing") of gear teeth, especially the P-V criterion of Almen [41]. He estimated the maximum conjunction temperatures reached at incipient scoring in several gear testing machines as well as in actual gear practice, based on the following two equations:

$$T_c = T_b + T_f \quad (9)$$

and

$$T_f = 1.11 \left[ \frac{\mu W' (V_1 - V_2)}{b_1 \sqrt{V_1} + b_2 \sqrt{V_2}} \right] \cdot \frac{1}{\sqrt{w'}} \quad (10)$$

where  $T_b$  is the bulk temperature,  $T_c$  is the maximum conjunction temperature,  $T_f$  is the maximum possible "flash temperature",  $\mu$  is the coefficient of friction,  $V_1$  and  $V_2$  are the tangential velocities of the two rubbing surfaces relative to the contact zone,  $W'$  is the load per unit width of the face of the wear track,  $w'$  is the width of the band-shaped conjunction zone, and  $b_1$  and  $b_2$  are thermal contact coefficients for the materials comprising the two specimens ( $b = \sqrt{k\rho c}$ ), where  $k$  is the thermal conductivity,  $\rho$  is the density and  $c$  is the specific heat, so

that  $\rho c$  is the heat content per unit volume.

It will be apparent that Equation (9) is similar to Equation (4). However, it should be remembered that Blok was interested in the temperature at which the oil film breaks down to produce scoring (or "scuffing" or "severe wear" as we would now call it). This "flash-temperature" may not, indeed is most unlikely to be, the same as the "hot-spot" temperature ( $\theta_m$ ) occurring in a system with no lubrication (other than the protection afforded by surface oxide films). However, the bulk temperature ( $T_b$ ) does seem to be very similar to the general surface temperature ( $T_s$ ) we have defined earlier, so that we must take  $T_c$  to be the same quantity in both equations, except that one would expect  $T_c$  to be lower for oil-lubricated systems than for dry systems (due to  $T_f$  being somewhat less than  $\theta_m$ ).

Blok's [40] "scoring criterion" is only applicable to oils with no extreme-pressure additives. In his review in 1970, Blok [42] re-appraised his approach regarding the postulate about the constancy of the scoring temperature for a given tribological system. His re-appraisal did not lead to any new conclusions, apart from the realization that the wide applicability of the postulate to non-additive oils makes it a "real boon" to gear designers. His 1970 review is interesting, however, from the point of view of this report, in that he makes some suggestions regarding possible scoring mechanisms which involve the replenishment of oxide layers on those parts where scoring (i.e., scuffing) starts. He suggests that competition occurs between the shearing and tearing at local failure areas and the "self-healing"

action of boundary layers (those which arise from adsorption from the oil and those which arise from the oxidation of the newly-exposed metal surface to form an oxide film). Blok further suggests that the scoring temperature (i.e., the critical conjunction temperature up to which protection from scoring persists) might vary with relative contribution of the bulk temperature and the flash temperature components.

If the main contribution to the conjunction temperature comes from the bulk temperature [as, for example, in the slow speed wear tests carried out by Boerlage and Blok [43] and Vinogradov, Arkharariva and Petrov [44]] and this temperature is equal or near to the desorption temperature, then one should readily obtain scoring. Blok [42] seems unconvinced that these slow speed determinations of the scoring temperature would be relevant to scoring temperatures in actual gear practice. This is the same type of misgivings expressed in the last section, where it described the work of the author [26] in which slow-speed unlubricated runs were carried out for the purposes of extrapolating to higher (more practical) speeds in order to deduce the contact temperature ( $T_c$ ).

If the bulk temperature is well below the desorption temperature, then Blok [42] envisages "a wide margin is left for frictional heating to provide a flash temperature component sufficient for reaching a critical temperature at which desorption and/or scoring will set in." These are just the sort of conditions for which the oxidational wear theory was originally proposed, namely where interaction can only occur at the real areas of contact (see Section 2.1 of this review).

Predictably, Blok [40] sees that, under these conditions, the scoring temperature will be "somewhat higher" than the desorption temperature obtained from slow-speed experiments. He quotes the work of Lancaster [45], who proposed that competition between (i) the local breakdown of an oxide layer (characterized by the rate of exposure of the virgin metals), and (ii) the self-healing of these local areas caused by oxidation (characterized by the rate of oxidation), can have a considerable effect upon the type of wear which occur. This is, of course, the self-same mechanism we have been considering for explaining the transition between severe metallic wear (i.e., scuffing or scoring) and mild oxidational wear. Blok [42] attempts to include this work (which was carried out under unlubricated sliding conditions) in his concept of a critical temperature. He suggests, without any real basis, that the removal rate increases more rapidly with conjunction temperature ( $T_c$ ) than does the replenishing rate through oxidation, so that there will occur a critical temperature at which the removal dominates the replenishment. This is, however, completely at variance with the typical behavior of steels sliding against each other, in which an increase in conjunction temperature usually brings about the production of a more protective oxide (viz.  $Fe_3O_4$  or the spinel oxide) in place of the low-temperature, more abrasive oxide (viz.  $\alpha-Fe_2O_3$  or the rhombohedral oxide), (see Reference [26]). The temperature at which  $Fe_3O_4$  begins to form rather than  $\alpha-Fe_2O_3$  is about  $300^\circ C^*$  (46), regardless of whether the oxidation occurs through oxygen in the air or in the lubricant. One would expect the oil to desorb well below this

\*Later work by Caplan and Cohen (53) suggests that this is a lower limit and that the transition temperature is nearer to  $400^\circ$  to  $450^\circ C$ .

temperature, in which case, the only protection at the real areas of contact will be through oxide films.

This leads one to believe that Blok's critical temperature hypothesis is of limited value, since it is the protection afforded by oxide films which determines whether or not a local area will fail, regardless of the temperature at which the oil desorbs. If the speed of sliding is so slow that only the bulk temperature contributes to  $T_c$ , then clearly it is the protection of the boundary layers of the oil which is important in determining when the surfaces will scuff. For more practical speeds, this author believes that, without any extreme-pressure additive, the type of oxide being formed at the conjunction temperature ( $T_c$ ) is what determines whether failure of the surfaces will occur. If  $T_c$  is less than the desorption temperature then failure cannot occur. If  $T_c$  is less than the formation temperature for the spinel oxide (with steel specimens) then failure will occur. Thus, for steels, we have a small range of possible values for the so-called "scoring temperature", namely it must lie below the transition temperature for  $\alpha\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$  and above the desorption temperature of the oil. The successes of the Blok [40] flash temperature criterion could be attributed to the possibility that the conjunction temperature attained in most gear machines is normally less than the  $\alpha\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$  transition temperature, so that, as soon as the oil desorbs from an incipient scuffing site, there is very little protection from the rhombohedral oxide film being produced at that site at the conjunction temperature.



Although some criticism has been made of Blok's [40] flash temperature criterion, there is no doubt that he has made a significant contribution to the knowledge insofar as his work relates to surface temperatures. Due possibly to the complexities of the subject, however, his publications are not easy to read. This is also true of the work of Jaeger [47] and tribologists are indebted to Archard [36] for producing his "plain man's guide to surface temperatures." A most thorough, and readable, review of "Contact Surface Temperature" has recently been written by Winer [48]. None of these, however, has been concerned with using heat flow calculations and measurements to deduce a surface model which would, of course, be the same surface model one would have to use in any wear theory which is produced to explain the measured wear rates. Actually, Grosberg and Molgaard [49] did publish an account of some heat flow work with steels sliding at high speeds, but the derivation of their equations was not at all clear. Also they did not attempt to use the model from their heat flow work to explain the wear rates. In the next two sub-sections, we will deal (i) with the derivation of surface temperature ( $T_s$ ) and heat flow during sliding (no external heating), and (ii) with the application of heat flow analysis, together with a suitable surface model, to provide an explanation of the wear rate in terms of the oxidational wear theory.

### 3.2. The Derivation of Surface Temperature ( $T_s$ ) and Heat Flow during Sliding (No External Heating)

The frictional heat flux generated at the real areas of contact

divides so that part of the heat flows into one specimen whilst the remainder flows into the second specimen. For a pin-on-disk configuration of specimens, as shown in Figure 1, the portion of the total frictional heat flow rate that enters the pin is  $H_1$ . This raises the temperature of the pin and if the heat flux, and hence the temperature of the pin, is sufficiently great, the metal of the contacting asperities of the pin undergoes parabolic oxidation so that, at equilibrium, contact between the two specimens is via an oxide film, the form of the oxide being dependent on the oxidation temperature, i.e., the temperature of the real areas of contact ( $T_c$ ). In order to use the oxidational theory to predict the wear rate of metals, the temperature ( $T_c$ ) of the real areas of contact must be computed. This may be done if the pin is mounted in a thermal insulator mounted within a copper calorimeter. By placing two thermocouples a known distance apart on the pin, as shown in Figure 1, and by measuring the temperature of the calorimeter, it is possible to deduce the heat flow rate at any position on the pin, in particular, at the interface between the pin and the disk. From this analysis of heat flow, it is possible to deduce a temperature ( $T_s$ ), which is the temperature at the surface of the pin, assuming the whole of the apparent area of contact is, in fact, in contact at any given moment. Such a situation is almost impossible to obtain in practice due, of course, to the microtopographical features which provide real areas of contact much smaller than the apparent area of contact. In fact, the total real area of contact ( $A$ ) can be four orders of magnitude

less than the apparent area of contact for the sliding of metals. Nevertheless, the calculation does give us an average surface temperature ( $T_s$ ) resulting from the dissipation of energy at the real areas of contact. Clearly, the temperature at the real area of contact ( $T_c$ ) can be considerably in excess of  $T_s$ , depending on the speed, the ambient temperature and, of course, the number of contacts ( $N$ ) and the thickness ( $\xi$ ) of any reacted film formed at the real area of contact.

### 3.2.1 Heat flow analysis for the pin

The analysis is divided into two parts. The first part relates to that portion of the pin within the thermal insulator and the second part for the portion of the pin that is not insulated (see Figure 1).

#### (i) The insulated portion of the pin

Figure 2 shows an element of the pin and insulator, in the area B of Figure 1.

Let the temperature of the pin at  $x$  be  $T_x$ . From elementary heat flow considerations, we know that the axial heat flow rate at  $x$ , i.e.,  $(H_A)_x$ , is given by:

$$(H_A)_x = -K_s \pi R_t^2 \left( \frac{dT_x}{dx} \right) \quad (i)$$

where the symbols have the meanings given in the Nomenclature. The axial heat flow at  $(x + \Delta x)$  is  $(H_A)_{x+\Delta x}$  and is given by:

$$(H_A)_{x+\Delta x} = -K_s \pi R_t^2 \left( \frac{dT_{x+\Delta x}}{dx} \right) .$$

This could be written as

$$(H_A)_{x+\Delta x} = - K_S \pi R_t^2 \left( \frac{dT_x}{dx} + \frac{d^2T_x \cdot \Delta x}{dx^2} \right) \quad (\text{ii})$$

Ignoring the change in temperature between  $x$  and  $x + \Delta x$ , the radial heat flow through an element of unit length is given by

$$H_R = \frac{2\pi K_i (T_x - T_o)}{\ln(R_a/R_t)} \quad (\text{iii) (a)}$$

∴ for element of length  $\Delta x$

$$(H_R)_x = \frac{2\pi K_i}{\ln(R_a/R_t)} (T_x - T_o) \cdot \Delta x \quad (\text{iii) (b)}$$

where  $T_o$  is the temperature at the outer surface of the insulator.

For equilibrium  $(H_A)_x = (H_A)_{x+\Delta x} + (H_R)_x$

$$\therefore K_S \pi R_t^2 \left( \frac{d^2T_x}{dx^2} \right) \cdot \Delta x = \frac{2\pi K_i (T_x - T_o) \cdot \Delta x}{\ln(R_a/R_t)} \quad (\text{iv})$$

$$\therefore \frac{d^2T_x}{dx^2} = \frac{2\pi K_i}{\pi K_S R_t^2 \ln(R_a/R_t)} (T_x - T_o) \quad (\text{v})$$

Writing

$$T_x - T_o = T \quad (\text{vi) (a)}$$

and putting

$$M^2 = \frac{2K_i}{K_S R_t^2 \ln(R_a/R_t)} \quad \text{(vi) (b)}$$

we get

$$\frac{d^2 T}{dx^2} = M^2 T \quad \text{(vii)}$$

The solution is of the form

$$T = B_1 \exp(Mx) + B_2 \exp(-Mx) \quad \text{(viii)}$$

The boundary conditions are

$$(i) \quad \text{at } x = 0, T_x = T_A$$

$$(ii) \quad \text{at } x = L_3, T_x = T_B$$

$$\therefore (T_A - T_0) = B_1 + B_2 \quad \text{(ix)}$$

and

$$(T_B - T_0) = B_1 \exp(ML_3) + B_2 \exp(-ML_3) \quad \text{(x)}$$

$$\therefore B_2 = \frac{(T_A - T_0) \exp(ML_3) - (T_B - T_0)}{2 \sinh(ML_3)} \quad \text{(xi)}$$

substituting in Equation (ix) gives:

$$B_1 = (T_A - T_O) - \left\{ \frac{(T_A - T_O) \exp(ML_3) - (T_B - T_O)}{2 \sinh(ML_3)} \right\}. \quad (\text{xii})$$

Hence from Equations (vi) and (viii) we get

$$T_x = \left[ (T_A - T_O) - \left\{ \frac{(T_A - T_O) \exp(ML_3) - (T_B - T_O)}{2 \sinh(ML_3)} \right\} \right] \exp(Mx) \\ + \left\{ \frac{(T_A - T_O) \exp(ML_3) - (T_B - T_O)}{2 \sinh(ML_3)} \right\} \exp(-Mx) + T_O \quad (\text{xiii})$$

