EFFECT OF ION IMPLANTATION ON SUBSEQUENT EROSION AND WEAR BEHAVIOR OF SOLIDS

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ABSTRACT

The removal of material from a solid surface by mechanical forces is influenced by material properties (hardness, fracture toughness, yield strength, surface free energy) as well as system parameters (force, velocity of loading, environment). Ion implantation can modify many of the material properties either by directly affecting the deformation characteristics or indirectly by affecting the chemical or phase composition at the surface. The various forms of wear and erosion are analyzed to determine the material and system parameters which control material removal. The effects of implantation on these critical parameters are noted and examples of changes in surface topography under various test conditions are discussed.

1. INTRODUCTION

Ion implantation has received much publicity as a technique for improving the resistance to wear and erosion and for decreasing the friction of material surfaces. The success of the first studies at Harwell (reviewed in reference 1) resulted in the study of ion implantation into a variety of materials but the observed wear and erosion behavior of implanted specimens was erratic. Eventually it was realized that a knowledge of the total metallurgical system, that is, the implant species, the substrate material, and the test environment must be used in designing the implantation conditions.

Erosion (wear) phenomena are not material properties but are characteristic of an engineering system which involves a complex interplay of material properties, test procedure, and environment. For ease of discussion, wear processes can be divided into four main types: (1) adhesive wear, (2) abrasive wear, (3) corrosion or oxidative wear, and (4) surface fatigue or fracture. Each of these may involve several steps which depend directly upon material properties, and thus may be modified by ion implantation. In many real systems, two or more wear processes may occur simultaneously. Since wear is a manifestation of the mechanical and chemical processes that occur at solid interfaces, the specific test procedure may strongly influence the conclusion drawn from laboratory or accelerated testing. Many of these features of wear (and erosion) have been recently reviewed by Yust (2).

This paper will first review the characteristics of the various wear processes in order to identify the material properties important to each, and discuss which of these properties might be altered by ion implantation. A limited number of examples will be drawn from the literature to

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illustrate the topographical features of implanted metals and ceramics, and some directions for future research will be mentioned.

2. FRICTION

Historically, the study of friction can be traced to very early periods. Leonardo de Vinci is known to have had an interest in friction. In 1699 Amontons performed experiments to seek the origin of friction in machines. Coulomb (1785) introduced the concepts of surface roughness, which plays an important part in today's models. Figure 1, after Tabor (3), illustrates Coulomb's view of interlocking surface asperities and their contribution to the friction of sliding bodies. Even today we associate high friction with rough surfaces and low friction with smooth surfaces.

By 1800, the "laws of friction" recognized that the friction force is proportional to the normal load applied to the sliding contact and that the friction force is independent of the area of the sliding surface. Friction is important to the subject of topography of surfaces in contact since it determines the load transfer from one component to another, that is, the stress distribution in the system.

Frictional processes involve the dissipation of energy, a fact not accommodated by the simple roughness model of Coulomb (3). Although Coulomb's simple roughness model was incomplete, the concept of surface irregularities is central to today's understanding of friction (and adhesive wear). Figure 2 illustrates the multiple scales of surface irregularity that are detected at various magnifications. Note the similarities to Fig. 1. At a magnification of 1X, a surface waviness and texture is detected. At 100X, the texture is manifest as a fine scale irregularity called the surface roughness. At a higher magnification, for example 1000X, the roughness contours may also be irregular. The average roughness, R_a , is found by averaging successive ordinate values. Because of this surface roughness, two surfaces nominally in contact actually meet only at surface asperities or high points.

The modern view of friction, summarized by Tabor (3), considers the important factors to be (1) the true contact area, (2) the type and strength of bonds formed at the contact areas, and (3) deformation and rupture at and around the contact areas.

Surface topography and its role in surface interactions has been studied in detail since the mid-1960s and many models for describing surface asperities and their response to the load have been developed. The relationship between the number of asperities and their area and the applied load depends upon the nature of the local deformation at the asperity tip, that is, whether it is elastic or plastic deformation, or brittle fracture.

As two clean pieces of a metal are brought into contact, bonds first form due to van der Waals forces. These increase as the separation distance decreases leading to screened van der Waals bonds. The much stronger metallic bond forms at a separation distance corresponding to about one interatomic distance. The bonding between dissimilar metals has often been discussed in terms of mutual solubility. The suggestion that mutually soluble pairs show strong adhesive bonding while insoluble pairs show weak adhesive bonding is useful as a general guideline but fails upon rigorous inspection.

Buckley (4,5) has determined the force to pull clean metal surfaces apart and correlated these measurements with friction. He discussed the results in terms of the number of d-electrons in the metal and their influence upon the strength of the bond. Metals with strong d-character

FIGURE 1. Illustrations of Coulomb's view of friction due to surface asperities (after ref. 3).

