

COMPUTERISED

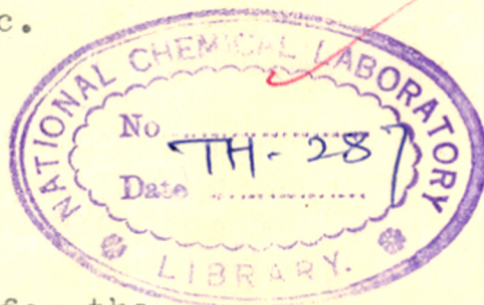
1002
1090

COMPUTERISE

The Effect of Surface Films on Sliding Metals.

By

R.T.Spurr, B.Sc.



A Thesis Submitted for the
Diploma of the Imperial College.

539.23 : 539.62 (043)
SPU

Applied Physical Chemistry Dept.

May, 1951.

Contents.

	Page.
Part 1. <u>Friction and Lubrication.</u>	
1. Theories of Friction	1
2. Significance and Measurement of μ	3
3. Variation of Friction with Sliding Conditions ○○○○○○	6
4. Lubrication	10
Part 2. <u>Adhesion between Metal Surfaces.</u>	
1. Introduction	16
2. Surfaces in Air	17
3. Pressure Welding	19
4. Welding by Sliding	20
Part 3. <u>Sliding of Metals</u>	
1. Introduction	25
2. Experimental Details	26
3. Results	27
4. Temperatures reached during Sliding	34
Part 4. <u>Films on Metal Surfaces.</u>	
1. Formation and Nature of Oxide Film	37
2. Films on Copper	39
3. Films on Iron	44
<u>Summary</u>	51

PART 1. FRICITION AND LUBRICATION.1. Theories of Friction.

When two surfaces are slid over one another Amonton's Law, according to which the resistance to sliding is proportional to the load and independent of the nominal area of contact, is in general obeyed. This led Coulomb to suggest that the frictional resistance was due to interlocking of surface asperities, and represented the work of lifting the load over the summits of these asperities. This theory was generally accepted up to about 1924 (See Encyclopaedia Britannica, 13th Edn.) and still finds adherents (Bikermann, 1944). Ewing (1892) seems to have been the first to question the Coulomb theory, and Hardy's (1932) experimental work suggested strongly that friction was due to adhesion between the opposing surfaces, though Hardy admitted the difficulty of reconciling an adhesion theory with Amonton's Law. Tomlinson (1929) suggested a molecular theory according to which the frictional resistance was due to the attractive and repulsive ^{forces between} molecules in the opposing surfaces.

A notable advance was made by Holm (1938) who recognised clearly the great difference between the nominal

and actual areas of contact between the two surfaces and its implications. Holm (1935) found experimentally that the frictional resistance was of the same order as the force required to shear welds of cross-sectional area equivalent to that of the real area of contact between two clean metal surfaces and so suggested that ~~the~~ welds were indeed formed at the isolated areas of contact and were responsible for the resistance to sliding. Ernst and Merchant (1940) arrived at a similar view, and also made allowance for the effect of surface roughness on the friction. Bowden and Tabor (1943) demonstrated the existence of intermetallic welds formed during sliding, and showed that the adhesion theory of friction was consistent with Amontons's law if the deformation at ~~the~~ highly stressed areas of contact was plastic rather than elastic. They also considered how the force required to plough asperities on the one surface through the opposing surface contributed towards the friction.

The surface film between two metals surfaces may act as a dielectric, and Schnurmann (1942) suggested that the sliding friction may include an electrostatic component but the experimental evidence brought forward in support seems very weak.

2. The Significance and Measurement of the Coefficient of Friction.

The coefficient of friction (μ) is defined as the ratio of the frictional force to the applied load and is constant for a given pair of surfaces.

Attempts have been made to relate the numerical value of the coefficient ~~from~~^{with} the bulk properties of the sliding surfaces. It follows directly from Bowden's hypothesis that it is equal to the sum of the ratio of the shear strength to the "flow pressure" of the metal concerned and a "ploughing" term due to the frictional resistance encountered on ploughing asperities on one surface through the opposing surface. Ernst and Merchant obtained a similar expression substituting the "actual mean pressure hardness" for the "flow pressure" and a "roughness" term for Bowden's "ploughing" term. They also found that some of their calculated coefficients of friction agreed reasonably well with the experimental values.

Measurement of Friction.

There are many ways of measuring friction. The nature of the sliding system, however, may change with the method of measuring the friction, and so the results

obtained with one type of instrument might be different to those obtained with another.

Friction measuring instruments can be divided into two classes :- (i) those in which a force is applied to one surface to make it move over the other, i.e. static friction is measured; and (ii) those in which a force is applied to keep one surface in continual motion over the other, i.e. dynamic friction is measured.

Static Friction - The simplest way to measure the static coefficient of friction (μ_s) is with the inclined plane, for here the coefficient is numerically equal to the tangent of the angle of inclination at which motion begins. Various arrangements of the inclined plane have been described (Dow, 1929, Shaw and Leavey, 1930).

Instead of using gravity to bring about motion a tangential force can be applied to horizontal surfaces (Campbell, 1939, Claypoole, 1943). But with all such instruments it is almost impossible to determine where motion begins and awkward to use heavy loads.

Dynamic Friction - The Bowden-Leben apparatus (1939) has been the forerunner of a number of similar machines. The lower surface is driven by e.g. a hydraulic ram at the required speed and the loaded upper specimen, usually hemispherical in shape, is prevented from moving with it

by an elastic bifilar suspension, the deflection of the suspension indicating the magnitude of the frictional resistance. Variations in the manner of measuring the deflection have been described by Brummage (1942), Barwell and Milne (1949), Bristowe (1949) and Whitehead (1950). If the dynamic coefficient of friction (μ) should decrease with velocity the upper surface may oscillate giving "stick-slip" motion (Bristowe, 1947).

The frictional force may also be measured directly by running a thread from the restrained surface over a pulley to a scale pan and weights (Chalmers et al., 1946).

In machines in which a rotating disc is driven by a constant speed electric motor the other surface may be fixed and the torque determined from the armature current so that after suitable calibration the friction can be obtained by measuring the current drawn. This method is used in some wear machines. Numerous other ways of measuring friction have been described (Viewig, 1924, Schnurmann, 1942, Dykos, 1946, Rideal, 1947, etc.).

The actual act of measuring the friction may alter the frictional system and so the observed friction, sometimes drastically. In the Bowden-Leben apparatus the upper surface is used throughout a run and so any surface film present initially may be rubbed off and the crystal structure

of the specimen altered. For machines with circular tracks not only is the constrained surface altered but the nature of the track may alter progressively after the first revolution (Strough and Repp, 1941). Such changes in the surfaces, however, may give some information concerning their wear properties.

3. Variation of Friction with Sliding Conditions.

Effect of Load.

Provided the sliding system does not change μ is independent of load. Thus Whitehead (1950) found that μ for aluminium or silver pairs was practically constant for loads varying from 10^{-2} to 10^4 grams. The load however may alter the sliding system. With loads of less than 1 gram Whitehead found that the μ for copper was constant at about 0.4, but rose with increasing loads to a constant value of about 1.2 for loads greater than 50 grams. The surface oxide was not penetrated with light loads and so oxide was sliding on oxide, whereas for heavy loads the surface films were ruptured and the sliding became metallic.

Effect of Velocity.

Coulomb stated that the friction is independent of velocity and this has been found to be the case over a wide range of velocities. At very high speeds μ decreases due

to the wedging effect of the air between the surfaces. Also at high speeds frictional heating may affect the properties of the surfaces.

The force to keep two surfaces sliding over one another is, in general, less than that required to bring about motion, i.e. dynamic friction is less than static friction.

The static friction of soft metals tends to increase with the time in which they remain in contact; also the difference between the coefficients is less for harder than for softer metals. Thus the difference may be due in part to the sliding surfaces having lesser opportunity in the dynamic case to attain equilibrium.