Now when  $x = 0$ ,  $(H_A)_x = H_3$

$$\therefore H_3 = -K_S \pi R_t^2 \left( \frac{dT_x}{dx} \right)_{x=0} \quad \text{from Equation (i)}$$

But from Equation (viii)  $\frac{dT_x}{dx} = M B_1 \exp(Mx) - M B_2 \exp(-Mx)$ , so that:

$$\left( \frac{dT_x}{dx} \right)_{x=0} = M (B_1 - B_2)$$

$$\therefore H_3 = -K_S \pi R_t^2 M (B_1 - B_2) .$$

Substituting for  $M$ ,  $B_2$  and  $B_1$  from Equations (vi)(b), (xi) and (xii) respectively, the following expression can be obtained for  $H_3$ , the axial heat flow rate leaving the element at  $x = 0$ :

$$H_3 = K_3 \pi R_t^2 M \left[ \frac{(T_A - T_O) \cosh(ML_3) - (T_B - T_O)}{\sinh(ML_3)} \right]. \quad (11)$$

If  $H_2$  is the heat flow rate entering the last uninsulated element of the pin, then

$$H_2 - H_3 = \frac{C(T_A - T_O)}{(R_a - R_t)}$$

is the heat flow along the thermocouple wires at that point (assuming that the wires at the outer surface of the insulator are at the temperature  $T_O$ ). Hence

$$\boxed{H_2 = H_3 + \frac{C(T_A - T_O)}{(R_a - R_t)}} \quad (12)$$

(ii) The heat flow in the exposed portion of the pin

In this part of the analysis, it will be assumed that the radial heat flow rate ( $H_R$ ) which is transferred from an element of unit length in the exposed portion of the pin (Area  $A$ ) to the surroundings, is given by the empirical relation:

$$H_R = 2\pi R_t \Delta x h (T_x - T_E) \quad (xiv)$$

where  $T_E$  is the temperature of the air flowing past the pin (well away from the boundary layer at the cylindrical surface of the pin) and  $h$  is the heat transfer coefficient. We will equate this transferred heat flow rate to the net axial heat flow rate through the element at  $x$  (taking our origin for  $x$  to be now at the end of the pin, where  $H_1$  is originating). We have already seen that this net axial heat flow rate will be given by the left handside of Equation (iv), hence:

$$K_S \pi R_t^2 \left( \frac{d^2 T_x}{dx^2} \right) \cdot \Delta x = 2\pi R_t (T_x - T_E) \cdot \Delta x \cdot h.$$

$$\therefore \frac{d^2 T_x}{dx^2} = \frac{2}{K_S R_t} \cdot h \cdot (T_x - T_E) \quad (xv)$$

Writing

$$T_x - T_E = T \text{ and } Z = \left( \frac{K_S}{2hR_t} \right)^{1/2} \quad (xvi)$$

we get

$$\frac{d^2 T}{dx^2} = \frac{T}{Z^2 R_t} \quad (xvii)$$

The solution is of the form

$$T = B_1 \exp\left(\frac{x}{ZR_t}\right) + B_2 \exp\left(\frac{-x}{ZR_t}\right) \quad (xviii)$$

$$\therefore T_x = B_1 \exp\left(\frac{x}{ZR_t}\right) + B_2 \exp\left(\frac{-x}{ZR_t}\right) + T_E \quad (xix)$$

$$\therefore \frac{dT_x}{dx} = \frac{1}{ZR_t} \left[ B_1 \exp\left(\frac{x}{ZR_t}\right) - B_2 \exp\left(\frac{-x}{ZR_t}\right) \right] \quad (xx)$$

Now axial heat flow  $(H_A)_x = -K_S R_t^2 \left( \frac{dT_x}{dx} \right)$  from Equation (i),



so that

$$(H_A)_x = \frac{-K_S R_t}{z} \left[ B_1 \exp\left(\frac{x}{zR_t}\right) - B_2 \exp\left(\frac{-x}{zR_t}\right) \right]. \quad (\text{xxi})$$

The boundary conditions at  $x = L_1$  are

$$T_x = T_A \text{ and } (H_A)_x = H_2$$

$$\therefore T_A = B_1 \exp\left(\frac{L_1}{zR_t}\right) + B_2 \exp\left(\frac{-L_1}{zR_t}\right) + T_E$$

from Equation (xix)

and

$$H_2 = \frac{K_S R_t}{z} \left[ B_2 \exp\left(\frac{-L_1}{zR_t}\right) - B_1 \exp\left(\frac{L_1}{zR_t}\right) \right] \text{ from Equation (xxi).}$$

The last two expressions for  $T_A$  and  $H_2$  are readily solved for  $B_1$  and  $B_2$ , namely:

$$B_1 = \frac{1}{2} \left\{ (T_A - T_E) - \frac{zH_2}{K_S \pi R_t} \right\} \exp\left(\frac{-L_1}{zR_t}\right) \quad (\text{xxii})$$

and

$$B_2 = \frac{1}{2} \left\{ (T_A - T_E) + \frac{zH_2}{K_S \pi R_t} \right\} \exp\left(\frac{L_1}{zR_t}\right). \quad (\text{xxiii})$$

A further set of boundary conditions relate to  $x = 0$ , namely

$$T_x = T_S, \quad (H_A)_x = H_1.$$

$$\therefore T_S = B_1 + B_2 + T_E$$

$$= \frac{1}{2} \left\{ (T_A - T_E) - \frac{ZH_2}{K_S \pi R_t} \right\} \exp\left(\frac{-L_1}{ZR_t}\right) \\ + \frac{1}{2} \left\{ (T_A - T_E) + \frac{ZH_2}{K_S \pi R_t} \right\} \exp\left(\frac{L_1}{ZR_t}\right) + T_E$$

$$T_S = (T_A - T_E) \cosh\left(\frac{L_1}{ZR_t}\right) + \frac{ZH_2}{K_S \pi R_t} \sinh\left(\frac{L_1}{ZR_t}\right) + T_E \quad (13)$$

$$\text{and } H_1 = \frac{K_S \pi R_t}{z} (B_2 - B_1).$$

Substitution from Equations (xxii) and (xxiii) gives us

$$H_1 = \frac{K_S \pi R_t}{z} \left[ (T_A - T_E) \sinh\left(\frac{L_1}{ZR_t}\right) + \frac{ZH_2}{K_S \pi R_t} \cosh\left(\frac{L_1}{ZR_t}\right) \right] \\ \therefore H_1 = \left(\frac{K_S \pi R_t}{z}\right) \cdot (T_A - T_E) \sinh\left(\frac{L_1}{ZR_t}\right) + H_2 \cosh\left(\frac{L_1}{ZR_t}\right). \quad (14)$$

If we assume that the air which flows past the pin has a temperature  $T_o$  instead of  $T_E$ , then we modify Equation (13) and Equation (14) accordingly.

'h' is deduced from the Nusselt Number ( $N_{Nu}$ ) and the Reynolds Number ( $N_{Re}$ ), (See McAdams [50]).

Thus, from Equation (14), in conjunction with Equations (11) and (12), it is possible to deduce the heat flow rate ( $H_1$ ) entering the pin by taking three thermocouple readings. Furthermore, if we know the equilibrium value of the force of friction ( $F$ ) at the interface between the pin and the disc, then we can deduce the division of heat ( $\delta_{\text{expt}}$ ) at this interface, since clearly

$$\delta_{\text{expt}} = \frac{H_1}{VF} \quad (15)$$

where  $V$  is the linear speed at the pin and  $F$  is the frictional force at the pin. Similarly, Equation (13) in conjunction with Equations (11) and (12) can be used to deduce the bulk surface temperature of the pin ( $T_s$ ) from the same three measurements.

### 3.3 The Application of Heat Flow Analysis to Oxidation during Wear

In order to apply the heat flow analysis to mild, oxidational wear experiments, for the purposes of increasing our knowledge about the interactions at the real areas of contact during wear, it is necessary to postulate a surface model. The model chosen is similar to that proposed by Grosberg et alia. [49], namely, that at any time there exists (on the average)  $N$  contacts beneath the pin. As far as the pin is concerned, these  $N$  contacts will be covered with an oxide film of thickness  $\xi$  (the critical oxide thickness). On the other hand, the disk will have several sets of  $N$  contacts, representing the various positions taken up by the pin as the disk rotates beneath it. As a first approximation, let us assume that it is unlikely that there is any appreciable oxide thickness on the contacts on the disk, due to

the large area over which the contacts could occur on the disk compared with the small area available on the pin. We will re-examine this assumption later on in this review. This model differs from that used by Archard [36], who calculated "flash temperatures" on the assumptions that all the load was being supported by one asperity ( $N = 1$ ) and there was no oxide film present on either surface (i.e.,  $\xi_{\text{pin}} = \xi_{\text{disk}} = 0$ ).

Junction growth is an unlikely feature to occur in any wear situation other than severe, adhesive wear. Hence one can assume that the total real area of contact ( $A$ ) supporting the load is given by  $(A/W_{\text{pm}})$ , and that this area comprises of a number ( $N$ ) of circular contacts, each of radius ( $a$ ), so that

$$A = N\pi a^2 \quad (16)$$

As the disk moves beneath the pin, frictional heating occurs. We are not, at this stage, interested in what causes that frictional heating. Current suggestions involve the work necessary to take the asperities through elastic hysteresis cycles. Regardless of how the heat is evolved at the interface, it is possible to deduce  $T_{\text{ox}}$  (the temperature difference between the sliding interface and the bottom of the oxide film on each asperity) since

$$H_1 = K_O (N\pi a^2) \left( \frac{\Delta T_{\text{ox}}}{\xi} \right) \quad (i)$$

It has been shown, from basic heat flow theory, by Blok [40], that  $T_b$  (the temperature difference between the bottom of the oxide film and

the general surface temperature,  $T_S$ ) is given by

$$H_1 = K_S \cdot (N\pi a) \cdot \Delta T_b \quad . \quad (ii)$$

Hence, the total temperature difference ( $\theta_m$ ) between the sliding interface (i.e., the top of the oxide film) and the general surface temperature ( $T_S$ ) is given by Equation (4), namely  $\theta_m = T_C - T_S$ . But  $\theta_m$  must also equal the sum of  $\Delta T_a$  and  $\Delta T_b$ . Hence, from (i) and (ii) we can readily obtain the following expression for  $T_C$

$$T_C = T_S + \frac{H_1}{N\pi K_S a} + \frac{H_1 \xi}{N\pi K_O a^2} \quad . \quad (17)$$

Thus we have an expression for  $T_C$ , the contact temperature, in terms of measured parameters such as  $T_S$  and  $H_1$ , material constants such as  $K_S$  and  $K_O$ , and the surface model features,  $N$ ,  $\xi$  and  $a$ . Now  $T_C$  has an important effect on how the surface will oxidize during mild oxidational wear, as we have already seen in Equation (3) (Section 2.3). Let us examine this wear equation to see where else it depends on the model. Clearly  $d = 2a$ , that is, the distance of a wearing contact is considered to be the diameter of that contact. (Archard [27] first suggested that the distance from complete conjunction between two circular areas of contact to the point where the contact is just over, should be considered as a good estimate of the distance of a sliding asperity contact). It already contains  $\xi$  explicitly as a squared term in the denominator. It also contains  $N$  implicitly through  $A$ , which is equal to  $N\pi a^2$  [See Equation (16)].

Thus, the oxidational wear equation is a rather complex function of  $N$ ,  $\xi$  and  $a$ .

Let us now consider the division of heat ( $\delta_{\text{theory}}$ ) at the pin interface in terms of  $N$ ,  $\xi$  and  $a$ . In order to do this, we can modify Archard's [36] expression for the average value of  $\delta_{\text{theory}}$ , namely

$$\delta_{\text{theory}} = \frac{T_D}{T_p + T_D} \quad (18)$$

where  $T_D$  is the "fictitious" flash temperature obtained with a heat flow rate of  $H_{\text{total}}$  supplied to the disc only, and  $T_p$  is a similar temperature deduced on the assumption that the heat is supplied at that rate to the pin only. Quinn [19] uses Equation (17) with  $H_{\text{total}}$  inserted in place of  $H_1$  to obtain  $T_p$ .  $T_D$ , on the other hand, is much more difficult to deduce, since this is the case of the moving heat source. In a recent paper, Quinn, Rowson and Sullivan [51] claim that  $T_D$  (for medium speeds) is probably suitable for most practical conditions, where  $T_D$  is given by

$$T_D = \left[ 0.86 - 0.10 \left( \frac{Ua}{2\chi_s} \right) \right] \left( \frac{H_{\text{total}}}{4Na K_s} \right) \quad (19)$$

where  $\chi_s$  is the thermal diffusivity of the underlying metal (in their case, it was steel). It will be apparent that this expression for  $T_D$  does not include a term involving the thickness of the oxide film; this omission will form the basis of further discussion later in the review.

Thus we see that we can deduce theoretical values for the division of heat in terms of  $T_D$  (a function of 'a' and 'N'),  $T_p$  (a function of 'a', 'N' and  $\xi$ ) to compare with the experimentally determined values of this division of heat. Since our theoretical expression for the oxidational wear rate is also a function of these three parameters, it would seem that there are two equations for three unknowns (after we insert experimental values for  $\delta$  and  $w$  into them). In fact, of course, there are only two unknowns, since "a" and "N" are related through Equation (16). Unfortunately, even with two unknowns, the solution of the division of heat and the oxidational wear equations is not analytically possible. Using an intuitive approach, combined with a computer search technique, the present author [19] managed to obtain consistent values of N,  $\xi$  and  $T_c$  for some experiments in which low-alloy, medium-carbon steels were slid against disks of the same materials, at loads from 6 to 30N and at a sliding speed of about 5 m/s.