FIGURE 2. Multiple scales of surface irregularity are detected as magnification of the surface is changed. The roughness average, R_a , is approximated by an averaging of successive ordinate values.

are less likely to interact. Figure 3 shows the coefficient of friction as a function of d-bond character for gold sliding on various metals. The large value indicates that the shearing force of bonded surfaces is being measured. Recent advances in the theory of solids suggest that questions regarding interfacial bonding could now be attacked from a sound fundamental base (6).

FIGURE 3. Coefficient of friction as a function of amount of d-bonding for gold sliding on various metals. Sliding velocity 0.7 mm/min, load 1 g, 23°C, and 10^{-8} N/m² (10^{-10} torr). (After Buckley, ref. 4.)

Since the metallic bond forms only at interatomic distances, the presence of a monolayer of absorbed gas may reduce the interaction between contacting forces to that of residual van der Waals forces, or by a factor of ten or more. The presence of a thin (1 nm) oxide also eliminates the metallic bonding.

The remaining factor to be considered in the discussion of friction is the deformation and rupture at and around the contact areas. The simplistic view considers failure or separation to occur at the weakest point — at the contact interface, randomly in both surfaces for similar pairs, or in the weaker component of dissimilar couples. If the interface junction is brittle, it fractures with little or no plastic deformation, and the work to break the bond should be close to the theoretical bond strength. If the junction is ductile, the work involved in plastically deforming the surrounding region must be considered, and the work-hardening characteristics of the materials become important. The presence of an interfacial layer, of course, adds a further complicating factor.

Following the arguments of Tabor (3), friction arising from interfacial bonds, in the absence of deformation or ploughing, is given as

$$F = A_o \tau = \frac{W}{\sigma_o} \tau \quad (1)$$

where F = friction force, A_o = true area of contact, W = normal force, σ_o = yield strength, and τ = interfacial shear strength. The coefficient of friction μ is then

$$\mu = F/W = \tau/\sigma_o \quad (2)$$

If there is a ploughing deformation, an additional term is to be added to this expression,

$$F = F_{\text{adhesion}} + F_{\text{deformation}}$$

The important feature for the current discussion is the dependence on the material parameters τ_0 (shear strength of interface) and σ_0 (yield stress).

3. ADHESIVE WEAR

Adhesive wear results from the formation of junctions at contacting asperities on the two surfaces and subsequent rupture of the junctions. It is characterized by the transfer of one material to the surface of the other. Figure 4 contains a photograph of a wear track made by a diamond pin sliding on a TiB_2 disk. The diamond adhered to the TiB_2 and exhibited a high wear rate, whereas only a small amount of TiB_2 was removed. The profilometer trace across the wear track also showed that a wear film had formed (7).

FIGURE 4. (a) Optical photograph of an adhesive wear track made by diamond sliding on TiB_2 . (b) Profilometer trace of (a). (Reference 7)

Junction formation is attributed to welding due to local temperature increases caused by the sliding of rough surfaces or to local adhesive bonding. Because of the small tip size of asperities and the very high local loads, the instantaneous temperature can be very high. Junction formation due to solid state bonding (adhesion) is the same as discussed above for friction. Thus, adhesive wear should decrease as one progresses from couples of the same metals and those that form solid solutions or inter-metallic compounds to incompatible metal couples to nonmetal-metal pairs, although there are many exceptions to this simple view.

Formation of adhesive bonds can also be described in terms of work of adhesion, first defined by Dupré (1869). The work of adhesion per unit area of contact required to separate two solid surfaces is given as

$$\Delta\gamma = \gamma_a + \gamma_b - \gamma_{ab} \quad (3)$$

In this relation, γ_a and γ_b are the surface free energies for the two free surfaces and γ_{ab} is that of the solid-solid interface.

More attention has been directed to the study of mechanisms involved in breaking the junctions than in forming them. In order to determine the

relationship between material properties that can be altered by implantation and material removal mechanisms, several proposed models will be examined. These are (i) shearing of the weaker material (8,9), (ii) minimization of surface energy (10), (iii) critical strain for crack growth (fracture toughness) (11), (iv) surface fatigue (12), and (v) the delamination process (13).