Barwell and Milne (1949) found that with lubricated surfaces $\mu = \mu_0 \left(\frac{v}{v_0} \right)^{\delta}$ for velocities less than about one cm./sec., but could not state what significance the expression had. Beek, Givens and Smith (1940) and Forrester (1946) have also found some variation of friction with velocity under conditions of supposed boundary lubrication, but some wedging effect probably occurred.

Effect of Hardness

For a given load the real area of contact between two surfaces will depend upon their plasticity, but the

shear strength of the metallic junction at the area of contact and the force required for ploughing (again depending upon the shear strength) are also related to the hardness of the surfaces, so that although μ decreases with the hardness, the range of μ under normal experimental conditions is small, e.g. for copper $\mu = 1.5$; for chromium $\mu = 0.4$. The increase in friction observed after the annealing of a previously work hardened surface shows the effect of hardness particularly well (Shaw and Levey, 1930) (Ernst and Merchant, 1940) as here the frictional system remains otherwise the same.

The advantages of a hard surface with its consequent small area of contact, and of soft metals with low shear strength are combined if a very thin film of a soft metal is formed on a hard substrate. Such a frictional system is used in the thin wall bearing (Finch, 1950) and in some duplex bearings where the softer constituent is smeared over the harder constituent (Heaton et al., 1942).

Effect of Surface Roughness.

Considerable work has been done on the effect of surface roughness on friction (Clayton, 1945, Strang and Lewis, 1949), but the experimental results and conclusions

are often confusing and even apparently contradictory. Thus Bikermann (1944) thinks that friction is entirely due to surface roughness whereas Hardy found that a ground glass plate had a smaller μ than a highly polished one. In the case of dry metals it appears that there is some increase in friction with surface roughness.

Some of the differences in results may be due to the specimen preparation. Thus altering the surface finish may alter other properties of the surface e.g. its hardness, the thickness and resistance to penetration of the surface oxide, the amount of a constituent present at the surface of an alloy, etc.

Also there is no satisfactory way of describing surface roughness and the shape of the asperities as well as their heights may be important.

With boundary lubricated surfaces there is again no simple correlation between μ and surface finish, although it appears there is an optimum surface finish which will keep the film spread but not penetrate it (Burwell, 1942).

Before engineering surfaces are made to carry working loads they are usually "run-in" with copious lubrication under light loads. This "running-in" operation at first wears down surface asperities and then as the surfaces becomes smoother wear decreases and metal from

high parts is "flowed" into recesses further smoothing the surfaces. The crystal structure near the surface is broken down and the metal surface layer "the Beilby Layer" becomes amorphous (Finch, 1936). Thus running-in smooths the surfaces, so promoting hydrodynamic lubrication; it also increases the rigidity of the surface and therefore the support given by the surface to the surface oxide and boundary lubricant film.

4. Lubrication.

If a film is interposed between two surfaces, the friction in general is reduced. All surfaces are covered with an oxide film but under most conditions of sliding this is not sufficient and lubrication is required. There are three main classes of lubrication : (i) hydrodynamic; (ii) boundary; and (iii) extreme pressure lubrication.

Hydrodynamic Lubrication.

In practice the engineer endeavours to obtain hydrodynamic lubrication. When a lubricant is drawn by the action of viscous forces through a constriction or wedge-shaped space such as exists, for example, between a shaft and its bearing, hydrodynamic forces appear which

tend to force the surfaces apart. Thus in a properly lubricated bearing the surfaces are kept apart by a film of oil, and the force of friction is the force required to shear the oil film.

Boundary Lubrication.

Under heavier loading and low sliding speeds, or if sufficient lubricant is not supplied, the surfaces may not be kept apart by the relatively thick oil film required for hydrodynamic lubrication. The friction, however, may be kept much lower than that for dry sliding by thin films of only molecular thickness adsorbed on the surfaces. Here the friction is independent of the viscosity of the oil, and the lubrication is called boundary.

Hardy obtained reproducible results showing a striking and simple relationship between the reduction of by a given member of a homologous series of normal paraffins, alcohols, etc. and the molecular weight of the lubricant. He suggested that the friction between two surfaces was due to the molecular forces acting across the interface of the metals and that the boundary lubricant molecules formed an orientated monolayer on the surfaces. The higher the molecular weight of the lubricant the

longer its molecules and so the further would the surfaces be forced apart with a consequent lowering of the friction.

Subsequent work has shown that the boundary lubricant does become adsorbed at the interface and is orientated and that the film is of a molecular order of thickness. The orientation of the molecules can be observed directly by electron diffraction, or inferred from trough measurements. Thin films of e.g. paraffins are crystalline with the basal plane of the long unit cell parallel to the surface and the molecules normal or steeply inclined to the surface. If these films are rubbed or heated as they must be during sliding the crystalline structure is broken down leaving a true monolayer of molecules perpendicular or nearly so to the surface (see Finch, 1950). There is some doubt as to the thickness of the film required. Langmuir found a monolayer of fatty acid reduced the friction of glass tenfold, but for the effective lubrication of metals more than one monolayer of lubricant is required, the number depending upon the metal and the lubricant. Lubricants that are needed in thicker films wear badly so, for example, the second and third monolayers of stearic acid required on copper are probably needed to maintain the first layer because the film is disturbed even before the slider reaches it.

The more strongly the molecules are adsorbed to the surface the more effective the lubricant, thus polar molecules are better than a straight chain paraffin and chemically adsorbed molecules more effective still. Fatty acids are particularly good lubricants with reactive metals, and Brummage (1947) has shown that the acid reacts with the oxide of the substrate to form a metallic soap. The molecules of the soap are firmly anchored and have good orientation and are thus difficult to displace and so reduce metal to metal contact.

Thus the boundary lubricant film is a solid film which is difficult to displace mechanically from the surfaces not only because of the cohesion across the interface, but also because of the attractive forces between the long parallel molecules, and as they depend upon the length of the molecules the coefficient of friction should decrease as the molecular weight of the lubricant for a given homologous series increases, which agrees with Hardy's early work.

Microscopic examination of the track left after sliding shows that the surface damage is much reduced, the surface being grooved rather than scratched with the film deforming with the metal and remaining practically intact. The boundary film, however, does not altogether prevent

intersurface contact, for sensitive radioactive methods show that though it is very much reduced some intersurface pick-up occurs. Interaction of the boundary films themselves contribute very little to the friction and can only be detected under very light loads (Whitehead, 1950).

Extreme Pressure Lubrication.

Under progressively increasing load the oil film between sliding metals eventually becomes discontinuous and oxide film contact begins to occur. The loading practicable without serious surface damage can be increased many fold by using a lubricant containing an additive capable of reacting chemically with the sliding surface to provide emergency protection. The reaction is accelerated by the sharply rising temperature associated with incipient seizure and the protective product is formed in just those places where temperature and pressures rise to values which are extreme relative to those typical of hydrodynamic or boundary lubrication.

Several theories have been advanced to explain how the chemical film prevents seizure. It has been suggested that the film simply has a lower shear strength than the substrate metal and so shearing occurs within its thin film minimizing damage. Beek, Givens and ~~Williams~~ (1940) have

shown that some of the extreme pressure lubricants can form eutectic films which are more fusible than the underlying metal and they suggest that the film is smeared out and the surface consequently smoothed and so restores hydrodynamical lubrication.

Finch (1950) has pointed out that the extreme-pressure film (unlike the oxide) is more fusible than the substrate metal. If the local temperature should rise sufficiently some of the film may smear and act as a temporary lubricant, but the primary oxide film will remain intact because the melting point of the compound is too low to impair the rigidity of the metal upon which the intactness of the oxide film depends.

PART 2.

ADHESION BETWEEN METAL SURFACES.1. Introduction.

The field of force of the atoms in the surface of a body is more or less satisfied by the adsorbed film of foreign matter (oxidation products, adsorbed water vapour and adsorbed gases generally). Therefore when two surfaces are brought together there is in general no adhesion across the interface (Landsberg, 1864). Some surfaces, however, can be sufficiently cleaned to demonstrate adhesion, e.g. freshly cleaved mica (Finch, 1950) or newly drawn glass fibres (Tomlinson, 1927).