Quinn, Rowson and Sullivan [51] have, more recently, used an iterative technique to solve these two equations (without any recourse to intuition). This was done by writing the oxidational wear theory in terms of the contact radius (a) only. This was done by taking Equations (18), (19) together with Equation (17) (with  $H_{total}$  written for  $H_1$ ) and Equation (15) (with  $H_{total}$  written for VF) to obtain an expression for  $\xi$ , namely

$$\xi = Ba (C - Ea) \quad (20(a))$$

where

$$B = \pi K_o / 4 \delta_{\text{expt}} K_s \quad (20(b))$$

$$C = 0.8605 (1 - \delta_{\text{expt}}) - \delta_{\text{expt}} \quad (20(c))$$

$$E = 0.1021 V(1 - \delta_{\text{expt}}) / 2 \chi_d \quad (20(d))$$

These authors then obtained an expression for  $T_c$ , as follows

$$T_c = Ga - Ia^2 + T_s \quad (21(a))$$

where

$$G = \frac{\delta_{\text{expt}} \cdot H_{\text{total}} \cdot \text{pm}}{W} \left( \frac{\pi}{4K_s} + \frac{BC}{K_o} \right) \quad (21(b))$$

and

$$I = \frac{\delta_{\text{expt}} \cdot H_{\text{total}} \cdot \text{pm} \cdot B \cdot E}{K_o W} \quad (21(c))$$

Inserting the expressions for  $\xi$  and  $T_c$  from Equations (20) and (21) into Equation (3), the oxidational wear equation, with '2a' written for 'd' and (W/pm) written for A, the following equation was obtained for  $w_{\text{theory}}$  in terms of 'a' only:

$$w_{\text{theory}} = \frac{J}{C^2 a - 2CEa^2 + E^2 a^3} \exp \left( - \frac{Q_p}{Ma - Sa^2 + U} \right) \quad (22(a))$$

where



$$J = 2WA_p/V_{pm} f_{o^o}^2 z_B^2 \quad (22(b))$$

$$M = RG \quad (22(c))$$

$$S = RI \quad (22(d))$$

$$U = R(T_s + 273) \quad (22(e))$$

where it is expected that  $T_s$  will be measured in deg. C. Setting  $w_{theory}$  equal to  $w_{expt}$ , Equation (22(a)) can be written as

$$-\frac{Q_p}{Ma - Sa^2 + u} = \ln (C^2 w_{expt}^a - 2CE w_{expt}^2 + E^2 w_{expt}^3) - \ln J \quad (23)$$

Unfortunately, Equation (23) does not lend itself to analytical solution. Hence an iterative solution had to be sought. Details of the solution, together with a computer program used to deduce values of 'a' from the experimentally-determined values of the division of heat and the wear rate, are given in the Appendix of Reference [51].

It is interesting to note that the trends of  $N$ ,  $\xi$  and  $T_c$  versus load ( $W$ ) as revealed by the new iterative technique were not significantly different from those revealed by the intuitive and computer search techniques [19]. However, the actual numbers assigned to  $N$ ,  $\xi$  and  $T_c$  were not in such close agreement. In fact, the numbers assigned to  $N$  and to the contact temperature ( $T_c$ ) were all considerably lower for the iterative approach. This was mainly due to the fact that, between the publication of Reference [19] in 1978 and that of the iterative solution

[51] in 1980, a new approach had been initiated towards clearing up the old problem related to whether or not one can use static oxidation data in trying to explain oxidation during wear. This approach, by Sullivan, Quinn and Rowson [52], will be discussed in the next section. It should be emphasized that this work mainly relates to steels. There is a real need for more confirmation of the applicability of the oxidational wear theory to other metal systems!

#### 4. ACTIVATION ENERGIES AND ARRHENIUS CONSTANTS FOR OXIDATIONAL WEAR

##### 4.1 Introduction

In static oxidation studies, one normally measures the mass uptake of oxygen per unit area ( $\Delta m$ ) of a metal surface during a time ( $t$ ). After an initial linear dependence upon time, it is most usual for a metal (especially iron) to oxidize according to the parabolic relation:

$$\Delta m^2 = k_p t \quad (24)$$

where  $k_p$  is the parabolic rate factor, which itself depends upon the temperature ( $T$ ) through Equation (8). This equation may be written in logarithmic form as:

$$\log_{10}(k_p) = \log_{10}(A_p) - \left(\frac{Q_p}{2.30R}\right) \left(\frac{1}{T}\right) . \quad (25)$$

By plotting  $\log_{10}(k_p)$  versus  $(1/T)$ , where  $T$  is expressed in absolute degrees (K), one obtains a straight line of slope  $(-Q_p/2.30R)$ . This is sometimes called an "Arrhenius Plot" and is used as a basis for determining  $Q_p$  (the Activation Energy for Oxidation).

Very rarely is the Arrhenius Plot a straight line over the range of temperatures for which Equation (24) has been shown to be valid. Most investigators of oxidation kinetics are only interested in the slope of these plots. Clearly, those portions of non-linearity indicate deviation from parabolic dependence upon time. However, they could also be related to ranges of temperature where the type of oxide changes

from one structure to another. For instance, when the author first used the static oxidation results of Caplan and Cohen [53] in his work with low-alloy, medium-carbon steel (EN31) [19], he did not appreciate that, instead of one straight line, there were, in fact, three straight lines relating to changes in oxide structure from the rhombohedral ( $\alpha\text{-Fe}_2\text{O}_3$ ) to the spinel ( $\text{Fe}_3\text{O}_4$ ) type at about  $450^\circ\text{C}$  and from the spinel to the wustite ( $\text{FeO}$ ) type at about  $600^\circ\text{C}$ . Very careful plotting of Caplan and Cohen's [53] oxidation rates versus the reciprocal of the absolute temperature revealed three regions of the Arrhenius plot, from which three combinations of  $A_p$  and  $Q_p$  values could be deduced, as shown in Table 2.

Table 2. Oxidation Constants (derived by the static oxidation of iron, 53)

| Temperature range<br>( $^\circ\text{C}$ )                           | < 450             | 450 to 600           | > 600             |
|---|-------------------|----------------------|-------------------|
| Arrhenius constant<br>( $\text{kg}^2 \text{m}^{-4} \text{s}^{-1}$ ) | $1.5 \times 10^6$ | $3.2 \times 10^{-2}$ | $1.1 \times 10^5$ |
| Activation Energy<br>( $\text{kJ} \cdot \text{mole}^{-1}$ )         | 208               | 96                   | 210               |

Although  $Q_p$  (the Activation Energy) only changes by a factor of 2 (and back again) when the temperature increases from below  $450^\circ\text{C}$  to above  $600^\circ\text{C}$ , the Arrhenius Factor changes through 8 orders of magnitude

(and 7 orders of magnitude back) for the same temperature range and the same oxidizing conditions. However, it should be realized that a two-fold decrease in  $Q_p$  around 450°C, leads to an 8-orders of magnitude increase in the value of the exponential. Clearly, these are only slight changes in  $k_p$  (which is the product of  $A_p$  and the exponential term) when going through an oxide transition in static oxidation experiments. Now  $k_p$  may be expected to be proportional to the diffusion coefficients ( $D$ ), where  $D$  may be written in the Arrhenius form equal to  $D_o \exp(-Q/RT)$ , of the various atomic species in the relevant oxide. In  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, it is the diffusion of oxygen only; in Fe<sub>3</sub>O<sub>4</sub>, both the iron and the oxygen diffuse; in FeO, it is the diffusion of the iron only. If this is so, the values of  $A_p$  and  $Q_p$  for oxide growth will depend upon  $D_o$  and  $Q$  for diffusion.  $Q$ , depending on relative potential barrier heights, is not expected to differ in static and tribological situations. On the other hand,  $D_o$  (and hence  $A_p$ ) will greatly depend upon surface conditioning, voids and dislocations and other factors [35], all of which lead to differences, even between static oxidation tests with the same metal. Such differences can occur over many orders of magnitude depending on the experimental conditions.

We may say, therefore, that activation energies will remain the same in both static and sliding cases, and hence statically-derived values may be applied to tribological situations, if the correct temperatures are chosen. (There is little point in applying statically derived values above 600°C, say, to sliding oxidation where the temperatures might not exceed 300°C and quite different oxides may be

produced). The Arrhenius constants, however, unlike the activation energies, will be very different in the tribological situation. Intuitively, one would expect the values of  $A_p$  to be greater, due to the greater degree of surface disruption which occurs during sliding. In the next two subsections, we will show (i) how the intuitive search technique used in reference [19] can be used to provide tribological values of  $A_p$  for those experiments with EN31 steels sliding against themselves with no lubrication, and (ii) how these values of  $A_p$  can be used with other low-alloy steels, to confirm the surface model and its relevance to mild, oxidational wear.

#### 4.2 An Experimental Evaluation of the Arrhenius Constants related to the Oxidational Wear of Steel

In the computer program used by the present author [19], a particular value of  $\xi$  (oxide film thickness) was chosen and tried with each of a wide range of  $N$  values to obtain a value for the theoretical division of heat ( $\delta_{\text{theory}}$ ) and a theoretical value for the oxidation contact temperature ( $T_c$ ). If the value of  $\delta_{\text{theory}}$  was within one percent of the measured value of the division of heat ( $\delta_{\text{expt}}$ ), then the computer used those values of  $N$ ,  $\xi$  and  $T_c$  to derive a set of several  $Q_p$  values which would be consistent with Equation (3), in which  $w_{\text{expt}}$  replaces  $w_{\text{theory}}$ ,  $A$  is set equal to  $(W/p_m)$ , and 'd', the distance of a wearing contact is taken to be '2a', where 'a' is given by Equation (16), that is:

$$d = 2a = 2(W/\pi N p_m)^{1/2} . \quad (26)$$

The approach was "intuitive" insofar as certain criteria were used for choosing a particular set of values of  $N$ ,  $\xi$ ,  $T_c$ ,  $\delta_{\text{theory}}$  and  $Q_p$  consistent with the experimental wear rate and division of heat for any particular experiment in reference [19]. These are given below:

- (i)  $\xi$  should be in the range  $0.5 \mu\text{m} < \xi < 15 \mu\text{m}$ .
- (ii)  $N$  should be in the range  $1 < N < 2000$ .
- (iii)  $T_c$  should be greater than  $T_s + 150^\circ\text{C}$  and less than  $1000^\circ\text{C}$ .

The reasons behind (i) and (ii) were based on electron microscope evidence [18] regarding the height ( $\sim 3 \mu\text{m}$ ) of the plateaux of contact between sliding surfaces. The limits of  $\xi$  are arbitrarily centered around this value. It is also intuitively considered that 'd' will be of the order of magnitude of  $\xi$ , i.e., about  $10^{-6}$  m. From Equation (26), this means that  $N'$  should be less than 2000 for most of the situations involved. Criterion (iii) arises from the x-ray diffraction work of the present author [26] which indicated that, for similar conditions, the oxidation temperature was about  $200^\circ\text{C}$  above the general surface temperature ( $T_s$ ) for the low  $T_c$ 's (i.e.,  $T_c < 450^\circ\text{C}$ ) obtained in these experiments. The criterion that  $T_c$  be less than  $1000^\circ\text{C}$  is arbitrary, although one would expect values almost half of this if we assume  $N < 1$ .

In reference [19], the present author used one particular value of  $A_p$  (namely  $3.2 \times 10^6 \text{ kg}^2 \text{ m}^{-4} \text{ s}^{-1}$ ) and then used the criteria above to produce a fairly large range of possible values of  $N$ ,  $\xi$  and  $T_c$  consistent with the  $Q_p$  values around the statically-determined value of  $96 \text{ kJ/mole}$ . In order to reverse this procedure, namely to produce

values of  $A_p$ , together with  $N$ ,  $\xi$  and  $T_c$ , which would be consistent with both the experimentally-determined division of heat and the wear rate, there was no guide available as to the "correct" order of magnitude of  $A_p$  (apart from expecting the tribological  $A_p$  to be somewhat greater than the statically-determined  $A_p$ ). Fortunately,  $A_p$  seems to be rather insensitive to slight increases in the wear rate with increasing load (for a given oxide range), so that one was able to obtain fairly good average values for the Tribological Arrhenius Constants for the three temperature ranges over which the three different iron oxides pre-dominate [52]. These  $A_p$  values (together with the appropriate  $Q_p$  values) are given in Table 3:

Table 3. Oxidation Constants (relevant to the wear of EN31 steel)

| Temperature Range<br>(°C)   | < 450     | 450 to 600 | > 600  |
|---|-----------|------------|--------|
| Tribological Arrhenius<br>Constant<br>( $\text{kg}^2 \text{m}^{-4} \text{s}^{-1}$ ) | $10^{16}$ | $10^3$     | $10^8$ |
| Activation Energy<br>( $\text{kJ.mole}^{-1}$ )                                      | 208       | 96         | 210    |

#### 4.3 Application of Arrhenius Constants for Oxidational Wear to other Systems

Although Sullivan et alia. [52] do show that the oxidation constants of Table 3 can be used to predict the wear rates of other



low-alloy steels and give information about the variation of  $N$ ,  $\xi$  and  $T_c$  with load at various speeds, a more complete analysis was published elsewhere at about the same time [51] which we will discuss here. In these experiments, another low-alloy steel (EN8) was worn against itself at speeds of 2, 3 and 4 m/s over a range of loads from 4 to 60 N. The wear was always mild, i.e., the oxidational wear theory was always applicable to these results. In all cases, a thorough analysis of the collected wear debris was undertaken using the X-Ray Powder Diffraction techniques, so that the three oxide regions could be clearly identified. Since this work vividly showed the effect of oxide structure upon both the wear rate and the general surface temperature (as deduced from heat flow and thermocouple measurements), the graphs of "wear rate versus load" and "surface temperature versus load" are reproduced here in Figures 3 and 4 respectively.