Starting with the premise that sliding causes the rupture of junctions formed due to contact of asperities (8), the volume of material removed, ΔV , should be given by

$$\Delta V = N A_t x, \quad (4)$$

where N = number of atoms removed per interaction, A_t = true contact area, and x = sliding distance. The true area of contact is related to the applied load L and yield stress σ_y as $A_z = L/\sigma_y$ (3), such that Eq. (4) becomes

$$\dot{W} = \Delta V/x = NL/\sigma_y, \quad (5)$$

where $\dot{W}$ is the wear rate. Archard (8) replaced N in Eq. (5) with K , the probability that a junction between the two surfaces would lead to the formation of a wear particle. Hence,

$$\dot{W} = KL/\sigma_y \quad (6)$$

or, as often assumed, if the hardness $H = 3\sigma_y$,

$$\dot{W} = K'L/H \quad (7)$$

and we have a simple relationship between wear rate and hardness of the deforming (weaker) material.

Rabinowicz (10) proposed that the size of loose particles removed or transferred from one surface to the other is determined by balancing the elastic volume energy against the surface free energy. This approach yields the average loose (removed) particle size as a function of interfacial energy, or

$$\bar{d}_L = \frac{6\gamma_{ab}}{\nu^2 Y \epsilon_m^2}, \quad (8)$$

where γ_{ab} = surface free energy of a-b interface, ν = Poisson's ratio, Y = Young's modulus, and ϵ_m = maximum elastic strain. Writing the true area of contact A_t as $n\pi r^2$, where n is the number of contacts and r is the average radius of the contacting asperities, Eqs. (4) and (8) can be rewritten as

$$\dot{W} = N \cdot n \pi \left[\frac{3\gamma_{ab}}{\nu^2 Y \epsilon_m^2} \right]^2, \quad (9)$$

which relates wear volume to interfacial free energy and the elastic properties of the solid. A similar expression can be written for the size of particles that adhere to one surface.

Hornbogen (11) modified Archard's expression in terms of fracture toughness for test conditions under which crack growth determines the removal of material. Archard's formulation gives a simple inverse relationship

between wear and hardness. Figure 5 shows that the relationship appears to hold within certain classes of materials but often fails. Hornbogen derived the relationship

$$\dot{W} = K' \frac{\gamma L^{3/2} m^2 \gamma_y}{K_I^2 H^{3/2}}, \quad (10)$$

where K' and γ are empirical constants, m the work hardening coefficient, γ_y the yield strength, K_I the fracture toughness, and H the hardness.

FIGURE 5. Wear resistance as a function of hardness for various classes of material. After Hornbogen (11).

Halling (12) attempted to relate the factor K' to the fatigue properties of the metal, observing that repeated adhesions and stressing should cause failure by fatigue mechanisms. For a particular failure criterion, he proposed that

$$\dot{W} = CL/H_1, \quad (11)$$

where H_1 is the initial hardness and C is a constant.

Perhaps the most detailed description of the material removal mechanism is given by the delamination model developed by Suh (13). According to this model, the asperities on the softer material are quickly removed by fracture and further wear occurs by asperity (harder material) contact on a plane (softer material). This introduces subsurface deformation which accumulates with repeat loading. Eventually, cracks form and propagate approximately parallel to the surface. When the cracks shear to the surface, long thin wear sheets "delaminate". This process leads to an expression of the form

$$\dot{W} \propto \frac{\mu}{HK_I}, \quad (12)$$

where μ = coefficient of friction.

Certain of the material properties that appear in these relationships can be altered by ion implantation. These are hardness, yield stress, and fracture toughness. Surface energies may be changed by altering the surface composition.

4. ABRASIVE WEAR

Abrasive wear is characterized by the removal of material from one of two surfaces in relative motion caused by the presence of hard protuberances or hard particles either between the surfaces or embedded in one of them. The action is primarily cutting or ploughing and the worn surface contains grooves or scratches, Fig. 6. Following the arguments of Archard (8) and Mulhearn and Samuels (14), the following expression for volume wear rate is obtained:

$$\dot{W} \propto \frac{BF\sigma_a}{H}, \quad (13)$$

where σ_a = applied stress (L/A), B = fraction of contacts that actually remove material, and F = fraction of groove volume removed.

FIGURE 6. Optical photograph of abrasive wear track made by diamond grit sliding on copper. Normal load = 50 g.

Again, there is implied a simple inverse relationship between volume of material removed and hardness; however, the data of Kruschov (15) show variations between classes of material similar to those found by Hornbogen (11) for adhesive wear and shown in Fig. 5. Evans and Wilshaw (16) found that the wear resistance of brittle solids varied as fracture toughness and hardness. There is a large amount of data that shows the importance of the relative hardness of the abrading and abraded materials.

Erosion is a special case of abrasive wear in which the abrading material is in the form of particles carried by a gas or liquid stream. In the case of brittle materials, material removal is the result of cracking

due to Hertzian contact stress during impact. Evans, Gulden, and Rosenblatt (17) expressed the wear volume in terms of impact velocity, particle size, particle density, fracture toughness, and hardness. The first three parameters are functions of the particular system and the last two are materials properties.