Metal surfaces can be cleaned sufficiently by heating in a vacuum or a hydrogen atmosphere. Bowden and Hughes (1939) found that metal surfaces after being heated in vacuum exhibited an abnormally high μ (which was largely determined by adhesion between the surfaces) and they showed that this was due to the removal of the surface films, for on admitting a trace of oxygen into the apparatus the μ fell immediately to a much lower value. With improved technique Bowden and Young (1949) found that surfaces of e.g. nickel, iron and platinum, seized

TH-287

completely when brought together, the surfaces being first heated by an induction furnace in a vacuum of the order of 10^{-7} mm. of mercury.

Parallel frictional results have been obtained by Jacobs (1912), Shaw and Leavey (1930) and seizure observed by Gwathmey ~~et al~~ Denton (1948) and ~~Knudsen and~~ Holme (1935).

2. Surfaces in Air.

When two surfaces meet asperities of small radii will in general lodge against much flatter surfaces. Under pressure an asperity might flow and spread and so disrupt its surface film but the pressure on the opposing surface will be much more widely distributed and its film remain more or less intact and prevent intermetallic contact. The surface film will be even more effective with flatter surfaces.

Even a very thin surface film will prevent adhesion. Carefully electropolished copper specimens will not adhere when pressed together under moderate loads in vacuo, although the electron diffraction patterns of the surfaces show that any surface film present must be limited to a few atom layers in thickness. In vacuo any water vapour present must be limited to a monolayer.

539.23:539.62(043)
SPL

But according to Bowden (1950) when two surfaces are brought together welds are formed between the surfaces at the isolated areas of contact, though with elastic surfaces, the adhesion cannot be detected for the minute welds break one by one on releasing the load because of the recovery of the elastically deformed asperities. With soft surfaces having little elastic recovery the adhesion should be detectable, and Dr. Bowden's laboratory have shown that when a copper ball is pressed into an indium block the two surfaces do, in fact, adhere.

However, there appears to be no conclusive evidence of the existence of appreciable welds or adhesion between stationary surfaces. For the elastic surfaces the metal in the hypothetical welds, being itself stressed to the elastic limit, would have the greatest range of recovery on release of the pressure, and so there would be little tendency for the welds to be pulled apart. In the copper-indium experiment relative motion must occur between the surfaces thus rupturing the surface films and permitting intermetallic contact, and so the surfaces weld strongly. Again, although there is no measurable adhesion between two metal surfaces in air, Bowden and Young have shown that if the surfaces are made sufficiently clean by heating in high vacuum and allowing to cool, they exhibit relatively

large adhesion although the area of contact and the elastic recovery of the surfaces is practically the same as in air.

Thus it appears that the adhesion between surfaces in air is not detectable not because of the bulk properties of the metal, but simply because the surface films reduce the adhesion to a very low value.

3. Pressure Welding.

Surfaces may be made to adhere if subjected to such pressure that general plastic flow occurs and film free surface is exposed at the interface. Such "pressure welding" of silver (Van Duzee and Thomas, 1940), aluminium (Tylecote, 1945) and copper base alloys (Davis and Holmes, 1950) has been described. Van Duzee and Thomas cleaned the silver of its oxide by heating to about 200°C. and found that two sheets could be cold welded by applying a load of 5000 Kg./sq.cm.

Davis and Holmes found that the amount of deformation at the interface of their copper specimens was the main determining factor of the strength of the weld. Their surfaces, however, were heated while under pressure, increasing the amount of flow, assisting the diffusion of the oxide away from the interface and the recrystallisation

of the metal across the interface.

During pressure welding relative motion occurs to a greater or lesser extent between the opposing surfaces and this helps to rupture the surface oxide.

4. Welding by Sliding.

So far the only definite examples of metallic adhesion have resulted from the absence of the surface film. But surfaces can also be made to adhere in another manner which is of interest because of the information it gives on friction and on sliding generally. Metals can also be made to adhere together by sliding them over one another, provided the surfaces are sufficiently free from films. Most metals can be brought to the required state of cleanliness by electrolytic polishing. The high degree of freedom from surface films of surfaces so treated can be inferred from their electron diffraction patterns. Figures 1 and 2 are patterns obtained from single crystals of copper and iron respectively. The absence of oxide rings and the sharpness of the Kikuchi lines show that any oxide film present must be only a few angstroms in thickness. The patterns also show that electropolishing gives an atomically smooth surface which has, however, a large scale waviness, and that the crystal structure continues

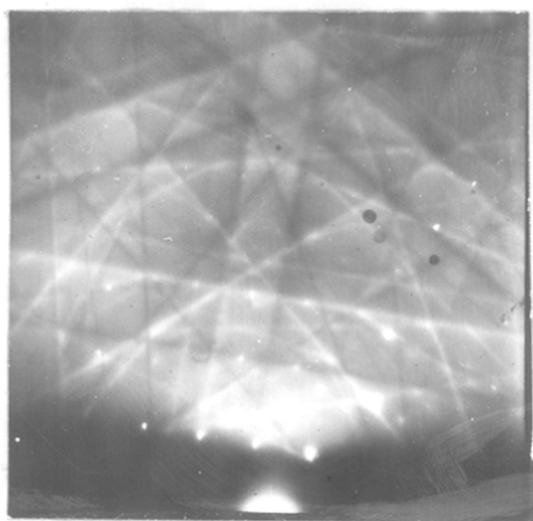


Fig. 1.

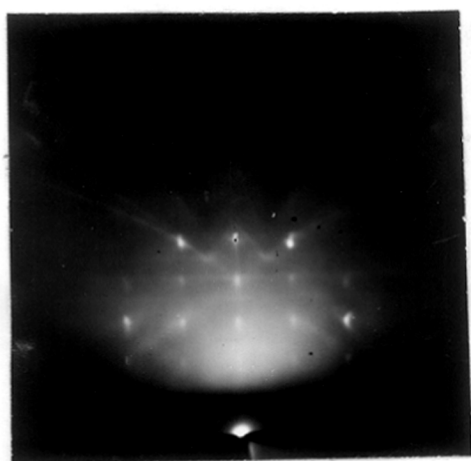


Fig. 2.

undisturbed to the surface.

The specimens after preparation are invariably covered with a thin layer of water molecules. In the diffraction camera this is largely removed because of the vacuum, and the electron beam itself scavenges the last tenaciously held monolayer. This film, however, does not give much protection during sliding, only a monolayer is strongly adsorbed and that to a lesser extent than the oxide. The specimens must be used immediately after polishing for usually they oxidise rapidly.

In some cases the metal may be sufficiently cleaned by suitable etchants e.g. dilute potassium cyanide or dilute nitric acid are suitable for copper. Some very soft metals, e.g. indium, can be scraped "clean". At about 180°C. the decomposition pressure of the oxide on silver is equal to the atmospheric pressure and so silver heated to this temperature is cleaned to a great extent of its oxide.

But despite such surface preparations a very thin film must still be present for, as stated earlier, when electropolished crystals are pressed together there is no intermetallic contact and consequent welding together of the surfaces provided the pressure is not sufficient to

produce extensive plastic flow. Similarly no adhesion has been detected between any other pairs of surfaces. The presence of thin films on electropolished surfaces other than water vapour has been shown in other ways, e.g. by the measurement of solution potential.

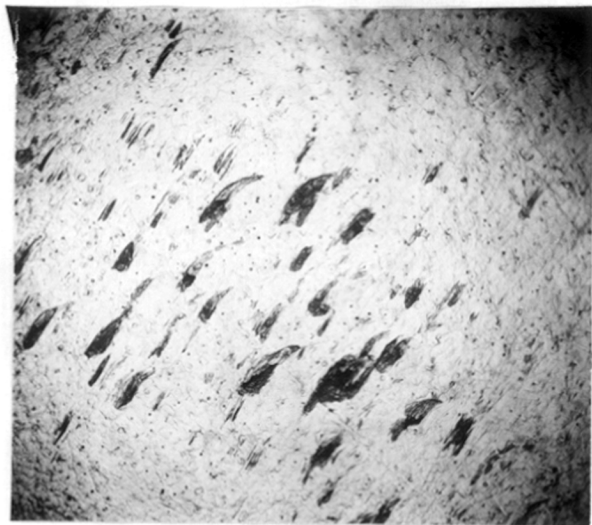
If, however, the copper crystals are slid over one another, ^{the} surface films are disrupted and cold welds are formed. Each weld grows rapidly. The first small welds are broken by the tangential force and they in turn disturb a larger amount of surface and so form larger welds and meanwhile fresh welds are formed until the applied force may no longer be able to shear the welds and total seizure occurs with a catastrophic increase in the coefficient of friction. Copper single crystals pressed together lightly, weld so strongly after sliding only a fraction of a millimetre that they are difficult to pull apart with the fingers. Adhesion to a greater or lesser degree has been observed for copper, gold, silver, aluminium, tin, lead, zinc and iron pairs and for various combinations of these metals.

