



Research Paper

INFLUENCE OF OXIDATION ON THE WEAR OF ALLOYS

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Wear is defined as a set of adhesion, transfer, abrasion, fatigue and oxidation. Sliding wear is influenced significantly by factors like heat, friction and oxidation of the metal or the alloy surface. This causes the decrease in the wear rate due to which the metallic debris may change to oxide debris. This research paper focusses on methods which account for generation of oxide during sliding and the effects of these oxides on the wear. This work also covers high speed unidirectional sliding where the frictional heat has a significant effect on surface temperatures. Wear is caused mainly due to spallation of oxide from asperities which in turn occur when the oxide attains a critical thickness. At high speed the oxide melts due to increase in surface temperature which leads to oxidational wear. On the other hand at low speed the oxidized metal debris is retained thereby giving a wear protection.

Keywords: Wear, High-temperature oxidation, Mild wear, Oxidationalwear, Wear debris

INTRODUCTION

Metals are thermodynamically unstable in air and react with oxygen to form an oxide. This oxide develops a layer on the surface of metal or alloy thereby giving it a protection from the gases by acting as a barrier. Oxidation requires the metal ions and oxygen to penetrate across the layer and form metal oxide at the interface. The process depends on the rate of diffusion of reactants, i.e., metal and oxygen, and also on temperature. There is an exponential relation between the rate of diffusion and temperature. For instance, iron and mild steel

form a layer of Fe_3O_4 at a temperature of 570 °C. Steel components can be used successfully at such temperatures for longer period of time. But at high temperature FeO becomes unstable and develops a layer at the interphase. The layer can be regarded as a defective oxide and is a poor barrier to diffusion of reactants. Therefore, above 570 °C the rate of oxidation increases very rapidly. Alloys should have a slow growing barrier layer for application at higher temperatures. The barrier layer gives effective protection against further oxidation and metal losses are usually

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acceptably low. Oxides also protect against loss of metal which causes due to mechanical damage in turn caused by sliding wear. Often at room temperature metal on metal sliding is accompanied by a severe wear followed by mild wear. It depends on a number of factors like low sliding speed, low load, high rate of oxidation and the transition temperature. The continuous oxide layer formed is often known as glaze. This layer gives reduced resistance to sliding and also protects against the wear damage. The mechanism of formation of this layer is much different from that of the barrier layer. Although under all mild wear condition a smooth layer may not develop but below the transition temperature a relatively low wear rate can be formed. This research paper presents the principles of oxidation and discuss the effects of oxidation on sliding wear.

EXPERIMENTAL STUDIES

The formation of oxide in an alloy occurs by nucleation and growth process. Nucleation initiates the process which is then followed by growth. The clean component has been exposed to an oxygen gas due to which thermodynamically stable oxides are formed on the surface. For instance an alloy like Ni-20%Cr at 1 atm. Air involves oxide which can be either single component oxide or complex oxide. A complete layer is formed when the nuclei of these oxides react rapidly. The rate of oxidation is rapid during the initial stage due to which the elements in the alloy oxidize and the amount of these oxides is proportional to the concentration of these elements. Due to diffusion of metal ions at the interface the growth of transient oxide layer takes place. The thickening rate of layer depends on a number

of factors like temperature, oxygen pressure, composition and structure of oxide phases.

Due to the thermodynamically favored oxide a complete layer is formed at the base of transient oxide scale. The temperature should be $> 650\text{ }^{\circ}\text{C}$. At the scale interface sufficient nuclei develop to coalesce and form a complete layer. At the transient oxide scale layer the oxygen activity is sufficiently high to oxidize the chromium (Cr) in the alloy (Cr_2O_3 on Ni-20%Cr). The rate of oxidation is controlled due to the transport of reactants across the Cr_2O_3 layer. Due to insufficient Cr it is not possible to form Cr_2O_3 layer in alloys containing less than 10% Cr. The Cr_2O_3 particles are insufficient in density to act as barriers to transport the reactants and moreover the oxidation rate is controlled by using a less protective nickel oxide. The steady state scale formed by oxide is dependent on a number of factors like alloy composition, growth rates of oxide, microstructure and surface condition of alloy. It is also dependent upon mechanical properties and oxidation condition.

Generally in oxidation of metals and alloys, there are parts where relative motion occurs and the contacting metal components are subjected to sliding stress. However at room temperature the development of oxide takes place which causes metal to metal interaction and sometimes mild wear. Another effect may include oxidation induced by frictional heat at room temperature which in turn causes unidirectional sliding. In jet engines oxidation induced by external heat is important which is mainly caused due to high temperature sliding. Lim and Ashby (1998) distinguished two regimes: mild-oxidationalwear and severe-

oxidational wear, where the prefixes, 'mild' and 'severe' refer to the extent of oxidation rather than wear; indeed the wear rate is often lower in the severe-oxidational wear regime and both regimes can give mild wear.

They indicated that sliding speeds of at least 1 m/s were required to give sufficient frictional heat for oxidation to become important, with a flash temperature approaching 700 °C being possible at 1 m/s. At lower speeds, the wear debris is mainly

Metallic; a drop in wear rate is associated with a change to oxide debris (Welsh, 1965; and Uetz and Sommer, 1977). At the higher velocities, an oxide film forms on the contacting surfaces (Nakajima and Mizutani, 1969) and, above a critical velocity, wear is caused by removal of the oxide (Quinn, 1987). In the mild-oxidational wear regime, oxidation at the points of contact is caused by frictional heat and the oxide formed grows until, at a critical

Oxide film thickness, about 10 nm for steel, it spalls off as wear debris. Lim and Ashby (1998) also proposed that, at velocities above about 10 m/s, oxidation becomes more extensive, resulting in a transition to severe-oxidational wear. During the high speed sliding mechanism of oxide generation show some similarities but there are no much similarities at low speed sliding. Due to oxidation of metals asperities oxides are formed. They are also formed when the metal asperities are in contact and the extent of such oxidation is dependent upon the temperature developed at the asperities contact. With the increase in surface temperatures the oxidation increases. The oxide developed during sliding can be removed only partially not all at once at high ambient temperatures. Moreover the thickness

of oxide layer gradually thickens with time. Due to this we can further protect an alloy or a metal with wear. Oxidation of metallic debris can also be regarded as source of oxide. Initially the wear debris particles which are produced in the earlier stages may be broken or they are reduced in size by sliding action due to which fresh areas of clean metal expose and oxidation occurs. As the rate of initial oxidation is rapid so the surface area of exposed metal is considerably large. The best examples can be iron or steel. The oxidation process increases during sliding due to the heat of deformation and also due to the increased energy of the particles which is basically due to the increase in surface energy. A considerable amount of oxide is generated during low speed sliding. The oxide debris developed can also act as a protective layer.

RESULTS AND DISCUSSION

The oxidation follows a parabolic kinetics, if m is the mass of oxygen taken up by the oxide film per unit area in time ' t ' then

$$m^2 = Ct$$

where C is the parabolic oxidation rate constant.

$$C = A \exp - (Q/RT)$$

A is the Arrhenius constant, Q is the activation energy, R is the gas constant and T is the absolute temperature.

A and Q can be treated as adjustable parameters which can fit the measurements of wear rate.

The uncertainties in the magnitude of flash temperature make it very complex for studying static oxidation. Other factors include temperature gradient, rate of temperature

decay and the mean size of wear particles. In oxidation of iron under static condition when the temperature is increased there is a change in mechanism. However at lower temperatures the oxidation rate becomes relatively low. The best example can be Fe_3O_4 layer which is formed thereby giving a good protection. FeO at high temperatures becomes thermodynamically stable and develops a layer between steel and Fe_3O_4 . The rate of oxidation is controlled by diffusion which takes place across the FeO layer.

The expression:

$$C = A \exp - (Q/RT)$$

is valid for temperatures up to 570 °C.

Lim and Ashby (1998) have also modelled the severe-oxidational wear regime in which continuous oxides develop over the surface and the frictional heat is reported to be sufficient to melt locally the oxide at the asperity tips. The melting asperity absorbs latent heat of melting and the molten material flows and spreads across the adjacent cooler surface where it solidifies, releasing its latent heat.

The wear of alloys depends on the presence of debris particles where the wear debris can be retained on contact surfaces. Wear particles are mainly generated due to the relative motion under load. When the wear particles are reduced to a small size then they are agglomerated at certain locations which are basically due to the adhesion forces between solid surfaces arising from surface energy. The fine particles may get sintered and form more solid layers.

We can say that tribo-oxidation and static oxidation are different processes and the activation energies in both the cases would

be similar. Low activation energy generally indicates that development of wear protective layers does not depend on oxidation process but depends on the adhesion which takes place between the debris particles.

CONCLUSION

In reducing wear during sliding of metals and alloys oxidation can have a beneficial effect there by preventing the metal-metal contact. The heat required by oxidation can be induced by friction. In case of high speed unidirectional sliding the surface temperature may cause melting of oxide which may lead to oxidational wear. During low speed reciprocating sliding, wear debris can be retained between the contacting surfaces thereby giving protection from wear. 🌀

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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