These graphs are important since they show (a) that wear rates and general surface temperatures are proportional to the load (in between transitions), and (b) a change of wear rate versus load occurs when the load increases through a transition load above which FeO is produced at the wearing interface. They give some support to the underlying premises of the oxidational wear theory. The results, then, give all the indications of being a reliable base on which to show that the tribological oxidation constants (of Table 3) give rise to "sensible" values of  $N$ ,  $\xi$  and  $T_c$  when applied to *other* sliding systems. "Sensible" values are primarily those which lie within the limits of the criteria mentioned in Sub-section 4.2. Admittedly, there is a need for a more

direct measurement of these three most important wear parameters and, in a later section dealing with different materials, some work will be described in which scanning electron microscopy has been used to determine the oxide thickness ( $\xi$ ). Measurement of  $N$  and  $T_c$  by direct measurement, of course, is only possible if one of the specimens is transparent (a state in which most practical materials, in particular steels, never find themselves!). With these restrictions in our mind, let us examine how the tribological oxidation constants fit in with the expected behavior of  $N$ ,  $\xi$  and  $T_c$  for a different low-alloy steel than EN31, namely for EN8 steel.

Using both the intuitive computer search technique [19] and the iterative solution technique [51], it is possible to generate values of  $N$ ,  $\xi$  and  $T_c$  for the wear experiments with EN8 steel summarized in Figures 3 and 4 of this review. For the sake of illustration, consider only the results obtained at 2 m/s. Table 4 compares the values of the surface model parameters as given by the two techniques. The column relating to the contact radius ( $a$ ) has been derived from the iterative technique only.

Most of the differences between  $N$  and  $T_c$  are trivial when plotted against the applied load. Figure 5 shows that the number of wearing asperities ( $N$ ) is proportional to the load within the appropriate oxide ranges, the factors of proportionality being 0.92 and 1.2 asperities/newton above the FeO transition, 3.57 and 4.5 asperities/newton between the FeO and  $Fe_3O_4$  transition, and 16.8 and 28.5 asperities/newton below the  $Fe_3O_4$  transition, according to either the computer search or the

Table 4. Comparison of  $N$ ,  $T_c$  and  $\xi$  values according to the computer search and iterative solution techniques

| Main Oxide                     | Load (N) | Contact Radius ( $\mu\text{m}$ ) | Computer Search |                         | Iterative Solution           |     |                         |                              |
|--------------------------------|----------|----------------------------------|-----------------|-------------------------|------------------------------|-----|-------------------------|------------------------------|
|                                |          |                                  | $N$             | $\xi$ ( $\mu\text{m}$ ) | $T_c$ ( $^{\circ}\text{C}$ ) | $N$ | $\xi$ ( $\mu\text{m}$ ) | $T_c$ ( $^{\circ}\text{C}$ ) |
| $\alpha\text{-Fe}_2\text{O}_3$ | 3.94     | 1.46                             | 113             | 0.89                    | 277                          | 180 | 0.82                    | 226                          |
|                                | 6.89     | 2.53                             | 65              | 2.66                    | 290                          | 105 | 2.67                    | 239                          |
|                                | 9.85     | 1.76                             | 184             | 1.17                    | 278                          | 310 | 1.07                    | 227                          |
|                                | 9.85     | 2.05                             | 140             | 1.69                    | 282                          | 228 | 1.54                    | 230                          |
| $\text{Fe}_3\text{O}_4$        | 14.78    | 4.47                             | 60              | 1.43                    | 368                          | 72  | 1.70                    | 371                          |
|                                | 14.78    | 3.94                             | 81              | 1.47                    | 406                          | 93  | 1.75                    | 409                          |
|                                | 19.70    | 4.94                             | 76              | 2.04                    | 440                          | 79  | 2.40                    | 443                          |
|                                | 24.63    | 5.16                             | 87              | 1.98                    | 444                          | 90  | 2.40                    | 449                          |
|                                | 29.55    | 7.84                             | 47              | 2.63                    | 442                          | 47  | 3.24                    | 448                          |
| $\text{FeO}$                   | 34.47    | 9.43                             | 34              | 0.94                    | 583                          | 38  | 1.14                    | 583                          |
|                                | 39.40    | 11.37                            | 28              | 1.38                    | 612                          | 30  | 1.75                    | 615                          |

iterative solution approach respectively. Graphs of contact temperature ( $T_c$ ) versus load are given in Figure 6. Since the contact radius seems to approximately constant at  $1.95 \pm 0.34 \mu\text{m}$ ,  $5.27 \pm 0.83 \mu\text{m}$  and  $10.40 \pm 0.97 \mu\text{m}$  for the  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and FeO oxide regimes respectively, Equation 21(a) indicates that  $T_c$  should be equal to  $T_s$  plus some constant. Hence,  $T_c$  should increase linearly with load in between oxide transitions in a similar fashion to the increase of  $T_s$  with load. Comparison of Figure 6 with Figure 4(a), shows that  $T_c$  does behave as expected. The differences in  $\xi$  values are even less significant than those apparent with the plots of  $T_c$  versus load. Although the value of  $\xi$  is supposed to be a constant for each load, the oxidational wear theory does not prevent the critical oxide thickness being dependent upon load. From this set of experiments, however, it seems that  $\xi$  is fairly insensitive to changes in load, the computer search technique giving an average of  $1.66 \pm 0.49 \mu\text{m}$  whilst the iterative solution gives an average of  $1.86 \pm 0.66 \mu\text{m}$ .

Similar results were obtained at 3 and 4 m/s using EN8 steel specimens [51,52]. These results are important in the evolution of the oxidational theory of mild wear under conditions where oxidation at the real areas of contact dominates over oxidation of the remainder of the surface for several reasons. Firstly, they showed that there is a difference between the Arrhenius Constant for static oxidation and that relating to oxidational wear. Secondly, the Arrhenius Constant for oxidational wear of EN31 steel can be applied to the oxidational wear of other low-alloy steels. Thirdly, the effects of

oxide structure can produce sharp transitions in the wear rate and the general surface temperature. Fourthly, the values of  $N$  and contact radius ( $a$ ) obtained by the application of the oxidational theory to these wear rates and surface temperatures, provide interesting confirmation of previously held ideas relating to the increase in the real area of contact with load. This is because it seems that  $N$  does increase linearly with load (in between oxide transitions) but the contact radius ( $a$ ) remains constant (also between oxide transitions). Since the contact radius also seems to be different according to the oxide, this could explain why it has been difficult to decide if the increase in real area of contact ( $A$ ) is due to an increase in  $N$  with load or an increase in contact radius with load or an increase in both. Fifthly, the constancy of critical oxide film thickness ( $\xi$ ) is confirmed, the values always lying between 1 and 3  $\mu\text{m}$  (the value observed in electron microscope examination of mild wear surfaces, 18). Finally, the actual values assigned to  $N$  and  $T_c$  are consistent with the asperity densities and contact temperatures currently being measured in direct measurements using interferometry [54] and infrared microscopy [55].

There are limitations we must place on using these Oxidational Wear Constants to other systems, apart from the obvious one involving a change in constants when one changes the material of the wearing pair! These limitations relate to conditions where "out-of-contact" oxidation cannot be neglected. In particular, these constants will be only partially relevant to wear under the high ambient temperatures induced

mainly by external heating. This is the big problem. Most practical situations involving oxidational wear (e.g., the wear of valve and valve-seat materials in the exhaust systems of diesel engines) also involve a situation in which high ambient temperatures occur, which is generally not due to frictional heating, or only partly so. Even in lubricated situations, such as scuffing of gears, the ambient temperatures can be around 300°C. This could be enough to make the oxidation of those parts of nominal area of contact which are not in actual contact significant compared with those parts forming the actual real areas of contact. Hence the next section of this review, dealing with the wear of metals at elevated temperatures.

## 5. WEAR OF METALS AT ELEVATED TEMPERATURES

### 5.1 The Oxidational Theory of Wear at Elevated Temperatures

In this sub-section, we will deal with the modifications required to make the Oxidational Wear Theory applicable to wear at elevated ambient temperatures. The treatment is based on the author's original paper [56] but it owes much to discussion with colleagues and students at Aston University, in particular to Athwal [57] and Allen [25].

In order to apply the oxidational theory of mild wear to elevated temperatures, account must be taken of the "out-of-contact" oxidation, that is, the oxidation of the real areas of contact in between the times they are in contact, and are, therefore, being exposed to the general surface temperature ( $T_s$ ). It is not possible to consider this aspect of wear without applying it to a particular system geometry. Let us, therefore, consider a pin-on-disk geometry, and assume that there are  $N$  asperities in contact at any instant. Furthermore, assume these contacts are of equal circular area ( $\pi a^2$ ). If we assume a uniform distribution of these contacts, each of the same height, then the number ( $n$ ) of contacts per unit area on both the pin and the disk is given by:

$$n = 4N/\pi D^2 \quad (27)$$

where  $D$  is the diameter of the pin ( $= 2R_t$ ).

In one revolution of the disk, an asperity on the pin will generate an annulus of width ( $d$ ) on the wear track of the disk, where  $d$  is the diameter of the asperity ( $= 2a$ ). Hence the number of contacts within this annulus is  $N_d$  given by:

$$N_d = n(2\pi R_d d) = 8R_d N d/D^2 \quad (28)$$

where  $R_d$  is the mean radius of the wear track. Hence, on the average, each asperity on the pin will make  $(8R_d N d/D^2)$  encounters in one revolution.

Analogous to Archard's [27] K-factor, let us define  $K'$  as the probability of producing a wear particle per revolution. This means it will take  $(1/K')$  revolutions to produce a wear particle. Hence, from Equation (28), the number of encounters  $(1/K)$  required to produce a wear particle is  $(1/K')(N_d)$ , that is:

$$\frac{1}{K} = \left(\frac{1}{K'}\right) \left(\frac{8d R_d N}{D^2}\right) .$$

Thus, the probability of forming a wear particle at a single encounter is  $K$ , the Archard K-factor, where  $K$  is given by:

$$K = K' \frac{D^2}{8d R_d N} . \quad (29)$$

We are now in a position to deduce expressions for the total times  $(t_c)$  and  $(t_s)$  for which the wearing asperity is at the contact temperature  $(T_c)$  and at the general surface temperature  $(T_s)$  respectively.

Consider one asperity on the pin surface. The time of oxidation at this asperity for one revolution  $(t_r)$  is given by:



$$t_r = t_{r_c} + t_{r_s} = \frac{2\pi R_d}{V} \quad (30)$$

where  $V$  is the speed of sliding at the pin surface,  $t_{r_c}$  is the time for which the asperity is in contact and  $t_{r_s}$  is the time it is "out-of-contact" during one revolution. From Equation (28), the contact time per revolution ( $t_{r_c}$ ) is:

$$t_{r_c} = \left[ \frac{8R_d Nd}{D^2} \right] \tau \quad (31)$$

where  $\tau$  is the time for a single asperity encounter which is given by  $\tau = d/V$ . Hence the total contact time ( $t_c$ ) needed before a wear particle is produced is:

$$t_c = (1/K')t_{r_c} = d/VK \quad (32)$$

Equation (32) could easily have been deduced from the Archard [27] interpretation of  $K$ , so that  $(1/K)$  encounters, each of duration  $\tau = (d/V)$ , give rise to a total contact time ( $t_c$ ) of  $(d/VK)$ . However, with the development as above, it is now easier to derive an expression for the total time ( $t_s$ ) that the asperity is out of contact (before it is removed in the wearing process after  $(1/K')$  revolutions). For example:

$$t_s = \left( \frac{1}{K'} \right) \cdot t_{r_s} \quad (33)$$

where

$$t_{r_s} = t_r - t_{r_c} = \frac{2\pi R_d}{V} - \frac{8R_d \cdot N \cdot d^2}{D^2 \cdot V}$$

i.e.,

$$t_s = \frac{D^2}{4dKN} \left[ \pi - 4N \left( \frac{d}{D} \right)^2 \right] . \quad (34)$$

This is the time that an asperity will be at the general surface temperature ( $T_c$ ) before it breaks off to form a wear particle. Remember that it will also be at the contact temperature ( $T_c$ ) for the total time ( $t_c$ ) given by Equation (32). It is reasonable to assume that, for most practical systems subjected to external heating whilst sliding, the general surface temperature ( $T_s$ ) will be greater than 100°C and it will oxidize with a parabolic dependence upon the time at both  $T_s$  and  $T_c$ . Hence the mass uptake ( $\Delta m_c$ ) of oxygen per unit area of oxide film at the contact temperature ( $T_c$ ) will be:

$$\Delta m_c^2 = k_p(T_c) t_c \quad (35)$$

where  $k_p(T_c)$  is the parabolic rate constant at  $T_c$ . Similarly, we can write an expression for ( $\Delta m_s$ ), the mass uptake of oxygen per unit area whilst the asperity is "out-of-contact", as follows:

$$\Delta m_s^2 = k_p(T_s) t_s \quad (36)$$

where  $k_p(T_S)$  is the parabolic rate constant at  $T_S$ .