The ease with which the surfaces weld on sliding depends mainly upon their plasticity. With a soft metal there is a greater area of contact under load, the metal

will deform more easily and so rob the surface film of its support and the area of intermetallic contact can grow more rapidly than for a harder and more elastic material. Thus under conditions of sliding which would cause copper surfaces to seize together strongly, iron pairs will adhere only moderately. Very soft metals like lead weld extensively, but the welds are weak and the force of friction does not increase with sliding to the same extent as with stronger harder materials. The damage due to welding is quite distinctive on parting the surfaces so the extent of welding can be determined from the damage (Figure 3) rather than from the friction or the load required to cause seizure.

The surface films on all these metals were very thin, and the properties of the films themselves were of little importance for the relatively heavy loads used (of the order of Kilograms/sq.cm.).

Sometimes during the electropolishing operation, particularly when washing and etching the specimens, the surfaces became covered with a relatively thick oxide film, usually amorphous and some hundreds of angstroms thick. Such thick films give very great protection to the harder metals, some of which for example, iron, could not be made to weld at all under the experimental conditions.



x 70

Fig. 3.

Heavily oxidised aluminium was difficult to weld. However, because the metal is so much softer than the oxide the latter can be easily broken up by vigorously rubbing the surfaces together, and welding then occurs easily. Even with a thick film the sliding process assists welding if once it begins on a fairly large scale, the seized metal ploughing under rather than scraping away or rupturing the surface film.

PART 3.

SLIDING OF METAL SURFACES.1. Introduction.

The first stages of sliding have recently been examined by Parker and Hatch (1950). They slid cast hemispheres of lead and indium over glass and examined the surface of the metals with the electron microscope. With no tangential force the surface features persisted under load, showing that the deformation was elastic, but on applying a small tangential force the asperities deformed plastically and were scratched, indicating that some relative motion had occurred. With increasing tangential load there was a proportional increase in this slip and in the real area of contact until the cohesive force was in equilibrium with the tangential force and motion ceased. Still increasing the ^{Tangential} load increased the real area of contact until it equalled the apparent area of contact and then large scale sliding occurred. These results agree with those of Claypoole (1943) and Campbell (1939).

According to Bowden, under normal conditions of steady sliding, small welds are formed between the surfaces.

To maintain sliding part of the applied tangential force has to shear these welds. The existence of these welds can be demonstrated in a number of ways (Bowden and Tabor, 1943, Sackmann et al., 1944, Bowden and Moore, 1945, Gregory, 1946) because they do not in general shear in the plane of sliding but within the weaker surface and so leave fragments of metal adhering to the other surface. The applied force must also plough irregularities of the harder surface through the softer, and possibly overcome other forms of frictional resistance.

2. Experimental Details.

Surfaces are usually prepared for the investigation of frictional effects by abrading with successively finer abrasives and often finally giving a metallographic polish. This treatment breaks up the crystal structure near the surface and in the case of polishing gives a Beilby layer and promotes oxidation. As mentioned previously, electropolishing gives an undisturbed surface with only a very thin surface_x film so that the various phenomena associated with sliding occur on a larger scale and can be more easily examined. If single crystal instead of polycrystalline specimens are used the surface damage is even more marked because of the very great work hardening

which accompanies the deformation of a single crystal.

Accordingly the experiments with electropolished specimens described earlier were continued, but the sliding conditions were varied, in some cases the static coefficient of friction measured, and the surfaces were examined microscopically and foreign films sometimes deliberately formed on the surfaces. The static coefficient of friction was measured on an inclined plane for loads of less than 50 grams and by direct measurement of the tangential force required to cause sliding for heavier loads. There was some spread in the results due possibly to slight movements occurring when putting the surfaces together and to the difficulty of determining when motion began. Also the specimens were either flat discs or plates and so contact occurred at three or more points and therefore the absolute load carried by any area of contact was considerably less than the overall load which alone could be measured.

3. Results.

Effect of Substrate.

As one would expect from the cold welding experiments the hardness of the surfaces largely determined the damage done during the sliding of electropolished specimens and

so to a certain extent the friction. Thus under moderate loads (order of 500 grams) single crystals of copper seized together on sliding. "Seizure" here and in future means that the μ increases very rapidly with further sliding through welding occurring on a large scale. When parted the surfaces showed a few large broken welds and the scratching was negligible. Electropolished polycrystalline specimens however did not seize quite as readily, for the polycrystalline surface is harder because the deformation of each crystal grain is resisted at its boundary by the neighbouring grains. The welds were smaller and more numerous and there was some scratching. Similarly mechanically polished polycrystalline specimens were more difficult again to seize, the welds smaller still and again there was more scratching. With loads short of that required for seizure, mechanically polished specimens had a slightly lower μ than the electropolished specimens. With hard iron surfaces under moderate conditions of loading a little scratching occurred and only occasionally welds, the coefficient of friction was again very low at about 0.2.

Effect of Surface Films.

After electropolished surfaces had been exposed to air heavier loads were necessary for seizure to occur on

sliding, and the effect of hardness was even more marked. After a period of time, depending upon the metal concerned the surfaces could not be made to seize at all under the experimental conditions. Microscopic examination showed that the nature of the surface damage had also changed. The surfaces were now much scratched, and any intermetallic welds were very small and occurred in the tracks of the scratches where the deformation had been greatest and so the surfaces occasionally scraped clean simultaneously. During sliding the surfaces must have been in intimate contact and so oxide-oxide or oxide-metal adhesion may have occurred and contributed to the frictional resistance, but such junctions would shear at the interface and so not be detected. The calculated work done in breaking welds and in causing plastic deformation is found to be considerably less than that measured during sliding, and such adhesion might account for some of the difference.

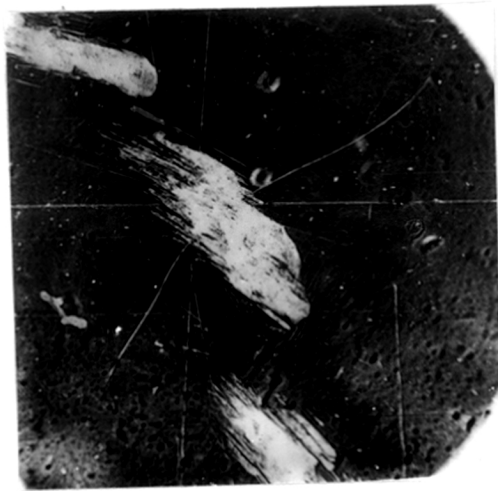
If the oxide has about the same hardness as the metal, metal and oxide deform more or less as one making penetration or removal of the oxide difficult; thus intermetallic welding is reduced and much scratching occurs. Indeed, for light loads no intermetallic welding occurs at all in many cases, e.g. Fe, Cu. But if the oxide is much harder than the metal the metal may deform under the

oxide, robbing it of its support and making intermetallic contact possible, e.g. aluminium, tin. This effect is shown in an exaggerated manner in Fig.4 where the obviously brittle oxide film on anodically oxidised Al has cracked about the weld.

When metals of differing hardness are slid over one another it appears that if the softer metal has the harder oxide its oxide fragments may help to penetrate the opposing surface and bring about welding, for example, Al welds more easily than Cu to Fe.