In ductile materials, wear occurs by a cutting process or by extrusion of lips around impact sites followed by fragmentation of these lips by subsequent impacting particles. A model by Sheldon and Kanhere (18) describes the wear volume in terms of the ratio of vertical to horizontal force on the particle, particle size, velocity and density, and eroding material hardness.

5. SURFACE FRACTURE

Material removal due to direct surface fracture is important for brittle solids and may occur during abrasive or adhesive wear conditions. Figure 7 shows a scratch made in α -SiC. There are many radial cracks which extend into the surrounding material for distances comparable to the groove width. Much of the material is removed in large pieces due to the lateral cracks caused by the tensile component of the stress which is present during unloading. The models of material removal cited above for erosive wear should be applicable, hence, the properties of yield strength, hardness, and fracture toughness should be important. Since the fracture mode of brittle solids is sensitive to the details of the stress state, being particularly susceptible to tensile stresses, the residual surface stresses introduced by ion implantation can affect the wear response.

FIGURE 7. Scanning electron micrograph of surface cracking on and around the wear track made in α -SiC.

6. OXIDATIVE-CORROSIVE WEAR

Oxidative (corrosive) wear is characterized by the formation of an oxide or other corrosion product layer and its subsequent removal by mechanical action. The tendency to form adhesive junctions between a metal and an oxide is much less than between metals. Thus, oxidation provides a hard surface layer with little tendency to adhere to an opposing material. On

the other hand, oxides tend to be brittle, and if the softer substrate fails to support the load applied to the thin oxide layer, the oxide will crack and perhaps spall. The wear rate will depend upon both the oxidation rate and the stresses in the oxide-substrate composite.

Dearnaley (19) modified earlier formulations used to describe oxidative wear to give

$$\dot{W} = \frac{k_o t L}{\delta_c \rho H}, \quad (14)$$

where k_o = linear oxidation rate, t = time of contact for a single junction encounter, δ_c = critical oxide thickness for spalling, ρ = oxide density, and H = oxide hardness. The parameter δ_c depends upon the stress state at the oxide-metal interface and thus is related to the substrate hardness or yield strength. These models assume that oxidation occurs due to the temperature rise at asperity contacts.

Equation (14) suggests ways in which implantation may reduce oxidative wear rates. Surface alloying or compositional changes may reduce the oxidation rate, k_o . The critical oxide thickness, δ_c , may be changed by reducing growth stresses, increasing fracture toughness of the oxide or matching the hardness of oxide layer and substrate. The first two might be changed by compositional effects and the last one by altering the mechanical properties of the substrate.

7. EFFECTS OF IMPLANTATION

The purpose of the above discussion is to identify the properties of materials which contribute to their wear by mechanical processes. In friction and adhesive wear, the type and strength of solid state bonding, and the mechanical properties near bonded junctions were identified as important. The mechanical properties of hardness and fracture toughness were specified as controlling wear during abrasion or erosion. Surface fractures depend upon strength (hardness), plasticity, fracture toughness, and residual stress states. Oxidative wear is controlled by the oxidation rate, the mechanical properties of the oxide and substrate hardness. The types of bonds formed and the oxidation rate may be altered by control of surface composition. The mechanical properties may be changed by use of the defect structure produced by the radiation damage, second-phase formation, or interaction of implanted species with defect and microstructural features.

Before discussing specific examples of the effect of ion implantation upon the surface topography of subsequently eroded materials, a discussion of property alteration by implantation will be given.

Roy Chowdhury et al. (20) used a mechanical microprobe technique to determine the Dupré adhesion energy, γ , for titanium before and after implantation. They determined γ between a titanium asperity and a titanium foil. Implantation of about 1.4×10^{17} N/cm² (200 keV N₂⁺) reduced the value of γ by a factor of three.

Hardness is defined as the resistance of a material to penetration by a loaded indenter. It has proved to be difficult to relate hardness to fundamental material properties, although it is generally related to yield strength in ductile metals. Many of the early attempts to determine the effect of implantation on hardness employed the Vickers or Knoop technique in which the depth of the hardness impression exceeded the depth of the implanted ions. These measurements indicated the direction of change but failed to give a quantitative measure of the effects. Table 1 summarizes

recent measurements. The data for metallic materials made with the ultra-low load equipment were obtained from load-displacement curves for penetration depths less than the ion range (21).

TABLE 1. Hardness Changes Due to Ion Implantation

Material	Implanted species	Hardness method*	Relative hardness (H_i/H_u)	Reference
Al	N	ULL	4.20	(22)
Be	B	KH5	4.00	(23)
Fe	N	ULL	1.84	(23)
Co	N	ULL	1.40	(22)
Ni	N	ULL	1.04	(22)
Ti-6Al-4V	N	ULL	2.00	(22)
Armco Fe	N	ULL	1.80	(22)
304 Stainless	N	ULL	1.25	(22)
Steel 12T(410)	N	ULL	1.20	(22)
52100	N	ULL	1.00	(22)
18-4-1 Tool Steel	B	VH10	1.80	(24)
Al ₂ O ₃	Cr (300K)	KH15	1.5	(25)
	Y (300K)	VH200	1.4	(26)
	Cr (77K)	KH15	0.6	(27)
		ULL	0.6	(28)
MgO	Cr,Ti	KH10	1.5	(29)
SiC	Cr,N	KH15	0.6	(30)
	N	VH200	0.7	(31)
TiB ₂	Ni	KH15	2.0	(32)
ZrO ₂	Al	KH20	1.2	(33)

*ULL = ultra-low load; VH10 = Vickers, 10 gf; KH15 = Knoop, 15 gf.

For metallic materials, the relative hardness (implanted $\div$ unimplanted) varies from 1.0 to 4.2. The variation results from the different hardening mechanisms activated by the implanted species and implantation damage. In the pure metals implanted with nitrogen, for example, Hutchings et al. (22) argued that the hardening of aluminum was due to nitride formation. The hardening of iron was due to interstitial solid solution strengthening, and the absence of an effect in nickel is due to lack of a hardening mechanism. Similar arguments were made for the metallic alloys. In the case of the ceramics, the softening of Al₂O₃ and SiC is attributed to the change from the crystalline to the amorphous state and a change in deformation mode.

The fracture toughness of implanted materials is very difficult to determine because of the small dimensions of the affected layer. Measurements for brittle materials (ceramics) have been reported for an indentation technique which gives a qualitative indication of the effects (25-30). Increases in the apparent K_I of 15 to 90% have been reported. In some instances, the apparent increase was attributed to the

residual compressive surface stresses that prevented cracks that were initiated in the interior from reaching the surface (26,27).

There have been few direct measurements of the effect of ion implantation upon yield stress because of the difficulties of testing. Tranchant et al. (34) performed tensile tests on copper single crystals pulled in the $\langle 111 \rangle$ direction. Implantation with aluminum increased the yield and rupture strengths by 42 and 26%, respectively. Hioki and co-workers (35) found that implantation of 300 keV nickel increased the rupture strength (in three-point bending) of single crystal Al_2O_3 by 30% and that 400 keV nitrogen increased it by 50%. Thus, it is clear that the mechanical properties which are important to wear (erosion) resistance are altered by implantation.

Phase changes caused by implantation might produce large differences in response to mechanical forces due to change in deformation mechanisms or surface reactivity. The literature contains many examples of crystalline to amorphous transformations, precipitate formation in the surface layer, and a surface compound layer. The cases cited here pertain to the wear results to be discussed later.

Coinplantation of titanium and carbon or titanium in a steel that contains sufficient carbon (36) or titanium in a vacuum chamber containing residual hydrocarbons (37) produces an amorphous surface on a wide variety of steels — ferritic, austenitic, and martensitic. In ceramics, amorphous surfaces have been prepared by implanting Al_2O_3 at 77 K and $\alpha\text{-SiC}$ at 300 K (27). As noted above, the hardness of the amorphous ceramics is 60% of their crystalline counterpart. Deformation occurs by viscous flow in the amorphous phases instead of dislocation motion.

Many of the improved mechanical properties of nitrogen-implanted steels have been attributed to the formation of a fine dispersion of nitride particles. The compounds Fe_2N , Fe_3N , and Fe_4N have been identified in ferritic steels (38). High chromium-containing steels (types 304 and 316 austenitic stainless steel) precipitate CrN (39) and martensitic stainless steels from Cr_2N (40).

Langer et al. (41) reported that a 100-nm thick TiC surface layer formed during high fluence ($5 \times 10^{17}/\text{cm}^2$) implantation of titanium into iron and M2 steel at substrate temperatures of 600 to 800°C. The carbon involved was contained in the substrate material for the steel but came from the specimen chamber atmosphere for the iron targets.

EerNisse developed a technique for determining the stresses lateral to the implantation surface by measuring the deflection of thin specimens (42). This technique has been used to determine the surface stresses introduced into Al_2O_3 (43), steel (44), and thin films of aluminum and gold (45). Implantation of argon into Al_2O_3 and nitrogen into steel produced stresses in excess of the yield strength.

8. EFFECTS OF IMPLANTATION ON SUBSEQUENT WEAR

The effects of implantation on the mechanical removal of material during wear or erosion processes will be illustrated in this section. An attempt will be made to classify the effects in terms of the various property changes discussed above. Since several wear mechanisms may be operative during a single test, results are seldom as clear-cut as the outline might indicate.

8.1. Change in mechanical properties

Implantation of nitrogen into aluminum reduced the amount of material removed in a pin-on-disk test (adhesive wear) by a factor of 35 for a fluence of $1 \times 10^{17} \text{ N/cm}^2$ (46). Figure 8 shows the wear improvement factor

FIGURE 8. The effect of nitrogen implantation on the wear resistance of aluminum. After Madakson and Smith (46).

as a function of ion fluence. Reference to Table 1 shows that a similar treatment increased the hardness of aluminum by a factor of 4.2 due to formation of nitride precipitates. Examination of the wear tracks revealed fewer cracks for the implanted samples. The wear and frictional behavior of aluminum depends on the formation and subsequent failure of the surface oxide film which is hard and brittle. It is proposed that the improvement in wear behavior caused by implantation of nitrogen derives from the increased support provided for the oxide film by the hardened substrate.

Figure 9 shows the increase in wear resistance and hardness as a function of boron fluence for the tool steel 18 W-4 Cr-1 V (24). Both properties increased approximately with fluence in the range of 10^{15} to $10^{18}/\text{cm}^2$. Implantation did not change the shape of the wear track, only the depth. These changes (170% increase in wear resistance and 40% increase in hardness at $10^{17}/\text{cm}^2$) were considered to be associated with interstitial solid solution strengthening of the steel by the boron. The implanted ions also occupy defect and dislocation sites to give further strengthening.

As noted above, implantation of Al_2O_3 with chromium at 300 K caused an increase in hardness (50%) and fracture toughness (15%). The SEM of Fig. 10 shows a scratch made by a diamond pin sliding across an Al_2O_3 surface under a normal force of 0.29 N (30 g), corresponding to abrasive or ploughing wear conditions (47). In this case the implanted region is crystalline but both sublattices are characterized by high damage levels. The number of radial cracks and the amount of material removed due to lateral cracks were much higher in the unimplanted region of the specimen. The measured tangential force on the moving pin increased by 20 to 30% as the pin passed from the unimplanted to the implanted region, indicating an increase in the work required to remove a unit of volume of material.

8.2. Change in surface composition

The change in near-surface composition can affect the wear by altering the surface energy, the type or strength of adhesive bonds, or the formation of a surface film.

As discussed above, Roy Chowdhury and co-workers found a reduction in surface energy (work of adhesion) by a factor of three after implanting titanium with nitrogen (20). It has been suggested that this reduction in the work of adhesion may be responsible for the observed reduction in the coefficient of friction for nitrogen-implanted titanium (1).

FIGURE 9. The effect of boron implantation on hardness and wear, and wear track profile in type 18-4-1 tool steel. After Madakson (24).

FIGURE 10. Suppression of surface cracks around a wear track by implantation of 2.6×10^{16} Cr/cm² into α -Al₂O₃. Yust and McHargue (47).

The implanted species can have a large effect on the wear process if it promotes the formation of an oxide layer such that the mechanism changes from adhesion or abrasion to oxidative wear. In the early studies by Hartley et al. (48), a variety of ions (Sn, In, Ag, Pb, Mo) were implanted to fluences greater than 10¹⁶/cm². Specimens implanted with tin and molybdenum showed greatly reduced coefficients of friction, Fig. 11, whereas those with Pb, In, and Ag had higher values. It was proposed that Sn and Mo enhanced the formation and retention of the oxide layer. Molybdenum showed greatly reduced coefficients of friction, Fig. 11, whereas those with Pb, In, and Ag had higher values. It was proposed that Sn and Mo enhanced the formation and retention of the oxide layer.

Hutchings and co-workers (22,49,50) studied the hardness, friction, appearance of wear tracks, and surface composition for nitrogen-implanted Ti-6 Al-4 V. Their results are summarized in Fig. 12. Implantation of 3.5×10^{17} N/cm² reduced the wear rate by more than two orders of magnitude. There was also a decrease in friction coefficient from 0.48 to 0.15. Long-term testing resulted in a return to the unimplanted wear rate. Inspection of the wear tracks [Fig. 12(b,c)] showed a marked difference between the unimplanted and implanted areas. The SEMs of tracks on unimplanted regions, or after long-term testing, showed deep grooves and

FIGURE 11. The effect of 2.8×10^{16} Sn/cm² on the coefficient of friction for En 352 steel. After Hartley et al. (48).

were very rough. The photographs of tracks in the implanted areas were smooth and covered by a thin polycrystalline film. The profilometer traces also showed these differences.

Results of an electron probe microanalysis of oxygen and nitrogen in the wear tracks are also shown in Figs. 12(b,c). There were no significant amounts of oxygen or nitrogen in the tracks made on unimplanted areas or after breakthrough of the implanted layer. The traces in Fig. 12(c) were obtained from a track after 1000 turns. From the variation in the oxygen signal and the profilometer trace, it is deduced that an uneven oxide layer had developed in the wear track. In addition, some nitrogen had been lost from the track (i.e., some wear of the nitrogen-containing material had occurred).

Oliver et al. proposed the following description for the wear process. The dominant mechanism of material loss in the unimplanted material is a cutting or machining process. This occurs because of transfer of material from the disk to the pin due to adhesive wear in the initial stage. This layer acts as the cutting edge for further wear. No material transfer was found for implanted disks and the formation of the oxide (or oxynitride) layer suggests wear occurs by an oxidative process. The authors proposed that the effects were largely due to chemical stabilization of the surface film or that chemical effects promote the rapid formation of this film.

8.3. Phase changes

Implantation may alter the phase composition of the near-surface region by formation of metastable solid solutions, formation of second-phase precipitate particles, formation of a compound layer, or promotion of a crystalline-to-amorphous phase change.

The formation of an amorphous surface would be expected to affect the response to the mechanical forces responsible for wear since the physical, chemical, and mechanical properties of amorphous and crystalline phases may be quite different, even for the same overall composition. Figure 13 gives the results of wear tests for 440C stainless steel (a martensitic steel) implanted with 2×10^{15} Ti/cm² and 2×10^{15} C/cm². For a normal load of 4.85 N (500 g), the coefficient of friction was reduced 40% and the wear depth was reduced 80% by implantation (51). The Hertzian stress in these tests often exceeded the yield stress of the crystalline (unimplanted) steel. These investigators concluded that abrasive wear occurred in the implanted (amorphous) region and adhesive wear occurred in the unimplanted (crystalline) region.

(a)

FIGURE 12. (a) The effect of 3.5×10^{17} N/cm² on the wear volume of Ti-6 V-4 Al. SEM, profile, and oxygen and nitrogen distribution in wear track of (b) after breakthrough, (c) after 1000 turns. After Hutchings, Oliver, and Pethica (49,50).

(b)

(c)

FIGURE 13. Effect of amorphous surface on wear of type 440C stainless steel. (a) Coefficient of friction, (b) wear depth. After Pope et al. (51).

The formation of an amorphous phase in ceramic materials may have two effects on the removal of material during wear. A large volume increase accompanies the crystalline to amorphous transformation in α -SiC. This causes high lateral compression stresses in the near-surface region; the deformation mechanism also changes. Figure 14 shows scratches made by a diamond pin sliding across a single crystal sample of α -SiC. The scratch in the unimplanted region is accompanied by a large number of radial cracks that extend into the surrounding material. Much of the debris consists of angular pieces fractured from the wear track. In Fig. 14(a), there are two regions of large segments removed or loosened due to formation of lateral cracks. In the amorphous region, produced by 2.6×10^{16} Cr/cm², the deformation occurred by viscous flow with ductile-appearing chips. A profilometer trace showed that a significant amount of material was present as ridges next to the groove. In this case, it is believed that cracks nucleated in the crystalline region below the wear track were prevented from reaching the surface by the surface compressive stresses, and that the applied stress was relieved by viscous flow (30,47).

Implantation under certain conditions may produce a surface layer of a new compound. Figure 15 contains the wear data of Singer and co-workers (41) and shows the TiC layer on hardened M2 steel to be three to ten times more resistant to abrasive wear than the substrate. In sliding tests where adhesive wear occurred for the substrate material, this TiC layer was free of grooving, cracking, and adhesive debris. The coefficient of friction for the TiC layer in these sliding tests was 40 to 60% lower than that of the hardened steel.

8.4. Surface stresses

Oliver, Hutchings, and Pethica studied the wear of nitrogen-implanted electrodeposited chromium (hard chromium plate) and attributed the improved wear properties to the effects of implantation-induced stresses (50). The wear volume was decreased by a factor of 20 for normal loads of 5.2 N (540 g) and 10.5 N (1080 g), (Fig. 16). There was no significant change in the coefficient of friction, but there was a 40% increase in hardness. Wear tracks in unimplanted material, implanted after 1000 turns at a load of 10.5 N where breakthrough did not occur, and implanted after 515 turns where breakthrough did happen are shown in Fig. 17.

FIGURE 14. Effect of amorphous surface on wear of α -SiC. (a) Crystalline, unimplanted, (b) amorphous, implanted with 2.6×10^{16} Cr/cm². McHargue and Williams (30).

FIGURE 15. Abrasive wear of M2 steel containing a near-surface layer of TiC formed by implanting Ti + C at 600 to 800°C. After Singer et al. (41).

The wear track in the unimplanted material shows a series of fine longitudinal grooves and a more widely spaced network of nearly transverse features. Higher magnifications revealed these transverse features to be small shear lips which delineate the microcracks which exist in hard chromium plate due to release of the large residual stresses produced by the plating process. In contrast, the wear track on the implanted material (before breakthrough) is much smaller and much smoother, having a maximum depth of around 0.1 μ m. The track in implanted chromium which broke through and was terminated after 515 turns was characterized by the

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FIGURE 16. Wear rates in electrodeposited chromium before and after implantation with $3.5 \times 10^{17} \text{ N/cm}^2$. After Oliver et al. (50).

FIGURE 17. Scanning electron micrographs of wear tracks in specimens of Fig. 16. (a) Unimplanted, 1000 turns; (b) implanted, 1000 turns, no breakthrough; (c) implanted, 515 turns, breakthrough. Load 10.4 N.

The wear track in the unimplanted material shows a series of fine features. Higher magnifications revealed these transverse features to be small shear lips which delineate the microcracks which exist in hard chromium plate due to release of the large residual stresses produced by the plating process. In contrast, the wear track on the implanted material (before breakthrough) is much smaller and much smoother, having a maximum depth of around $0.1\text{ }\mu\text{m}$. The track in implanted chromium which broke through and was terminated after 515 turns was characterized by the appearance of the microcracking at the center of the wear track and fine longitudinal grooving towards the edges.

These results for chromium show that its wear resistance was improved by nitrogen implantation. This improvement was associated with a change in wear mechanism, but in this case it was the role of the microcracks inherent in the plated chromium that was critical. The introduction of a large fraction of nitrogen into a metal lattice causes an expansion of that lattice. For example, the formation of Cr_2N from chromium metal is accompanied by a volume increase of approximately 25%. Such a volume increase will close the microcracks in the implanted region. Thus, the initial wear of implanted chromium occurred by the adhesive wear of two hard materials, and was therefore very slow.

Once the implanted layer was penetrated (or in the unimplanted material), the dominant wear mode changed. As seen in Fig. 17(c), breaking through the implanted layer coincided with the appearance of striations along the wear track. It was suggested that these striations were the product of abrasive wear by fine particles which originate at the shear lips associated with the microcracks. Thus, the wear mode for unimplanted chromium plate may be explained in terms of the shearing of particles from the vicinity of the microcracks combined with abrasive wear by these particles.

Another example in which the residual surface stress state controls the removal of material during wear is given by McHargue et al. for TiB_2 (ref. 7). Figure 18 is a SEM of the wear track made by a diamond pin on a TiB_2 disk. There is a large adhesive component to wear in this system which caused a carbon (diamond) layer to be transferred to the TiB_2 . The removal of TiB_2 occurred primarily by the pull-out of the entire grains as a result of grain boundary cracking. It is thought that this cracking was caused by the tensile component of the stress during the unloading stage as the diamond pin passed a given point. The presence of large residual compressive stresses would counter this tensile component. Examination of the wear tracks at high magnification showed profuse cracking in the unimplanted region but very little in the implanted sections.

9. SUMMARY AND CONCLUSIONS

This paper has discussed the major features of wear processes and identified the material properties important to the material removal step. Then these effects of implantation on structure and properties were examined to determine how implantation might affect the wear process. Finally, several examples of wear studies on implanted materials were given to illustrate the range of responses observed.

It is clear that the wear rate for a given mechanism can be altered in a systematic manner. Following the arguments of Rabinowicz (52), Dearnaley (19) suggested improvements in adhesive wear by factors of 2 to 3, abrasive wear by factors of 10^4 , and oxidative wear by 10^2 to 10^3 can be achieved by implantation. The most effective treatment is one that changes the wear mode to a less aggressive one. Most studies to date have focused on the mechanical property-wear relationship.

FIGURE 18. Scanning electron micrograph of wear track in TiB_2 . The unimplanted region is to the left and implanted with $1 \times 10^{17} \text{ Ni/cm}^2$ is to the right. McHargue et al. (7).

A number of cases have been cited in which oxidative wear has been promoted at the expense of adhesive wear. Unfortunately, the manner in which the implanted species causes this change remains unknown. Since this route holds the most promise, there is a great need for careful studies to establish a scientific basis. Likewise, in most instances, the reason for improved wear resistance of amorphous metallic surfaces has not been established.

Few attempts to control wear by alteration of surface composition have been reported. Since chemical species that lower surface energy tend to segregate to surfaces and interfaces, adhesive wear might be addressed by selectively doping, that is, ion implantation.

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