The critical oxide film thickness ( $\xi$ ) which builds up upon the asperity after  $(1/K')$  revolutions, is simply given by:

$$\xi = \xi_C + \xi_S \quad (37)$$

where  $\xi_C$  and  $\xi_S$  are the total oxide film thicknesses produced at temperatures  $(T_C)$  and  $(T_S)$  respectively. To a good approximation,  $\xi_C$  and  $\xi_S$  are related to  $\Delta m_C$  and  $\Delta m_S$  through the relations:

$$\Delta m_C = f_o(T_C) \cdot \rho_o(T_C) \cdot \xi_C \quad (38a)$$

$$\Delta m_S = f_o(T_S) \cdot \rho_o(T_S) \cdot \xi_S \quad (38b)$$

where  $f_o$  is the mass fraction of oxide which is oxygen and  $\rho_o$  is the density of the oxide film. Both quantities depend upon the temperature of oxidation ( $T_S$  or  $T_C$ ), since there is usually more than one oxide type formed when the temperature goes from room temperature to 600°C or more. Combining Equations (37) and (38) we get:

$$\xi = \frac{\Delta m_C}{f_o(T_C) \cdot \rho_o(T_C)} + \frac{\Delta m_S}{f_o(T_S) \cdot \rho_o(T_S)} \cdot$$

Substituting for  $\Delta m_C$  and  $\Delta m_S$  from Equations (35) and (36) one obtains:

$$\xi = \frac{[k_p(T_C)t_C]^{1/2}}{f_o(T_C)\rho_o(T_C)} + \frac{[k_p(T_S)t_S]^{1/2}}{f_o(T_S)\rho_o(T_S)} \quad (39)$$

Putting in expressions for  $t_c$  [from Equation (32)] and  $t_s$  [from Equation (34)], the following expression for critical oxide film thickness ( $\xi$ ) emerges:

$$\xi = \left( \frac{k_p(T_c) \cdot d}{V \cdot K} \right)^{1/2} \left( \frac{1}{f_o(T_c) \cdot \rho_o(T_c)} \right) + \left\{ \frac{k_p(T_s) \cdot D^2}{4d \cdot KN} \left[ \pi - 4N \left( \frac{d}{D} \right)^2 \right] \right\} \left( \frac{1}{f_o(T_s) \cdot \rho_o(T_s)} \right) \quad (40)$$

Squaring this equation and rearranging, we eventually obtain an expression for the K-factor which takes into account oxidation at the general surface temperature ( $T_s$ ), namely:

$$K = \frac{d \cdot k_p(T_c)}{V \cdot f_o^2(T_c) \cdot \rho_o^2(T_c) \cdot \xi^2} + \left[ \frac{D^2 \cdot k_p(T_s)}{4d \cdot KN} \left\{ \pi - 4N \left( \frac{d}{D} \right)^2 \right\} \right] \frac{1}{f_o^2(T_s) \cdot \rho_o(T_s) \cdot \xi^2} + \frac{D}{V \cdot f_o(T_c) \cdot \rho_o(T_c) \cdot f_o(T_s) \cdot \rho_o(T_s) \cdot \xi^2} \left[ \frac{k_p(T_c) \cdot k_p(T_s)}{N} \left\{ \pi - 4N \left( \frac{d}{D} \right)^2 \right\} \right]^{1/2} \quad (41)$$

Putting this value for K into Equation (1), we obtain the general oxidational wear equation. Assuming  $A = W/p_m$  (from Bowden and Tabor [12])

we can write it in the following form:

$$\begin{aligned}
 w = & \frac{W \cdot d \cdot k_p(T_C)}{V f_o^2(T_C) \cdot \rho_o^2(T_C) \cdot p_m(T_S) \xi^2} \\
 & + \frac{W}{p_m(T_S)} \cdot \left[ \frac{D^2 \cdot k_p(T_S)}{4d \sqrt{N}} \left\{ \pi - 4N \left( \frac{d}{D} \right)^2 \right\} \right] \cdot \left( \frac{1}{f_o^2(T_S) \cdot \rho_o^2(T_S) \cdot \xi^2} \right) \\
 & + \frac{WD}{V \cdot f_o(T_C) \cdot \rho_o(T_C) \cdot f_o(T_S) \cdot \rho_o(T_S) \cdot p_m(T_S) \cdot \xi^2} \left[ \frac{k_p(T_C) \cdot k_p(T_S)}{N} \left\{ \pi - 4N \left( \frac{d}{N} \right)^2 \right\} \right]^{1/2} \quad (42)
 \end{aligned}$$

In Equation (42), we have written  $p_m(T_S)$  for  $p_m$  to denote that the real area of contact (A) is determined by the value of the hardness of the underlying metal (and not the oxide), and this hardness depends mainly on the general surface temperature ( $T_S$ ).

The first term of Equation (42) is, of course, the expression for the wear rate as given in the original oxidational wear equation (Equation (3)) with  $[W/p_m(T_S)]$  substituted for A. This expression ignores any oxidation which may occur away from the actual areas of contact during the life-time of a wearing contact. The second and third terms of Equation (42) are due to the effect of significant "out-of-contact" oxidation at the general surface temperature ( $T_S$ ) upon the wearing processes occurring at the real areas of contact. One way of examining this expression as regards its validity to real wear processes, is to apply it to frictionally-heated systems in which the surface temperature

$(T_s)$  is not insignificant. The present author [56] used this approach with an expression for the oxidational wear rate somewhat similar to Equation (42), to show that the second or third terms could be neglected for EN8 steel systems sliding at speeds less than 5 m/s and loads less than about 40N, provided  $T_s$  was less than about 300°C. The argument is somewhat circuitous, since the values assigned to  $k_p(T_c)$  in these additional terms had been obtained from calculations in which the "out-of-contact" oxidation was assumed to be negligible! For the argument [56] to be truly valid, we should apply the processes described in Section 4 of this review to the general equation [Equation (42)] and deduce the tribological Arrhenius Constants suitable for insertion into  $k_p(T_c)$ . These processes will clearly become very tedious for such a complex expression. There is a need for us to put in more measured data into both the wear equation [Equation(42)] and the heat flow analysis. Such data can be provided by using the scanning electron microscope to measure the oxide film thicknesses on both the pin and disk surfaces. We can then use Equation (17) together with an equation similar to Equation (19) to obtain the contact temperature in terms related to heat flow down the pin and into the disk respectively. Since the contact temperature must be the same for both the pin and disk, we can equate these expressions and solve for the contact radius ( $a$ ), remembering that  $N$  is related to the contact radius through Equation (16). This is done in the next subsection.

## 5.2 The Measurement of Oxide Film Thickness and its Use in Deducing the Contact Temperature and other Surface Parameters

If we can measure the oxide film thickness on both the pin and disk surface, then we will have reduced the number of variables in Equation (42). Previously, when deducing Equation (19) for the fictitious disk temperature ( $T_D$ ) which one would obtain assuming all the heat ( $H_{total}$ ) evolved at the interface goes into the disk, it was assumed (for convenience) that the average area of contact on the disk would not have very much oxide film. It is not necessary to make this assumption and certainly, recent examinations [25] by Scanning Electron Microscopy have shown that the oxide film thicknesses on the pin ( $\xi$ ) and on the disk ( $\xi'$ ) are of the same order of magnitude. We can therefore modify Equation (19) to give us the general surface temperature of the disk ( $T_d$ ), by putting  $(VF - H_1)$  for  $H_{total}$  and adding a term representing the temperature drop across the oxide film, of thickness  $\xi'$ , upon the real areas of contact of the disk surface.  $(T_c - T_d)$  must be equal to the temperature drop across the film together with that across the metal between the underside of the oxide and the bulk of the metal of the disk surfaces. This is summarized in the following expression:

$$T_c = T_d + \frac{\alpha(VF - H_1)}{N\pi K_d \cdot a} + \frac{\alpha(VF - H_1)\xi'}{N\pi K_o a^2} \quad (43)$$

where  $\alpha$  is a dimensionless parameter which is related to the speed parameter ( $L$ ) which is defined as:

$$L = \frac{Va}{2\chi_d} \quad (44)$$

According to Archard [36],  $\alpha$  varies linearly with  $L$  in the range of  $0.1 < L < 9.0$  from approximately 0.85 at  $L = 0.1$  down to about 0.35 at  $L = 5$ . Thus, we may write  $\alpha$  as:

$$\alpha = 0.86 - 0.10 L . \quad (45)$$

In the above equations,  $K_d$  is the thermal conductivity of the disk material and  $\chi_d$  is the thermal diffusivity given by the relation:

$$\chi_d = \frac{K_d}{\rho_d c_d} \quad (46)$$

where  $\rho_d$  is the density of the disk material and  $c_d$  is the specific heat capacity of that material. Note that we have changed our subscript from 's' to 'd' to allow for the fact that it is quite probable that the disk material will not be the same as the pin material, in respect of which we had used the subscript 's' to denote the property of the material of both the pin and the disk, namely steel. With this in mind, let us write Equation (17) in terms of subscripts 'p' and 'o', instead of 's' and 'o', for the appropriate terms, namely:

$$T_c = T_s + \frac{p_m(T_s) \cdot H_1 \cdot a}{K_p W} + \frac{p_m(T_s) \cdot H_1 \cdot \xi}{W \cdot K_o} \quad (47)$$

In this equation, we have substituted for  $N$  from Equation (16) together with the well known relation  $A = W/p_m$ . Now let us compare Equation (43) with Equation (47), after substituting for  $\alpha$  in Equation (43), and get:



$$\left[ \frac{p_m(T_s) \cdot V \cdot (VF - H_1)}{20 W \chi_o K_d} \right] a^2 - \frac{p_m(T_s)}{W} \left[ \frac{0.86(VF - H_1)}{K_d} + \frac{H_1}{K_p} - \frac{V(VF - H_1)\xi'}{20 \chi_o K_o} \right] a - \left[ \frac{p_m(T_s)}{W} \left\{ \frac{0.86(VF - H_1)\xi'}{K_o} - \frac{H_1\xi}{K_o} \right\} - (T_s - T_d) \right] = 0 \quad (48)$$

This is a quadratic equation in the contact radius (a) of the form  $Ax^2 + Bx + C = 0$ . Hence, Equation (48) will have two solutions if  $B^2 > 4AC$ . The correct solution will have to be chosen by inspection.

All the parameters of Equation (48) are measured or known, with the possible exception of  $\chi_o$ , the thermal diffusivity of the oxide. Only estimates are known for  $K_o$ ,  $\rho_o$  and  $c_o$ , which all vary with temperature. Since  $\rho_o$  and  $c_o$  vary in opposition with temperature, we need only concern ourselves with  $K_o$  and its variation with temperature. Molgaard and Smeltzer [58] have shown that for hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ),  $K_o$  varies according to the following relations:

$$\begin{aligned} \alpha\text{-Fe}_2\text{O}_3: \quad K_o &= (8.39 - 6.63 \times 10^{-3} T) \text{ Wm}^{-1}\text{K}^{-1} \\ \text{Fe}_3\text{O}_4: \quad K_o &= (4.23 - 1.37 \times 10^{-3} T) \text{ Wm}^{-1}\text{K}^{-1} \end{aligned}$$

With most steels, it may be sufficient to use these relations to get  $K_o$ . However, for steels with high chromium content, or for other materials, it is better to use the value of  $K_o$  which gives the best agreement between  $\delta_{\text{expt}}$  and  $\delta_{\text{theory}}$ , where  $\delta_{\text{expt}}$  is given by Equation (15) and  $\delta_{\text{theory}}$  is given by Equation (18) and  $T_p$  and  $T_D$  are given by:

$$T_p = \frac{p_m(T_s) \cdot V.F.a}{W K_p} + \frac{p_m(T_s) \cdot V.F.\xi'}{W K_o} \quad (49)$$

and

$$T_D = \frac{\alpha \cdot p_m(T_s) \cdot V.F.a}{W K_d} + \frac{p_m(T_s) \cdot V.F.\xi}{W K_o} \quad (50)$$

The above analysis is mainly due to Allen [25] who has, in fact, used Scanning Electron Microscopy applied to the Oxidational Wear of austenitic stainless steel (Brico 65) pins against ferritic steel (21-4N) disks. Figure 7 shows a typical electron micrograph of one of these worn surfaces from which the oxide thickness can obviously be measured with very little difficulty. In experiments carried out between 12.5 and 87.5N, with no external heating, Allen [25] used the quadratic equation [Equation (48)] to derive values of the contact radius (a),  $\delta_{\text{theory}}$ , N and  $T_c$ , using the  $K_o$  values giving the best fit between  $\delta_{\text{theory}}$  and  $\delta_{\text{expt}}$  and the values of  $p_m(T_s)$  found from Figure 8 (a plot of the bulk hardness versus temperature). These calculations are summarized in Table 5:

Table 5. Variation of various surface parameters with load for Brico 65  
versus 21-4N (2 m/s)

| LOAD<br>(Newtons) | $K_0$<br>( $W m^{-1} K^{-1}$ ) | a<br>( $\mu m$ ) | $\delta_{expt}$<br>(%) | $\delta_{theory}$<br>(%) | N   | $T_c$ ( $^{\circ}C$ ) |
|-------------------|--------------------------------|------------------|------------------------|--------------------------|-----|-----------------------|
| 12.50             | 5.0                            | 9.15             | 9.8                    | 4.2                      | 13  | 319                   |
| 31.25             | 5.0                            | 8.90             | 11.6                   | 6.8                      | 36  | 452                   |
| 37.50             | 4.9                            | 8.90             | 7.7                    | 5.0                      | 43  | 315                   |
| 50.00             | 4.8                            | 8.58             | 8.3                    | 6.7                      | 61  | 413                   |
| 62.50             | 4.8                            | 8.40             | 10.5                   | 7.0                      | 80  | 519                   |
| 67.00             | 4.5                            | 7.90             | 11.6                   | 9.5                      | 97  | 437                   |
| 75.00             | 4.2                            | 7.30             | 14.0                   | 12.6                     | 131 | 509                   |
| 81.25             | 4.2                            | 7.30             | 13.0                   | 12.6                     | 142 | 516                   |
| 87.50             | 4.2                            | 7.30             | 12.8                   | 12.6                     | 153 | 511                   |

### 5.3 The Feasibility of using the Oxidational Theory of Wear at Elevated Temperatures for Predicting Wear

Now we have seen (in Section 5.2) that direct electron microscope measurements of oxide film thicknesses at the real areas of contact can lead to estimates of  $N$ ,  $a$  and  $T_c$ , the general oxidational Wear Equation [Equation (42)] does not seem so untractable. Let us examine each factor in turn and see what we know about each one:

- (i)  $D$ ,  $V$  and  $W$ : can be measured directly
- (ii)  $w_{\text{expt}}$ : measured directly
- (iii)  $T_s$ : obtained through thermocouple measurements  
plus calculations
- (iv)  $f_o(T_s)$ ,  $\rho_o(T_s)$ ,  $p_m(T_s)$ : readily obtained from  $T_s$
- (v)  $k_p(T_s)$ : it seems reasonable to assume the 'out-of-contact' regions oxidize in a similar manner to static oxidation. Hence, take static oxidation values at  $T_s$ .
- (vi)  $\xi$ : can be measured by scanning electron microscopy  
(also  $\xi'$ , the oxide thickness on the disk).
- (vii)  $N$ ,  $a$ ,  $T_c$ : Obtained from  $\xi$ ,  $\xi'$  and the analysis given in Section 5.2
- (viii)  $d$ : is equal to  $2a$ .
- (ix)  $k_p(T_c)$ : it is reasonable to assume that  $Q_p$  is the same as the Activation Energy at  $T_c$  but  $A_p$  (the Arrhenius constant for tribological oxidation) is unknown.

Thus we have only one unknown which, if we equate  $w_{\text{theory}}$  to  $w_{\text{expt}}$ , will be found from Equation (42). Repeating this process for all wear experiments in which values of  $T_c$  lie within a given oxide range, should give an average value of the Tribological Arrhenius Constant. Unfortunately, Allen [25] did not have the static value of the Activation Energy ( $Q_p$ ) for either Brico 65 or 21-4N, so he was unable to use this approach. In fact, Equation (42), the general oxidational wear equation, still awaits validation. It is included in this "in-depth" review since it shows the present position in the development of a general oxidational wear equation. We must await the analysis of the elevated temperature wear experiments of Allen [25], together with an independent estimate of  $Q_p$  for his particular steels. Clearly, this is an area of great interest to diesel engine manufacturers, so one should expect a breakthrough within the next few years.

The general oxidational wear theory, with its inclusion of oxidation of the out-of-contact regions of the real area of contact, is more relevant to scuffing failure than the original oxidational wear theory. If  $T_s$ , the general surface temperature, is sufficiently high to cause breakdown of the oil film, then oxidational wear will ensue in those regions of breakdown at a rate determined by both  $T_s$  and  $T_c$ . It remains to be proved that the 'out-of-contact' oxidational terms of Equation (42) are relevant at  $T_s$  values around 300°C, but initial calculations [56] indicate that they might well be relevant, in which case the wear (or scuff resistance) of lubricated steel surfaces will then depend on the nature of the oxide film being formed and the speed with which the

oxidation proceeds. If the oil contains an extreme-pressure additive, then, of course, Equation (42) cannot be applied, since there are components of the additive (possibly released through the processes occurring at the real areas of contact) which will compete with the oxygen to produce protective surface films. Possibly, this competition could be included by having extra terms in Equation (42) involving the formation of additive-reacted films at the real areas of contact. These terms could possibly have the same form as the three terms of the oxidational wear equation with different values (and powers) for parameters such as  $k_p$  and  $f_o$ , which would now relate to the time dependence of additive film increase in mass per unit area and also how much of the film was due to the component of the additive reacting with the surface (which may or may not be oxidized!).  $k_p$  would itself have the Arrhenius form, namely  $Ae^{-Q/RT}$ , but now  $Q$  would be an activation energy related to the reaction between the additive component and the surface.

## 6. THE EFFECT OF PARTIAL OXYGEN PRESSURE UPON THE WEAR OF METALS

Possibly the most comprehensive work on the effects of partial oxygen pressure on the wear of metals was carried out by Habig, Kirschke, Maennig and Tischer [59]. These authors mixed oxygen and nitrogen in 20/80 percentage mixtures from 760 Torr down to about  $2 \times 10^{-7}$  Torr. It is not clear whether the authors were actually getting these percentages at the lower (i.e., vacuum) pressures, where impurities arising from the wearing surface might well affect the partial pressures. Their experiments were carried out at 0.02, 0.1 and 1 m/s, the load being chosen so as to ensure that the real area of contact (as defined by the relation  $A = W/p_m$ ) was the same for each experiment, namely about  $0.03 \text{ mm}^2$ , where  $p_m$  was the hardness (in units of force per unit area). They rubbed "like-on-like" (Fe, Co, Cu, Ag, Mg and Al), and selected combinations of "unlike" rubbing pairs (Co, Cu, Ag, Mg and Al pins on Fe disks; Fe pins on Co, Cu, Ag, Mg and Al disks). They produced graphs of friction coefficient versus  $\log(P_{O_2})$ , where  $P_{O_2}$  is the partial oxygen pressure of the ambient atmosphere, but no significant differences were found. This was reflected in the small effect of  $P_{O_2}$  upon the surface temperature. For example, for Fe on Fe at 0.94 m/s and a load of 23.7N, the  $T_s$  values range from about  $105^\circ\text{C}$  at 1 Torr, up to about  $160^\circ\text{C}$  at ambient pressures of  $10^{-3}$ ,  $5 \times 10^{-5}$  and  $10^{-6}$  Torr. The one exception seemed to be Fe on Cu, where the value of  $T_s$  went from about  $155^\circ\text{C}$  at  $5 \times 10^{-5}$  Torr up to  $245^\circ\text{C}$  at  $5 \times 10^{-7}$  Torr. [These values are based on a room temperature of  $20^\circ\text{C}$ .]

Habig et alia. [59] plotted wear rates in terms of Archard [27] K-factors. They rewrote Equation (1) in terms of the volume ( $v$ ) removed from a wearing partner over the distance ( $\zeta$ ) of the wear run, namely:

$$K = \frac{v P_m}{\zeta W} . \quad (51)$$

Habig, et alia [59] quote the original oxidational wear theory [16,17] and they suggest that since  $k_p$  (which they describe as the "velocity constant of oxidation" and to which they assign the symbol,  $k'$ ) must be proportional to a constant power ( $c'$ ) of the oxygen partial pressure, then so also must  $K$  (for a given speed and load).

Thus

$$K \propto k_p \propto (P_{O_2})^{c'} \quad (52(a))$$

so that

$$K = a' (P_{O_2})^b \quad (52(b))$$

where  $a'$  and  $b$  are constants to be evaluated from actual new experiments. Table 6 is a summary of some of the constants obtained by Habig et alia [59] over ranges where  $\log(K)$  appeared to be approximately proportional to  $\log(P_{O_2})$ , in accordance with Equation (52(b)).

One might, at first glance, suggest that since the highest power to which we must raise  $(P_{O_2})$  is 0.14 (for Fe/Fe at 0.02 m/s for pressures



Table 6. Numerical values for a' and b of Equation 52(b)

| Wearing Partner | Pair pin/disk | Normal Load (N) | Speed (m/s)   | Pressure Range (Torr)     | $10^5 a'$   | b    |
|-----------------|---------------|-----------------|---|---------------------------|---|------|
| Fe pin          | Fe/Fe         | 23.7            | 0.02  |                           | 18.3  | 0.14 |
| Fe pin          | Fe/Fe         | 23.7            | 0.10  | $2 \times 10^{-7}$ to 1   | 12.2  | 0.10 |
| Co pin          | Co/Fe         | 28.0            | 0.02  | $5 \times 10^{-5}$ to 760 | 7.0   | 0.09 |
| Co pin          | Co/Fe         | 28.0            | 0.1   | $5 \times 10^{-6}$ to 760 | 4.8   | 0.15 |
| Co pin          | Co/Fe         | 28.0            | 1.0   | $2 \times 10^{-7}$ to 760 | 1.3   | 0.11 |
| Co disk         | Fe/Co         | 28.0            | $\left\{ \begin{array}{l} 0.02 \\ 0.10 \\ 1.0 \end{array} \right\}$ | $2 \times 10^{-7}$ to 760 | 4.0   | 0.12 |
| Cu pin          | Cu/Cu         | 12.1            | 0.02  | $4 \times 10^{-7}$ to 760 | 22.3  | 0.07 |
| Cu pin          | Cu/Cu         | 12.1            | 0.10  |                           | 15.2  | 0.04 |
| Cu pin          | Cu/Cu         | 12.1            | 1.0   |                           | 33.9  | 0.08 |
| Cu disk         | Cu/Cu         | 12.1            | $\left\{ \begin{array}{l} 0.02 \\ 0.10 \\ 1.0 \end{array} \right\}$ | $10^{-3}$ to 760          | 19.1  | 0.13 |
| Cu pin          | Cu/Fe         | 11.70           | 0.02  | $5 \times 10^{-6}$ to 760 | 1.6   | 0.03 |
| Cu pin          | Cu/Fe         | 11.70           | 0.1   | $3 \times 10^{-7}$ to 760 | 1.3   | 0.01 |
| Fe pin          | Fe/Cu         | 11.70           | 0.02  | $5 \times 10^{-5}$ to 760 | 1.3   | 0.11 |
| Fe pin          | Fe/Cu         | 11.70           | 0.1   | $5 \times 10^{-5}$ to 760 | 1.7   | 0.08 |
| Cu disk         | Fe/Cu         | 11.70           | $\left\{ \begin{array}{l} 0.02 \\ 0.10 \\ 1.0 \end{array} \right\}$ | $10^{-3}$ to 760          | 4.8   | 0.01 |
| Fe pin          | Fe/Ay         | 9.43            | $\left\{ \begin{array}{l} 0.02 \\ 0.10 \\ 1.0 \end{array} \right\}$ | $2 \times 10^{-7}$ to 760 | 0.01  | 0.03 |
| Al pin          | Al/Fe         | 4.56            | 0.02  | $5 \times 10^{-5}$ to 760 | 4.0   | 0.03 |
| Al pin          | Al/Fe         | 4.56            | 0.1   | $10^{-3}$ to 760          | 3.1   | 0.04 |
| Al pin          | Al/Fe         | 4.56            | 1.0   | $2 \times 10^{-7}$ to 760 | 2.3   | 0.01 |
| Al disk         | Fe/Al         | 4.56            | $\left\{ \begin{array}{l} 0.02 \\ 0.1 \\ 1.0 \end{array} \right\}$  | $2 \times 10^{-7}$ to 760 | $\left\{ \begin{array}{l} 4.8 \end{array} \right\}$ | 0.06 |

less than about 1 Torr), then, in general, the wear of metals is insensitive to partial oxygen pressures down to about  $10^{-7}$  Torr. One must ask oneself, however, if the wear rates used by Habig et alia [59] were equilibrium mild, i.e., oxidational, wear rates. Perhaps some of the combinations do not exhibit mild wear. Certainly, Cu on Cu would be expected to be severe wear. To some extent, this is reflected in the large values of  $a'$  for Cu on Cu (about  $25 \times 10^{-5}$ ). A similar value for  $a'$  for Fe on Fe (about  $20 \times 10^{-5}$ ) leads to the conclusion that the Fe on Fe experiments were probably running-in under the usual severe wear conditions which occur for the first hour or so of mild wear runs. This is also confirmed by the x-ray diffraction evidence, in which Habig et alia [59] show us that  $\alpha$ -Fe only was in the wear debris for all partial pressures less than 1 Torr. In fact, oxides were noticeably absent from many of the experiments carried out with the other wearing pairs apart from Co on Fe between 760 Torr and 1 Torr and Cu on Fe at 760 Torr. The present author considers that Habig et alia [59] have merely been showing that *severe wear* does not depend much on partial oxygen pressure.

There is a real need to repeat Habig et alia's experiments, at least with low-alloy steels, to ensure that mild wear is obtained, so that the  $a'$  and  $b$  values can be (i) quoted with some confidence, and (ii) checked against values expected from the oxidational wear theory. Clearly,  $a'$  values relate to both the oxidational wear theory and the theory of oxidational kinetics, whereas  $b$  relates mainly to the latter. What is the relationship between  $b$  and  $c$ ? Many investigators think

that  $c$  approaches zero (Rahmel and Engell [60] find the oxidation rate of iron at 700-950°C is independent of the oxygen pressure if  $\text{Fe}_3\text{O}_4$  and  $\alpha\text{-Fe}_2\text{O}_3$  are present). However, when one is considering oxidation which occurs during wear, then one must expect differences from such static oxidational behavior. Even Rahmel and Engell [60] show that at low oxygen potentials (when in equilibrium with  $\text{CO}/\text{CO}_2$ ) where only  $\text{FeO}$  can exist on the surface, then  $k_1$  becomes equal to a constant times the 0.7th power of the partial oxygen pressure. It is quite feasible that at the real areas of contacts where most of the available oxygen is quickly used up to provide the wear plateau, the oxidation may be occurring under conditions of low oxygen potentials.

Finally, it is reasonable to assume that, under lubricated conditions, there might also be an effect of limited access to the oxygen present in the oil. This means that when a certain temperature is reached between the sliding surfaces, and the oil breaks down according to the Blok [40] hypothesis, the oxide film already formed before the breakdown might be of the thickness and type of oxide relevant to low oxygen pressures. This could lead to catastrophic failure (scuffing), especially since  $\text{FeO}$  seems to be associated with poor wear resistance [32]. Also, it should be pointed out that wear occurs between lubricated gears even when no scuffing ensues. This wear could be mild oxidational wear occurring at low partial oxygen pressures. There is thus a strong incentive for more work to be done on the effect of partial oxygen pressures on wear.

## 7. OXIDATIONAL WEAR IN THE 1980'S

In this review, we have traced the development of oxidational wear from the early 1930's, when the German school of investigators carried out much of the pioneer experimental work; through the 1960's, when the first theoretical experiments were published and when the complexities of mild oxidational wear became apparent; through to the 1970's, when increased instrumentation and heat-flow analyses were introduced together with computerization of the data, to lead to the present position. This position is one in which, for low-alloy steels at least, there seems to be a consistent oxidational theory of mild wear which gives information about the initial thickness ( $\xi$ ) of the oxide films formed at the real areas of contact, the temperature ( $T_c$ ) at which those areas oxidize during wear and the number of asperities ( $N$ ) forming the contact at any given moment. Oxidation constants for Oxidational Wear have been evolved for the low-alloy steels. We can thus say that, in principle, we can predict the mild oxidational wear of low-alloy steels, given enough information about the geometry of the wearing system, and the thermal and crystallographic properties of the interacting surfaces. This also assumes that there is no external heating nor external lubrication applied to the system, and that the system is running under conditions where oxidation of the "out-of-contact" regions can be ignored.

In the next few years, it should be clear from this review that oxidational wear should now be concerned with mild wear in its most general forms. For instance, the ideas and results obtained with the

low-alloy steels should be applied (suitably modified) to other systems, in particular other steels and other metals. Also, we should be considering what modifications will have to be made for the original theory to be applicable to lubricated conditions. Should we develop an expression which allows for the decreased partial oxygen pressures which might occur under lubricated conditions? How does "pitting" and "scuffing" fit in with the theory? Both of these are catastrophic phenomena which occur when the wear is no longer "well-behaved". Certainly, some form of "benevolent" wear is occurring under normal running conditions before pitting occurs [61]. This could be mild oxidational wear under reduced partial oxygen pressures. "Scuffing" is probably what happens when the initial severe wear of "running-in" does not ameliorate, due perhaps to the low oxygen pressures yet again.

The most important strides in the development of the oxidational wear theory over the next few years will probably be taken in the confirmation and validification of the general oxidational wear theory expressed in Equation (42) [or some similar expression]. This takes into account the "out-of-contact" oxidation; that is, the oxidation of the real areas of contact in between the times they are in contact and are, therefore, being exposed to the general surface temperature ( $T_s$ ). Normally, the amount of 'out-of-contact' oxidation (at  $T_s$ ) is insignificant compared with the 'in-contact' oxidation (at  $T_c$ ). However, there is an increasing number of practical situations where elevated ambient temperatures occur, for example, in nuclear reactors, in the exhaust valve systems of diesel engines, in rolling mills to name but

a few of the hostile environments in which tribological systems have to reliably operate. Under these circumstances, the 'out-of-contact' oxidation must affect the wear behavior of the sliding system. Although the relevance of 'out-of-contact' oxidation to scuffing might appear to be tenuous, it is probably here that the strands connecting the two phenomena should be drawn together. Blok's [40] hypothesis relates to the temperature at which the oil breaks down at the real areas of contact. It is most probable that the 'out-of-contact' temperature of these areas will be strongly connected with the general temperature of the oil, which will be fairly high in a scuffing situation. Oxidation will occur at these temperatures and, when breakdown occurs, the general oxidational wear equation may be relevant to whether or not mild or severe wear becomes the operative mode of wear, i.e., whether or not scuffing will occur. Similarly, the ambient temperatures in incipient pitting conditions could determine whether 'benevolent' wear occurs ('benevolent' because it wears away the cracks before they can propagate!) or not. If they are high enough, these ambient temperatures should affect the oxidational mild wear rate through an equation similar to Equation (42). There is, therefore, plenty of scope for the oxidational theory of mild wear to be applied to many important wear problems that are still awaiting solution.

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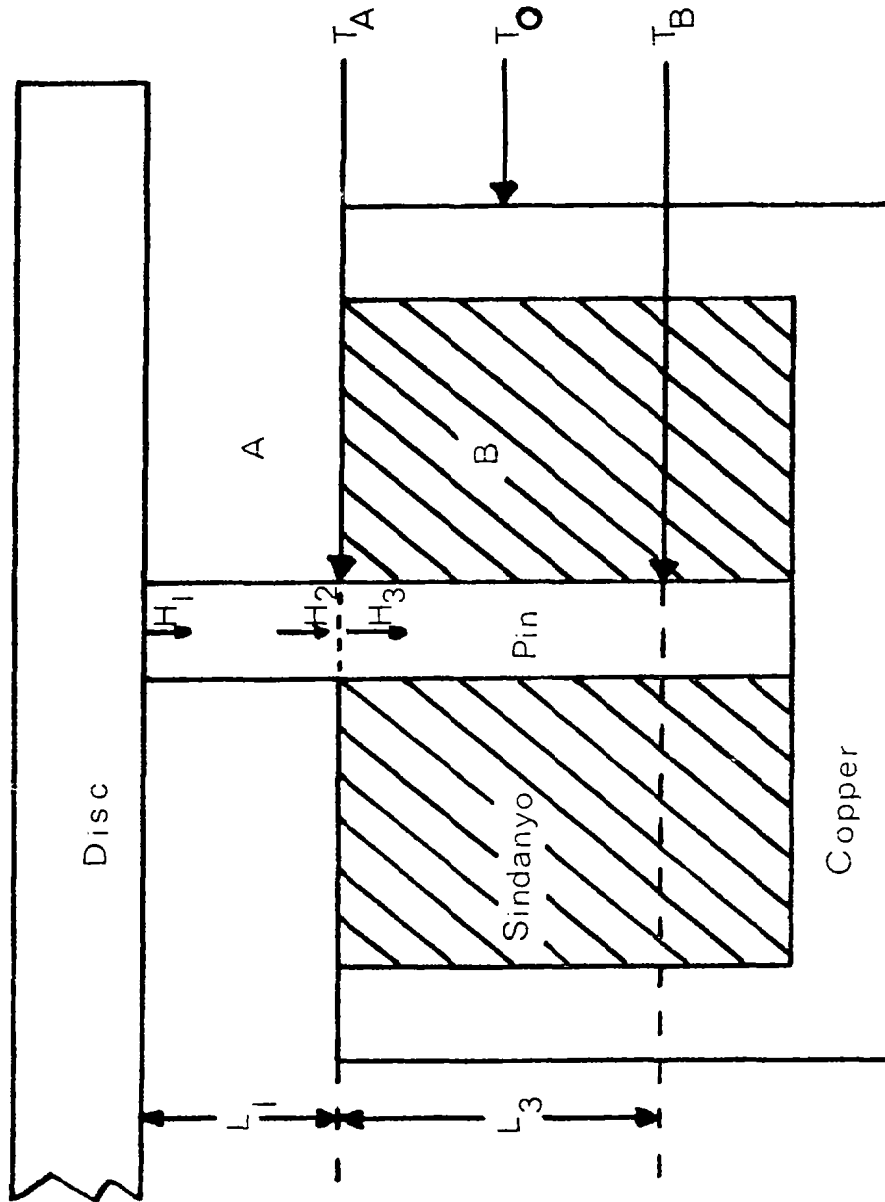


Figure 1. Heat flow diagram for pin loaded against a disc rotating about an axis parallel to pin but situated some distance to the left of this diagram.

Table 5. Variation of various surface parameters with load for Brico 65  
versus 21-4N (2 m/s)

| LOAD<br>(Newtons) | $K_0$<br>( $W m^{-1} K^{-1}$ ) | a<br>( $\mu m$ ) | $\delta_{expt}$<br>(%) | $\delta_{theory}$<br>(%) | N   | $T_c$ ( $^{\circ}C$ ) |
|-------------------|--------------------------------|------------------|------------------------|--------------------------|-----|-----------------------|
| 12.50             | 5.0                            | 9.15             | 9.8                    | 4.2                      | 13  | 319                   |
| 31.25             | 5.0                            | 8.90             | 11.6                   | 6.8                      | 36  | 452                   |
| 37.50             | 4.9                            | 8.90             | 7.7                    | 5.0                      | 43  | 315                   |
| 50.00             | 4.8                            | 8.58             | 8.3                    | 6.7                      | 61  | 413                   |
| 62.50             | 4.8                            | 8.40             | 10.5                   | 7.0                      | 80  | 519                   |
| 67.00             | 4.5                            | 7.90             | 11.6                   | 9.5                      | 97  | 437                   |
| 75.00             | 4.2                            | 7.30             | 14.0                   | 12.6                     | 131 | 509                   |
| 81.25             | 4.2                            | 7.30             | 13.0                   | 12.6                     | 142 | 516                   |
| 87.50             | 4.2                            | 7.30             | 12.8                   | 12.6                     | 153 | 511                   |

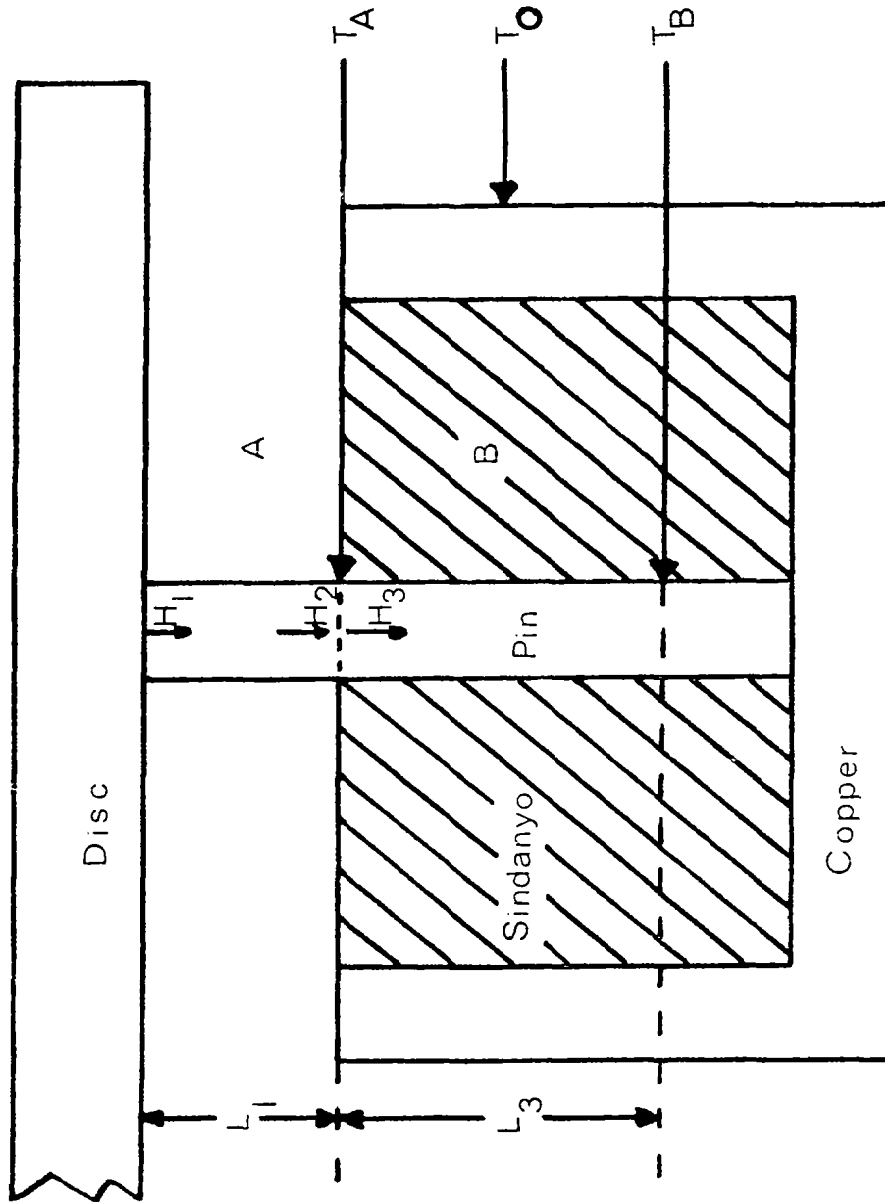


Figure 1. Heat flow diagram for pin loaded against a disc rotating about an axis parallel to pin but situated some distance to the left of this diagram.

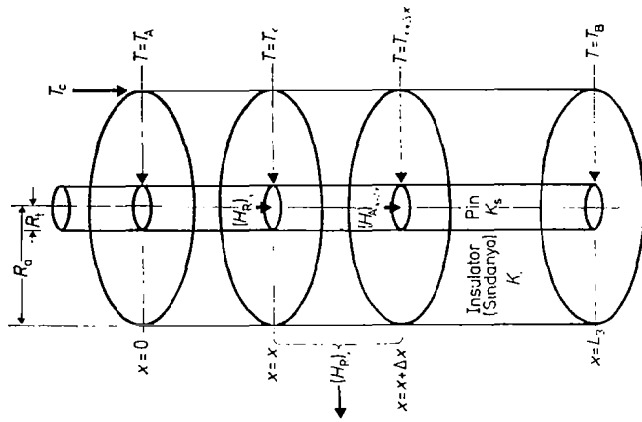


Figure 2. Perspective drawing of pin and insulator, showing an element  $\Delta x$  of both pin and insulator ( $T_A$ ,  $T_B$ ,  $T_x$  and  $T_{x+\Delta x}$  are the temperatures of the pin at the positions shown;  $T_C$  is the temperature of the outside (cylindrical) surface of the insulator).

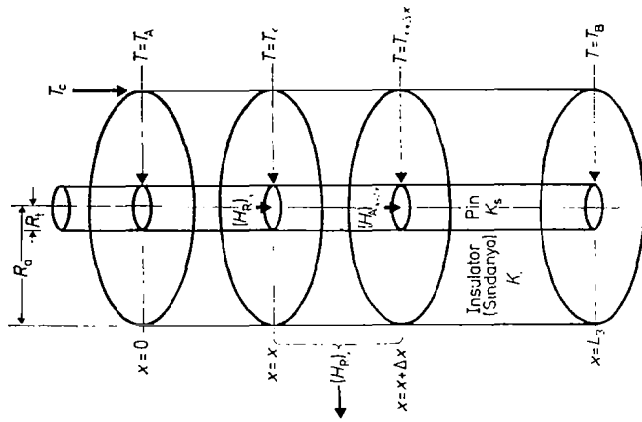


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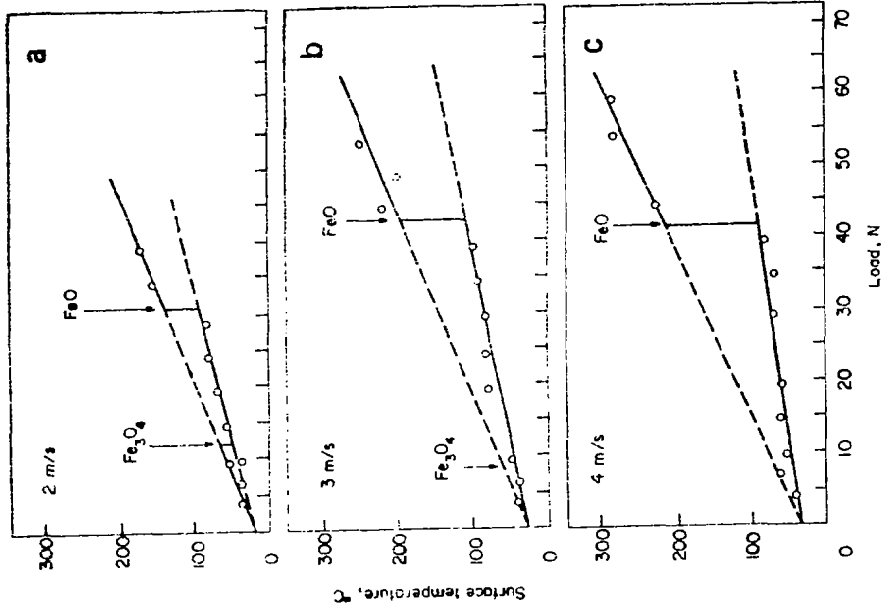


Figure 4. Surface temperature versus load for EN8 pins sliding against discs (a) at 2 m s<sup>-1</sup>, (b) at 3 m s<sup>-1</sup> and (c) at 4 m s<sup>-1</sup>.

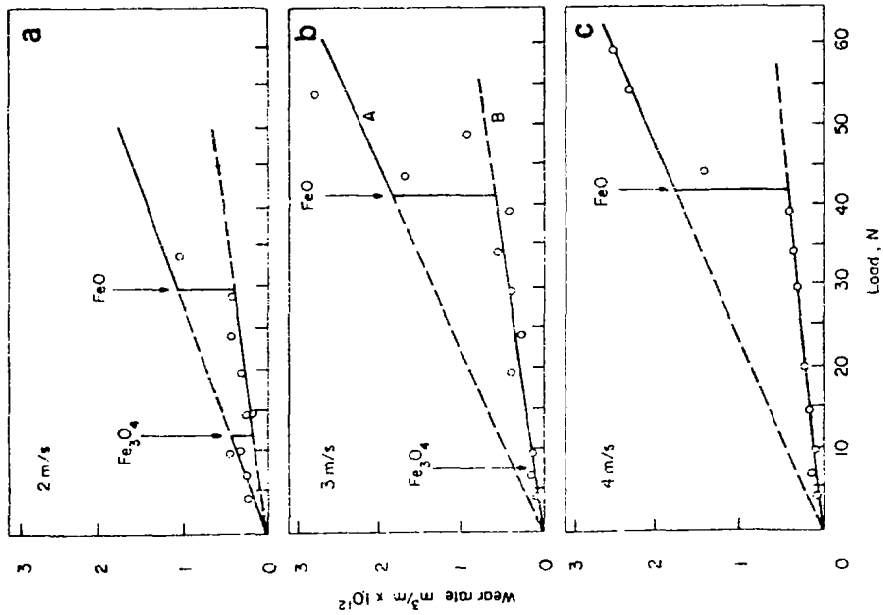
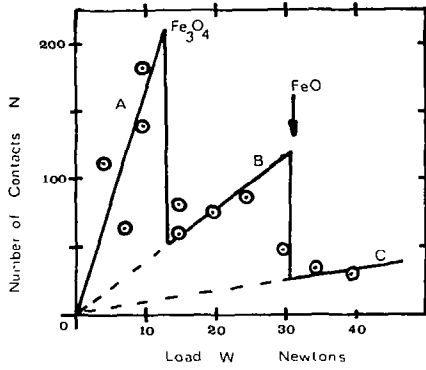
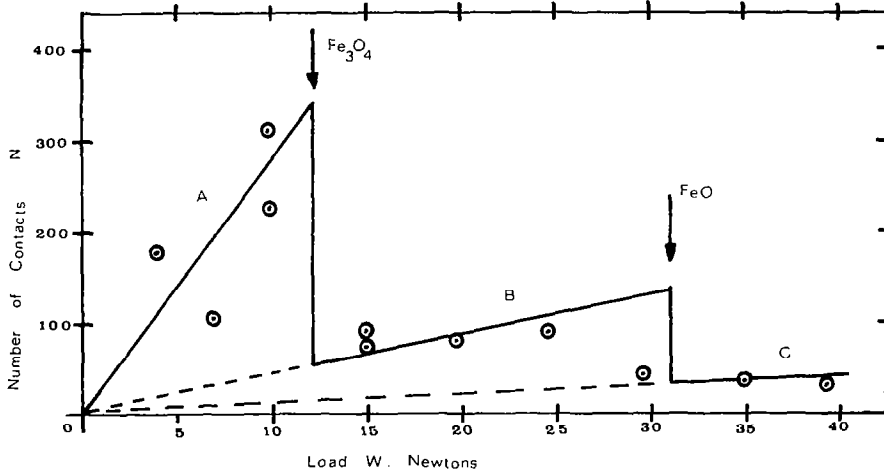


Figure 3. Wear rate, m<sup>3</sup> m<sup>-2</sup>, versus load, N, for EN8 steel (a) at 2 m s<sup>-1</sup>, (b) at 3 m s<sup>-1</sup> and (c) at 4 m s<sup>-1</sup>.

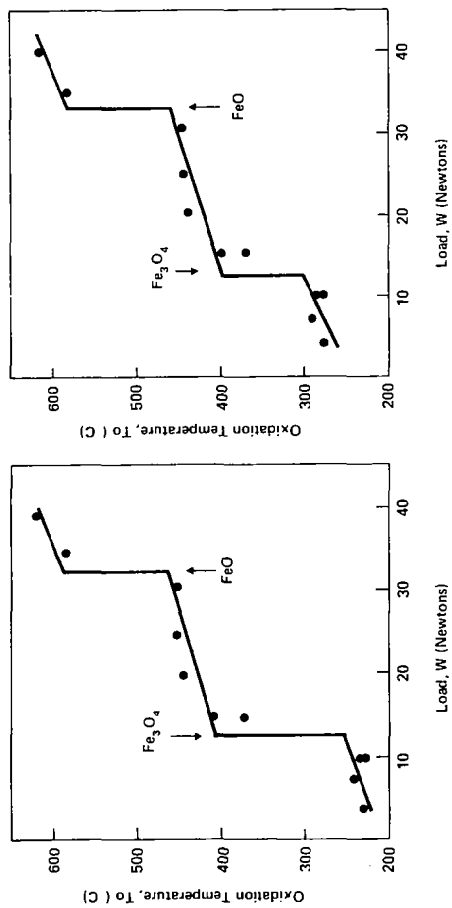


(a)



(b)

Figure 5. Number  $N$  of asperities vs. load  $W$  for EN8 at  $2 \text{ m s}^{-1}$  from (a) the intuitive search program and (b) the iterative solution program.



(a) intuitive (computer search) technique; (b) iterative technique.

Figure 6. Oxidation temperature  $T_o$  vs. load  $W$  for EN8 at  $2 \text{ m s}^{-1}$ : (a) intuitive (computer search) technique; (b) iterative technique.



Figure 7. Scanning Electron Micrograph of BRICO 65 pin surface showing oxide thickness.

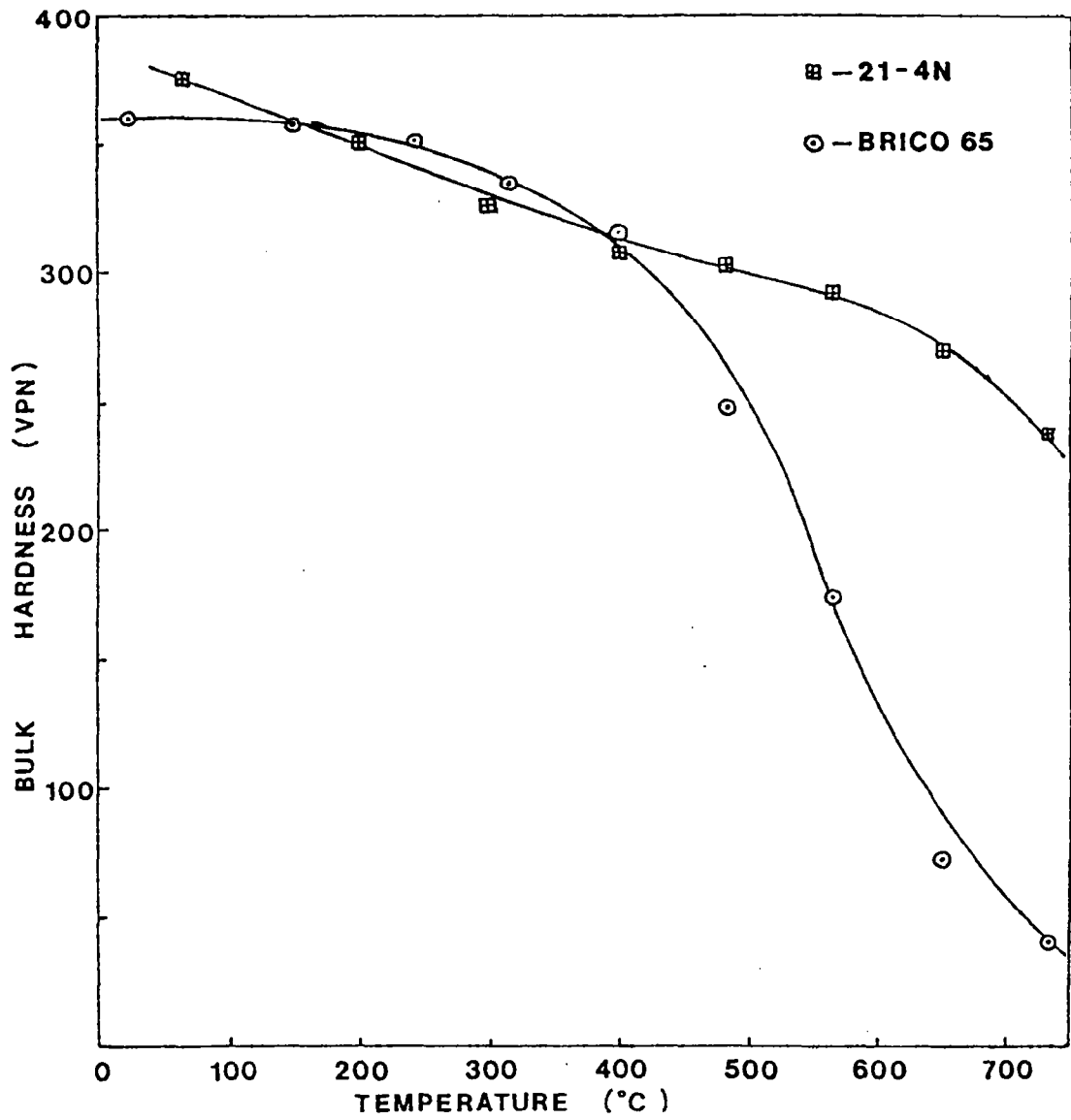


Figure 8. Variation of bulk hardness with temperature

|   |  |   |                                 |
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| 16. Abstract<br>An in-depth review of oxidational wear of metals is presented as part of the work under NASA Cooperative Agreement NCC 3-14 "Interdisciplinary Collaboration in Tribology--Thermo-mechanical Interactions". Special emphasis is given to a description of the concept of oxidational wear and the formulation of an Oxidational Wear Theory. The parallelism between the formation of an oxide film for dry contact conditions and the formation of other surface films for a lubricated contact is discussed. The description of oxidational wear is prefaced with a unification of wear modes into two major classes of mild and severe wear including both lubricated and dry contacts. Oxidational wear of metals is a class of mild wear where protective oxide films are formed at real areas of contact and during the time of contact at temperature $T_c$ . When the oxide reaches a critical thickness, frequently in the range of 1 to 3 $\mu\text{m}$ , the oxide breaks up and eventually appears as a wear particle. These oxides are preferentially formed on plateaux which alternately carry the load as they reach their critical thickness and are removed. If the system is operated at elevated temperatures, thick oxides can form both out of contact and between the plateaux. Temperature is important in determining the structure of the oxide film present. Spinel oxide ( $\text{Fe}_3\text{O}_4$ ) which forms above 300° C is more protective than the lower temperature rhombohedral ( $\alpha\text{-Fe}_2\text{O}_3$ ) oxide which is abrasive. An Oxidational Wear Theory is derived using a modified Archard wear law expressed in terms of activation energy ( $Q_p$ ) and Arrhenius constant ( $A_p$ ). A parabolic dependence of mass uptake of oxygen is assumed. The prediction of oxidational wear requires a surface model giving the number of contacting asperities (N) and the radius of the contact between asperities (a). A heat flow analysis is presented to derive the temperature ( $T_c$ ) at the contacting asperities. Oxidation constants ( $Q_p$ , $A_p$ ) for three oxide structures are evaluated for low-alloy steel. The Arrhenius constant for oxidational wear is found to be different than that for static oxidation tests. Values of the various parameters are calculated from oxidational wear experiments. The theory is extended to include oxidation wear at elevated temperature. The possible connection between the general Oxidational Wear Theory for dry contacts and lubricated contact is discussed. |  |   |                                 |
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