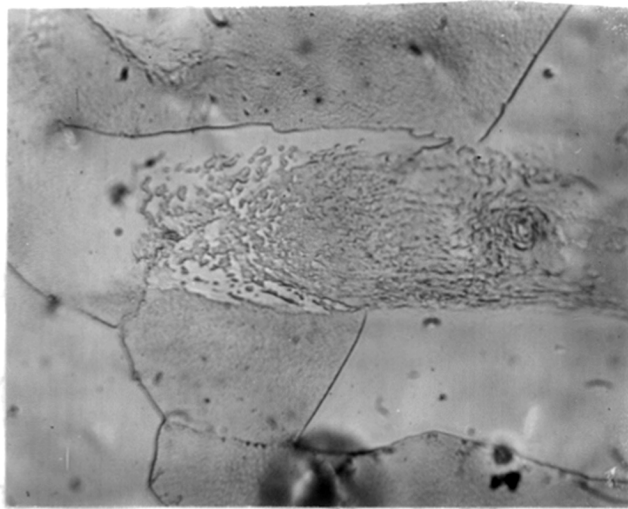
Surface Damage of Very Clean Surfaces.

The crystal structure of the rubbing high spots is broken down during sliding and so the weld junctions are hardened. This can be shown by abrading the top of a ^{weld} fragment flat, electropolishing to remove the metal disturbed during abrading and then etching the surface (Fig.5). Consequently the weld shears not at the interface but within the softer of the two metals. The distribution of stress about the weld during shearing also tends to cause fracture within the metal rather than at the surface. If both surfaces are of the one metal the scratching protuberance on the one will be hardened and pluck metal out of the other. (Thus fragments of Al will



x 100

Fig. 4.



x 250

Fig. 5.

be left adhering to copper, silver to iron, etc.) In the case of mixed metal pairs, fragments of the harder surface have never been observed on the softer. The difference in colour between e.g. copper and aluminium enable fragments ~~hardly~~^{scarcely} resolvable with oil immersion to be definitely distinguishable. Thus some pick-up of aluminium by copper has been observed even with loads of the order of a gram, and with lubricated surfaces (Fig.6).

Large welds once formed tend to part the surfaces and to localise the damage to the weld itself, therefore the weld grows in height rather than laterally, after reaching an optimum width. Often the growth in height is discontinuous giving the weld a stepped appearance.


In mutually soluble metal pairs it appears that the actual interface of the metals forming the weld has the composition of the eutectic. Blocks of tin and lead were welded together by sliding and then heated in vacuo in such a way that one block was supported entirely by the weld. The blocks were found to fall apart at the melting-point of the tin-lead eutectic and not at the melting point of the tin. The surfaces showed no sign of pick-up, a tiny patch of alloy indicating the actual area of contact. Similarly lead and bismuth parted near



x 3000

Fig.6.

the lead-bismuth eutectic melting point. But if the two blocks were heated when only resting on one another, nothing happened until the bismuth melted. Cold welding the surfaces together and heating them to a temperature just below the bismuth melting point formed a small molten pool of eutectic, the original tiny patch of eutectic having acted as a seed. Copper and aluminium were also observed to fall apart at temperatures below the melting point of the aluminium but some 20 or 30°C. above the eutectic melting point. In this case, however, results were complicated by the adhesion between the copper and aluminium oxides as these surfaces had to be heated in air because of the high temperatures required.

The actual weld interface can be examined when different metals are used by dissolving away the adherent fragment, using, for example, NaOH for aluminium on copper. The actual area of contact is smaller than the plan area of the fragment and the profile of the weld fragment appears to be 

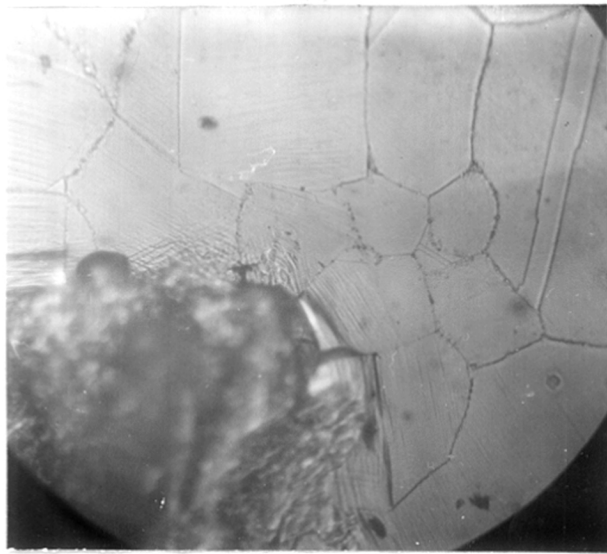
Damage to the surface is not confined to the weld junction itself. Slip lines surround the weld changing directions at the crystal boundaries to follow the appropriate glide planes in neighbouring crystals

(Fig.7), and particularly with single crystals (Fig.8) extend far across the surface and into the bulk of the metal. If welds are formed near the edge of a single crystal the slip lines cover relatively large areas. In some cases the metal immediately ahead of a weld is crumpled into folds (Fig.9).

Surface Damage to Exposed Surfaces.

As stated earlier, if the sliding surfaces are allowed to oxidise in air welding is much reduced and scratching occurs instead. Under normal loads the surface film is penetrated and metal exposed in the track of the scratch, but welding does not occur for the debris is caught up and embedded in the scratching protuberance which becomes progressively more contaminated and welds can only form when both rubbing spots are simultaneously clean of film. The exposed surfaces will however again weld easily if treated with potassium cyanide.

The metal at the surface of a scratch has a flowed and polished appearance. Underneath this flowed material the metal is polycrystalline, and between this region and the original crystalline structure there may be a zone in which rotational slip or other deformation has occurred. Recrystallisation is possible, particularly with very soft



x 450

Fig. 7



x 450

Fig. 8



x 450

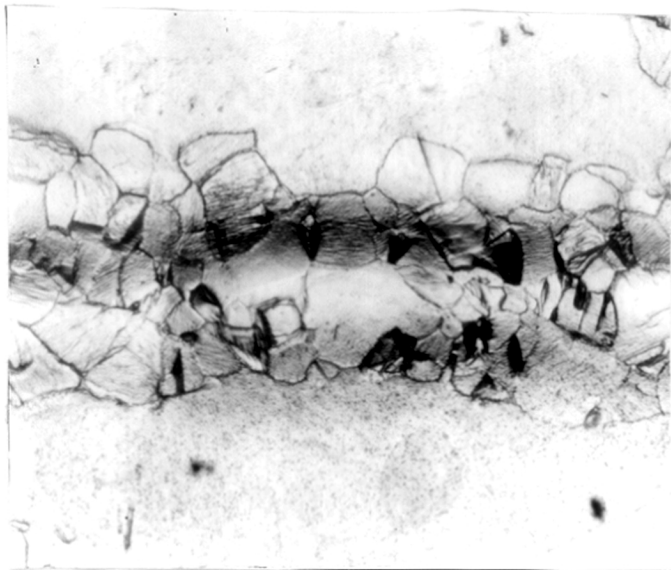
Fig. 9.

metals. This is shown in Fig.10, where the flowed material in the track of a scratch has been electropolished away. Characteristic markings are often observed in the beds of scratches after light etching, because of the way in which the metal has deformed. To scratch a crystal surface in different directions, varying amounts of work are required, depending upon the orientation of the scratch with respect to the translational and other, e.g. rotational, slip systems, but these average out in polycrystalline surfaces.

Oxide fragments themselves cause scratching. When lead is compressed and caused to flow between electropolished slightly etched copper discs, debris begins to scratch the lead and gets caught up in the copper grain boundaries so that when motion stops and the surfaces are parted a pattern of the copper grain boundaries appears on the lead.

4. Temperatures reached during Sliding.

Bowden (1950) ran small cylinders of e.g. Woods alloy gallium and tin against a steel disc revolving at high speeds, and measured the temperatures reached at the interface by using the sliding surfaces as thermocouple elements. He found that the temperatures obtained were never greater than the melting point of the more fusible metal of the pair,



x 250

Fig. 10

and that this metal became polished.

But when a nitrided steel shaft, for example, is run against a soft low melting point bearing both surfaces eventually become polished. A possible explanation is this - the more fusible metal is first polished and smoothed, the asperities on the other surface then form small areas of contact which continue to rub in relatively long tracks on the other smooth surface and so reach temperatures which are ^{high} enough to cause them to soften; that is, ^{reach} temperatures above the melting point of the lower melting metal, and are thus in their turn smoothed and polished (Finch, 1950).

To check whether higher temperatures would be reached small specimens of the higher melting material were run against discs of the other metal - that is Bowden's experimental conditions were in effect reversed. The specimens were very small, about 1/8" cubes, and the thermocouple embedded in them. They were mounted in plastic holders and carried a load of some pounds weight, and were moved radially across a Woods metal disc (8" diameter) rotating at about 1,000 r.p.m.

It was found that metals which had a higher melting point and were harder than the Woods metal actually reached a temperature above the melting point

of the disc ⁽⁶⁶⁾ for example copper reached up to 120°C. In a few seconds, however, the specimens became smeared with Woods metal and the temperature fell back to that of the melting point of the Woods metal. The thermocouple indicated the temperature of the specimen about 1/16" away from the rubbing faces, the surface temperatures must have been much higher still.

If the specimen had a higher melting point than the disc, but was softer, higher temperatures were again reached but results were rather inconclusive, for the specimen smeared the track rapidly, and even with a spiral track one could not be sure whether the disc was clean or not.

PART 4.FILMS ON METAL SURFACES.1. Formation and Nature of Oxide Films.

When an oxygen-free metal surface is exposed to dry air a monolayer of oxygen molecules is very rapidly bonded to the surface by Van der Waals forces. Above this monolayer there is a thin film of less strongly adsorbed molecules which can be removed by evacuation. The oxygen molecules dissociate into atoms, the reaction being strongly exothermic so that once begun by e.g. photons, catalytic reactions, etc. it will continue. If sufficient energy is available the atoms ionise and the ions take up mutual positions appropriate to the oxide.

The oxidation begins at favoured sites and the oxide grows laterally over the surface. When a coherent layer of oxide has formed, the metal and the oxygen become separated, and the reaction can only continue in so far as the reactants can diffuse through discontinuities in the film, or across the film itself. Wagner (1938) has suggested that the latter is possible because the film is not of stoichiometric composition and so permits the diffusion of cations outwards (or anions inwards)

with the electrical balance being preserved by the conduction of electrons outwards. But there is considerable evidence that oxidation proceeds mainly through discontinuities in the film.

At room temperature most oxides formed in dry air are amorphous. On heating the behaviour of oxide films varies widely. Those on aluminium and chromium remain amorphous up to about 600°C. and grow very slowly, but on copper the film becomes crystalline at about 150°C. and grows rapidly. Depending upon the conditions of oxidation, the oxide may be epitaxial with its substrate, show no preferred orientation or take up an orientation determined by the oxide and not by the metal. With increasing temperature higher oxides may be formed.

The oxidation of iron was studied briefly to determine whether the condition of oxidations would affect the frictional behaviour of the oxide film. Single crystals of iron were heated under varying conditions of temperature and pressure and the resulting oxide film examined in an electron diffraction camera. At temperatures of about 100°C. the oxide film was too thin to identify with certainty and was epitaxial, probably Fe_2O_3 . At higher temperatures very small random crystals of Fe_2O_3 were formed, these crystals becoming much larger

at about 300°C. At about 350°C., α -Fe₂O₃ was formed, this oxide had one degree of orientation due to preferred lattice rows growing out from the surface. Films formed above 500° were not examined. The pressure (varying from 10⁻¹ mm. to atmospheric pressure) had no noticeable effect on the rate of oxidation. However, the particular crystal face in the surface of the specimen and the nature of the surface finish had considerable effect on the rate of oxidation and probably also on the transition temperatures, thus abraded specimens oxidised more rapidly than electropolished specimens.

2. Films on Copper.

Various films were formed on electropolished copper surfaces and their effect on the static coefficient of friction and the proneness to welding of the surfaces examined. The friction was measured on an inclined plane with loads of about 20 grams. Some of the results are given below:-

Treatment	Welding	μ_s
Exposure to H ₂ S fumes	None	.29
Exposure to HCl fumes	"	.33
Exposure to H ₂ SO ₄ fumes	"	.38
Exposure to air for 36 hours	"	.36

Treatment	Welding	
Exposure to dry air for 36 hours	None	.53
Oxidised at 150°C. and exposed to air for 36 hours	"	.42
Oxidised at 150°C. and exposed to dry air for 36 hours	"	.48
Oxidised at 500°C. and scales removed	"	.29
Immersed in water for 36 hours	"	.42
Exposure to fuming HNO ₃	Slight	.38
Etched in H ₂ SO ₄	"	.36
Etched in HCl	Welding	.46
Oxidised in air at 150°C.	"	.53
Anodically oxidised	"	.70
Etched in HNO ₃	Very easy	
Plated with Cu	"	
Noble metal film evaporated on	"	

The greater the welding ability the higher the friction, but under the experimental conditions the converse was not necessarily true, for surfaces which show little tendency to form cold welds might give a high friction due to scratching, or to Coulomb friction. In particular it was observed that cuprous oxide surfaces gave easy welding and a high coefficient of friction, whereas

sulphided surfaces showed no sign of intermetallic welding and exhibited a low friction. Consequently the sliding of these films was investigated and compared.

Oxide Films on Copper.

The frictional behaviour of oxide films on copper has been examined by Campbell (1943), Tingle (1950) and Whitehead (1950), and Hughes and Whittingham (1942). With ordinary loads the oxide film reduced the friction but Whitehead found that for light loads (< 1 gm.) even the very thin oxide film after electropolishing was not penetrated and that this film had the same coefficient of friction as an oxide film hundreds of angstroms thick.

In the present work electropolished copper discs were oxidised in air at about 180°C . and the static coefficients of friction of the resulting cuprous oxide films measured with an inclined plane. The μ_s was found to be independent of the load and approximating .8 for loads of less than about 15 grams, and to increase with the thickness of the film, the main increase occurring before the film was thick enough to give interference colours. The surfaces always welded together very easily on sliding, the oxide in fact seemed to assist welding.

The surfaces were examined with the microscope after sliding and several kinds of damage observed, viz.

broken metallic welds with the oxide film extending right up to the weld; scratches penetrating the film, the oxide being displaced to the edges of the scratch; occasionally the film peeled away from the metal, sometimes rolling up in a spiral ahead of a scratching protuberance; particles of oxide etc. were often caught up between the surfaces and formed "gear wheel" tracks (Fig.11).

The above oxide films were crystalline. The film formed on exposure to air at room temperature was amorphous and inhibited seizure, but if this film was heated and so caused to crystallise the surfaces again welded easily. If the crystalline oxide was exposed to air for some time corrosion occurred within the film and welding again was prevented.

Thus it appears that the crystalline oxide film is weak and easily removed during sliding. At light loads the film gives less protection than the amorphous oxide and so its coefficient of friction is considerably greater. Provided the film is crystalline, the thickness of the oxide has little effect, indeed there is considerable evidence that the oxide fails at the metal-oxide interface. The amorphous oxide film, however, is isotropic and tough, and deforms with the substrate metal and so is difficult to penetrate or rupture.



x 250

Fig. 11.

Sulphide Films on Copper.

Electropolished copper surfaces were exposed to ammonium polysulphide vapour and the frictional properties of the films formed examined. For light loads the coefficient of friction was very low (about 0.30). Provided the film was sufficiently thick the damage done during sliding under all experimental loads (10 grams to 1000 grams) was largely confined to the film itself. There is considerable evidence that the film formed consisted mainly of cupric sulphide, and this compound has a layer lattice permitting relatively easy slip.

Adhesion between Films.

If clean copper specimens are clamped together and heated in air at temperatures above a definite minimum, the oxide films grow together and the specimens adhere together strongly. The surfaces must be initially clean and free from oxide and be heated to above about 180°C., heating for hours at a lower temperature being ineffective, and must be clamped together, otherwise the growing oxide merely forces the surfaces apart. Microscopic examination shows that no intermetallic contact occurs. Heating oxidised specimens clamped together in vacuo to bring about recrystallisation does not cause adhesion. The oxide

formed on single crystals of copper at about 180°C is well orientated cuprous oxide. Adhesion also occurs between copper and aluminium blocks in which case fragments of metal were torn out of the aluminium block and left adhering to the oxide, but not between aluminium pairs, or iron pairs. Similar adhesion was observed when bolted together copper specimens were exposed to ammonium polysulphide fumes.

3. Films on Iron.

The frictional properties of oxide and sulphide films on iron were also examined. To measure the friction a new type of instrument was built in which an annulus sliding against a coaxial rubbing disc was restrained from moving with the disc by a thread running over a pulley to a scale pan and weights. The load was variable from 100 to 2,000 grams, and the speed from 0 to 180 r.p.m.

Frictional Oxidation.

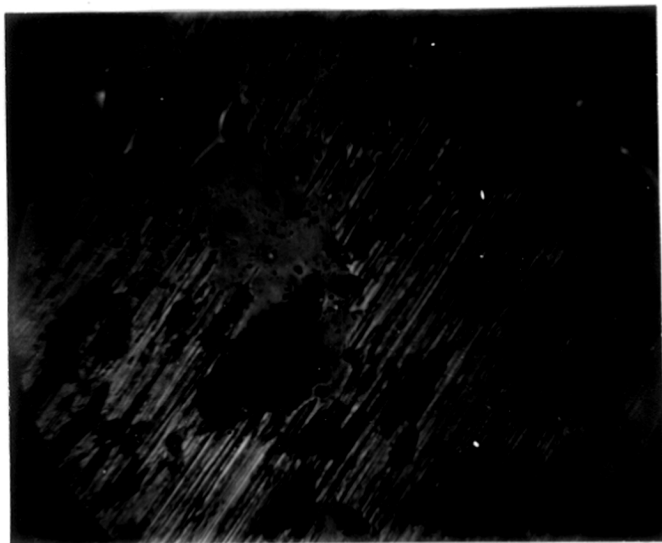
The instrument was first used to measure the friction of freshly electropolished iron surfaces. The friction was found to be independent of the velocity, to increase slightly with increasing surface roughness and to vary with load at low loads.

Although the surfaces were very carefully prepared

they became microscopically dirty after a few minutes sliding and a grey film eventually formed in the track of the scratches. After half an hour the film was very thick and composed of grey matter which compacted and piled up to form plateaux at surface irregularities (Fig.12), the plateaux finally carrying most of the load. The plateaux were often divided by a network of cracks, small plates flaking off at the cracks. Occasionally fragments of metallic iron were embedded in the compacted grey matter. The initial film speckled the surfaces black or brown, then sometimes becoming reddish, and finally grey. The electron diffraction camera showed that the film was crystalline Fe_2O_3 .

This "frictional oxidation" has been observed by Fink (1934), and Rosenberg and Jordan (1935), and occurs in some bearings (Ackermann, 1937). It has not yet been satisfactorily explained.

Attempts were made to relate the oxide formation with the rubbing conditions. The friction of the surfaces appeared to depend upon the amount of oxide present so as to determine the effect of load the variation of μ with time for various loads was measured. The μ fell fairly regularly with increasing load. The effect of velocity (to which the frictional heating is related) was next



x 100

Fig. 12.

examined. The amount of oxide formed seemed to be the same whether the instrument was run at top speed or at very low speeds. The top annulus was therefore replaced by a disc in which were embedded three equally spaced ball bearings and a small step was fixed to the lower surface in such a way that the bearings could not slide over the lower disc, but small movements due to vibration from the electric motor were possible. Again frictional oxidation occurred, and on much the same scale as in the other experiments. The optical microscope showed that very small scratches had been made by the ball bearings, but occasionally small patches of oxide were observed remote from scratches, but these may have been displaced from where they were formed or be themselves covering tiny scratches. The surfaces were next prepared in the usual way and left in contact in a vibration free place for a week. No visible oxidation occurred in this period. Thus the oxidation is caused, not by the large scale sliding, but by the very small movements due to vibration: that is, it is a form of the "fretting corrosion" described by Tomlinson (1927).

The mild steel annulus was run against a number of metals: frictional oxidation occurred for iron, mild steel, copper, aluminium, Woods alloy and lead. Microscopic pick-up occurred of the Woods alloy and to a lesser extent of the lead, and in the former case reduced the amount of frictional

oxidation.

Oxide Films on Iron.

The variation of friction with load of iron surfaces oxidised in dry air under varying conditions of pressure and temperature was measured with the annulus machine. An attempt was made to relate the friction of the oxide film with its structure, which was determined in each case with an electron diffraction camera.

The majority of the μ/L curves fell within three families. In the first type the μ remained constant up to about 200 grams, then increased suddenly to a higher value and then increased slightly with increasing load, the sudden jump being caused by the oxide beginning to fragment and clog the surfaces. Reducing the load did not reduce μ . The curves were roughly parallel with the thicker film giving higher coefficients of friction.

The second type of μ/L curve was similar in shape to that of clean electropolished surfaces, with the curves again more or less parallel and the thicker films giving the higher μ .

In the third type of curve, the friction appeared to increase linearly with time and to be independent of the load. Thus these films began to break up almost

immediately sliding began. All the curves were clustered together.

The results were irreproducible; it could not be predicted what particular type of curve would result from a given specimen from a knowledge of its chemical composition (Fe_2O_3 , Fe_3O_4 , FeO , etc.) structure, or thickness. Thus there must be some other significant variable or variables. The results were also further complicated by the occurrence of frictional oxidation once the metal was cleaned of its oxide at rubbing areas; both the frictional oxide and the prepared oxide compacted in the same way and could not be distinguished from each other. The oxide film on copper also piled up in the same manner.

The surfaces were examined microscopically after each run and some idea how the oxide film broke up obtained. In Fig.13 the scratching protuberance in the opposing surface has not penetrated the oxide film but peeled it away at the side of the scratch and formed fissures in the bed of the scratch. Fissures may also form in the neighbourhood of the scratch. With further rubbing the oxide flakes outlined by the cracks become detached from the surface, probably parting at the iron-iron oxide interface because of the epitaxial strain in this region (the diffraction camera shows that the oxide formed on single crystals of



x 450

Fig. 13.

iron heated to 450°C. scales off at the interface.) The oxide fragments then get further broken up and tend to get caught up in irregularities in the surface and pile up into grey plateaux, which may eventually carry the entire load. These plateaux sometimes break up themselves. Consequently the area of contact increases and therefore the friction.

There is some correlation between the friction and the thickness of the oxide film. It appears that the film is divided into a network of fine sub-microscopical latent discontinuities and that these are more frequent the thicker the film; their number also depends upon the way and rate the oxidation is carried out and so is very variable. During sliding cracks form at these discontinuities and they therefore determine the mechanical strength and so therefore the frictional properties of the film.

Oxide films lubricated with paraffin gave a very low and constant μ of about 0.1 which is the same as that of lubricated unoxidised surfaces. Although the oxide was removed quite rapidly, the substrate metal suffered very slight damage.

When iron surfaces are passivated in nitric acid, for example, the oxide film is compact and free from flaws. The frictional properties of such films appear similar to surfaces oxidised by exposure to air.

Iron surfaces were also run together in a pool of concentrated acid in the annulus machine so that the protective oxide film could be reformed almost immediately whenever penetrated. Heavy loads of one or two kilogram and low sliding speeds were used to minimise viscosity effects. A number of different acids were tried. Phosphoric and sulphuric acids both gave very low coefficients of friction of about 0.02 after a few minutes running and the surface damage was extremely slight. Both these acids are viscous, but viscous lubricants such as glycerol and paraffin gave much higher coefficients (0.10) under the same sliding conditions. There appeared to be little obvious reaction between the iron and the acids. Hydrochloric acid, however, attacked the surface vigorously and gave a coefficient of about 0.1 Nitric acid reduced the coefficient of friction to a steady value of about 0.25 after a few minutes, the track was little damaged except for a few large etch cavities.

Sulphide films on iron gave a higher initial friction than oxide films and the friction increased more rapidly, indeed, on a number of occasions thick sulphide films adhered together when sliding ceased. Sulphide films lubricated with benzene gave about the same coefficient of friction as lubricated oxide films.

Summary.

When two surfaces are brought together intermetallic contact is in general prevented by their surface films. With sufficiently clean surfaces, however, even a slight sliding motion will rupture the surface film and bring about large scale welding, the extent of which depends primarily upon the plasticity of the metal. But after the surfaces have been oxidised, the properties of the film themselves become important. If the oxide is much harder than the metal the latter may deform under the oxide, robbing it of its support and making intermetallic contact possible. But if the oxide has about the same hardness as the metal, metal and oxide deform more or less as one making rupture or penetration of the oxide film difficult, and so intermetallic welding is reduced or even inhibited.

Thus the amorphous oxide formed at room temperature on copper deforms with the metal and so for light loads the oxide films are not penetrated and the coefficient of friction is low. The crystalline oxide formed by heating in air, however, is easily removed from the metal permitting intermetallic contact and so gives a higher coefficient of friction. The sulphide film on copper is also crystalline

but because of its well-developed cleavage-plane and consequent low shear strength most of the damage due to sliding is confined to the film and the coefficient of friction is very low.

The damage done to very clean surfaces during sliding is quite distinctive. The intermetallic welds once formed do not in general shear in the plane of sliding, for the distribution of stress about the body of the weld is such that failure occurs within the bulk of the metal and so fragments of the one surface are left adhering to the other. Slip lines surround the broken welds extending across the surface and into the bulk of the metal. But if the surfaces have been allowed to oxidise there is a great increase in the amount of scratching and the number of broken welds are reduced and in some metals none can be observed.

The frictional behaviour of films on iron were examined by sliding flat discs against a loaded annulus, and measuring the force required to restrain the annulus from moving with the disc. The sliding action caused oxidation of the surfaces, and this "frictional oxidation" is a manifestation of "fretting corrosion". The crystalline oxide formed on iron by heating in air is weak and easily removed in the annulus machine, the strength of the film

being related to the way in which it is formed. A low coefficient of friction can be obtained by sliding the surfaces together under concentrated acids as in this way the tough amorphous oxide on iron is reformed whenever ruptured and so intermetallic contact reduced. Thick sulphide films on iron exhibit some mutual adhesion and give a high coefficient of friction.

Acknowledgements.

The author is deeply grateful to Professor G.I.Finch, M.B.E., D.Sc., F.R.S. for his constant interest and encouragement.

Thanks are also due to Messrs C.C.Wakefield and Co. for a maintenance grant for a part of the time during which this research was carried out.

References.

- Barwell and Milne, J.Inst.Petroleum, 1949, 35, 307.
- Beek, Givens and Smith, Proc.Roy.Soc., 1940, A.177, 90.
- Beek, Givens and Williams, Proc.Roy.Soc., 1940, A.177, 103.
- Bikerman, Rev.Mod.Phys., 1944, 16, 53.
- Bowden, "The Friction and Lubrication of Solids", Clarendon
1950. Press,
- Bowden and Hughes, Proc.Roy.Soc., 1939, A.172, 263.
- Bowden and Leben, Proc.Roy.Soc., 1939, A.169, 371.
- Bowden and Moore, Nature, 1945, 155, 451.
- Bowden and Tabor, J.Appl.Phys., 1942, 14, 80.
- Bowden and Young, Nature, 1949, 164, 1089.
- Bristowe, Proc.Roy.Soc., 1947, A.189, 88.
Proc.Inst.Mech.Eng., 1949, 160, 385.
- Brummage, Proc.Roy.Soc., 1947, A.181, 243.
- Burwell, Trans. S.A.E., 1942, 50, 450.
- Campbell, Trans. A.S.M.E., 1939, 61, 633.
- Chalmers et al., Proc.Roy.Soc., 1946, A.187, 430.
- Claypoole, Trans.A.S.M.E., 1939, 61, 323.
Trans.A.S.M.E., 1943, 65, 317.
- Clayton, Proc.Inst.Mech.Eng., 1945, 153, 332.
- Davis and Holmes, J.Inst.Metals, 1950, 77, 185.
- Dow, Phys.Rev., 1929, 33, 282.
- Dykes, J.Appl.Mech., 1946, 13, (2), A-148.
- Ernst and Merchant, Conf. Friction and Surface Finish,
M.I.T., 1940, 73.

- Ewing, *Not.Proc.Roy.Inst.*, 1892, 13, 387.
- Finch, *Proc.Phys.Soc.*, 1950, B,63, 465.
Nature, 1936, 137, 516.
- Fink, *Metallwirtschaft*, 1934, 13, 633.
- Forrester, *Proc.Roy.Soc.*, 1946, A,187, 430.
- Gregory, *Nature*, 1946, 157, 442.
- Gwathmey et al., *N.A.C.A. Tech.Note* 1461 (1948).
- Hardy, *Trans.Roy.Soc.*, 1932, A,230, 1.
- Heaton et al., *Nature*, 1942, 150, 520.
- Helm, *Wiss.Veroff.Siemens Werk.*, 1938, 17/4, 38.
1936, 15/1, 122.
- Hughes and Whittingham, *Trans.Farad.Soc.*, 1942, 38, 9.
- Jacobs, *Ann.der Phys.*, 1912, 38, 126.
- Landsberg, *Ann.der Phys.*, 1864, 121, 283.
- Palmer, *A.S.T.M. Symposium on Wear of Metals*, 1937.
- Parker and Hatch, *Proc.Phys.Soc.*, 1950, 63, 185.
- Rideal, *Trans.Faraday Soc.*, 1947, 63, 435.
- Rosenberg and Jordan, *Trans.A.S.M.E.*, 1935, 23, 577.
- Sackmann et al., *J.Appl.Phys.*, 1944, 15, 459.
- Schnurmann and Warlow-Davies, *Proc.Phys.Soc.*, 1942, 54, 14.
- Shaw and Leaver, *Phil.Mag.*, 1930, 10, 809.
- Strang and Lewis, *J.Appl.Phys.*, 1949, 20, 1164.
- Strough and Rapp, *Phys.Rev.*, 1941, 59, 65A.

- Tingle, Trans. Faraday Soc., 1950, 46, 92.
- Tomlinson, Phil.Mag., 1929, 7, 905.
Proc.Roy.Soc., 1927, A.115, 472.
- Tylecote, Trans.Inst.Welding, 1945, 8, 163.
- Van Duzee and Thomas, Trans.Electrochem.Soc., 1940, 87, 341
- Viewig, Pet., 1924, 20, 899.
- Wagner, Z.Phys.Chem., 1938, B.40, 455.
- Whitehead, Proc.Roy.Soc., 1950, A.201, 109.

References.

- Barwell and Milne, J.Inst.Petroleum, 1949, 35, 307.
- Beek, Givens and Smith, Proc.Roy.Soc., 1940, A.177, 90.
- Beek, Givens and Williams, Proc.Roy.Soc., 1940, A.177, 103.
- Bikerman, Rev.Mod.Phys., 1944, 16, 53.
- Bowden, "The Friction and Lubrication of Solids", Clarendon Press, 1950.
- Bowden and Hughes, Proc.Roy.Soc., 1939, A.172, 263.
- Bowden and Leben, Proc.Roy.Soc., 1939, A.169, 371.
- Bowden and Moore, Nature, 1945, 155, 451.
- Bowden and Tabor, J.Appl.Phys., 1942, 14, 80.
- Bowden and Young, Nature, 1949, 164, 1089.
- Bristowe, Proc.Roy.Soc., 1947, A.189, 88.
Proc.Inst.Mech.Eng., 1949, 160, 385.
- Brummage, Proc.Roy.Soc., 1947, A.181, 243.
- Burwell, Trans. S.A.E., 1942, 50, 450.
- Campbell, Trans. A.S.M.E., 1939, 61, 633.
- Chalmers et al., