



Research Paper

OXIDATION, OXIDE THICKNESS AND OXIDE TRANSFER IN WEAR

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Wear is defined as a set of adhesion, transfer, abrasion, fatigue and oxidation. Due to these processes transfer of matter takes place from one state to another. The final transformation in wear is a collection of free debris particles. Oxidation is a wear of metals in which oxide layer is formed. Oxidation rate is inversely dependent on the thickness of oxide layer. Mechanical characteristics of oxide layer is the basic factor in determining the wear process. Theoretically it can be shown that oxidation temperature is lower than the contact temperature at the contact regions. Also the oxidation rate may decrease with the increasing oxidation temperature because of increase in thickness of oxide layer.

Keywords: Wear, Oxidation, Oxide thickness, Oxide transfer

INTRODUCTION

Oxidation has clearly been a part of wear process of metals and in recent year several research work have been done on it to develop a theory for this wear process. This research work involves dependence of wear rate on load and sliding velocity. An attention has been given to the theories of wear with oxidation. The role of the oxide layer thickness and the possible transfer of oxide between the rubbing surfaces has also been discussed. Several physical and chemical processes are involved in wear occurring within a tribological system. Due to these processes the material of rubbing

surface undergoes a series of transformations. The material which is worn away is transformed from its initial state to one or more intermediate states. These states include deformed material, oxidized material and debris. The final transformation includes formation of free debris. Adhesion is the first stage in transformation of material, which leads to deformation and possibility of transfer. Adhesion cannot be regarded as an attrition process as attrition may occur through multiple fractures of a deformed adhesive bond or through subsequent fatigue of deformed material. In case of Fatigue, attrition takes

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place through a gradual propagation of fractures in rubbing surface caused due to periodical fluctuations of fractures in rubbing surface. This process is then followed by plastic deformation.

Oxidation can also be classified as a possible component of wear process. It is then accompanied or followed by adhesion and attrition and may occur through a multiple fractures, abrasion or fatigue.

EXPERIMENTAL STUDIES

During the oxidation of metals the reaction product tends to form a barrier between reacting gas and the metals. The process includes adsorption of oxygen molecules, dissociation of oxygen molecules and the ionization of both metal and adsorbed oxygen at the metal/oxygen which in turn lead to diffusion of ions. The diffusion of one species may be more rapid than diffusion of the other.

If one of the surface reactions at the oxide/gas interface is the slowest of all the reactions then following equation is applied:

$$dr/dt = k$$

which is an integrated form of:

$r = kt + c$; where c is the constant of integration and k is the constant which is independent of elapsed time t .

If the diffusion process is the slowest of several processes then the rate of diffusion and hence the rate of oxidation depends inversely on the oxide thickness:

$$dr/dt = kd/2r$$

On integration, we will get the parabolic rate law:

$$r^2 = k_d t + c_1$$

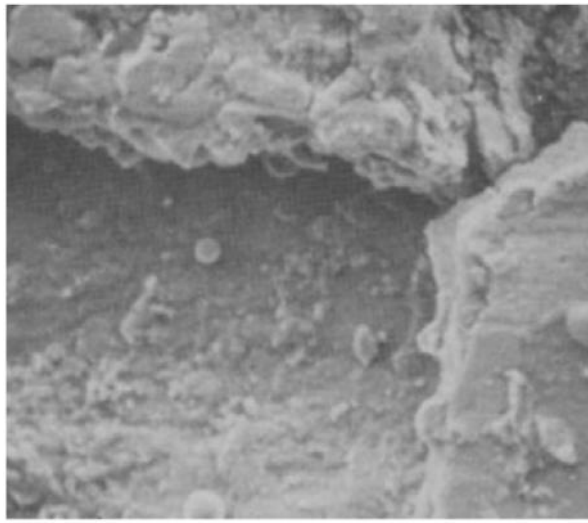
The parabolic and linear oxidation laws are perhaps the most common and best understood relationships for oxide layers.

There is no need of oxide layer to cover the whole nominal contact surface. For very thin oxide layers, there is a strong interaction between oxidation and other components of wear. We can agree on the point that the metal surface is activated in the wear process. Caplan and Cohen (1966) have found that the cold-working of iron through abrasion prior to oxidation does increase the oxidation rate of the metal in the temperature range 400-600 °C. The explanation provided is that the diffusion of metal ion vacancies to the oxide/metal interface will tend to produce pores at the interface if the metal is in an annealed state. Such pores were observed and they had clearly disturbed the oxidation process. The surface of the deformed metal can be expected to have a large number of dislocations and steps which could act as sinks absorbing the vacancies; this would account for the absence of pores at the interface of the deformed metal and the oxide.

Svedung *et al.* (1973) confirm this effect of pores at an oxide/metal interface on iron and also report a lack of influence of prior mechanical deformation on oxidation above 600 °C. However, they found that cold-rolled metal had, at 500 °C a greater tendency to form interfacial pores than was evident for cold-rolled metal which had been annealed prior to oxidation. This appears to contradict the influence of cold-work found by Caplan and Cohen (1966).

Oxidation rate is a function of temperature which can be expressed as:

Figure 1: Effect of Sliding Speed on Coefficient of Friction and Mean Surface Temperature



$$k_d = k_d^0 e^{(-Q/Rt)}$$

where t is the absolute temperature, R is the universal gas constant is the activation energy and k_d^0 a constant.

Some metals like iron have the ability to form multilayer oxides. The relative thickness of the layers depends on the relative rate of diffusion. For instance, an outer oxide layer on iron has a lower diffusivity than an inner oxide. In case of wear, removal and fragmentation of outer layer takes place due to which the overall oxidation rate may increase. Another significant effect that we can consider is the effect of fractures and grain boundaries in oxide layers. They may form surface along which oxygen may diffuse.

RESULTS AND DISCUSSION

In the range of 300-800 °C parabolic oxidation equations are applied than linear equations.

The equation us as follows:

$$dr/dt = k_d^0 / 2r^* e^{(-Q/Rt)}$$

This equation refers to the oxidation situation in which an oxide layer is able to grow continuously without wear. In case of wear with oxidation, it has been assumed that there is a maximum or critical thickness to which the oxide can grow. Once oxide reaches this thickness, it is abraded so that further growth is removed. If r_c is the critical thickness and t_c is the time that oxide takes to reach thickness r_c then the mean rate of growth is given by:

$$\text{Mean}(dr/dt) = r_c / t_c = (k_d^0 / r_c) e^{(-q/rt)} \quad \dots(1)$$

Substituting r by r_c we obtain the following equation:

$$dr/dt = (k_d^0 / 2r_c) e^{(-q/Rt)} \quad \dots(2)$$

Equations (1 and 2) refer to the growth rate of an oxide layer thickness. The oxide is formed from metal and from oxygen and the removal of an oxide involves the removal of both metal and previously added oxygen from the surface.

Let the rate of conversion of metal to oxide per unit nominal contact area on a sliding surface be denoted by S ,

Multiplying Equation (1) by oxide density (p_o), mass fraction (m) of the metal in oxide, (A) as the fraction of the nominal contact area on which oxide is actually being formed and dividing by (p_m) which is the density of the metal.

The following equation is obtained:

$$S = Am(p_o/p_m) (k_d^0 / r_c) e^{(-q/rt)}$$

On partially differentiating with respect to t and then with respect to r_c the following equation is obtained:

$$dS = Am(p_o/p_m) (k_d^0 / r_c) e^{(-q/rt)} \{ (Q/Rt^2) dt - (1/r_c) dr_c \}$$

Hence we can say that for a simultaneous change in both t and r_c when the sliding velocity is altered,

ds is positive if:

$$dr_c/dt < r_c Q/R^2$$

and ds is negative if:

$$dr_c/dt > r_c Q/R^2 \quad \dots(3)$$

Relation (3) shows that oxidation rate may decrease in wear, even if there is an increase in oxidation temperature.

It must be stressed that these particular mathematical relationships only apply if the oxidation follows a parabolic equation.

The transfer of metal between rubbing surface can be regarded as an important component of wear process with adhesion. It can be evident from the fact that oxide can transfer between surfaces in sliding contact. Transfer may involve embedment of fragments of a hard brittle oxide in the opposing surface or through adhesion of oxide formed on one surface on to either metal or oxide on the other surface, followed by plastic deformation and an appropriate fracture, similar to the mechanism by which metal can be transferred.

The transfer of oxide is a significant component of wear process and a step preceding towards the formation of oxide debris.

The nomenclature of all symbols is given in the following table:

Table 1: Nomenclature of Symbols	
A	Fraction of the nominal contact area which is oxidizing
k	Rate constant in linear oxidation equation
k_d	Rate constant in parabolic oxidation equation

Table 1 (Cont.)

k_d^0	Constant in Arrhenius equation.
m	Mass of metal from which one mass unit of oxide is formed
r	Oxide thickness
r_c	Critical or maximum oxide thickness in wear
S	Volume of metal transformed to oxide per unit nominal contact area, per unit elapsed time

CONCLUSION

Apart from an initial general treatment of the wear process, this discussion of oxidation in wear is restricted to a limited range of circumstances, notably those in which the oxide can form a layer on the metal surfaces. Particular attention has been paid to situations in which the layer thickness affects oxidation rates.

Analysis shows that the oxidation process itself is unlikely to be a controlling process in wear. The basic factors are likely to be the physical and mechanical properties of the oxide formed in wear, notably shear stress, fracture stress, ductility and adhesion to the substrate. Oxidation is likely to occur below an outer layer of oxide, and therefore at a lower temperature than the contact temperature. The transfer of oxide, is possibly an additional factor in the wear process. 🌀

ACKNOWLEDGMENT

I would also like to dedicate this research work to my father late R S Mishra and mother K L Mishra.

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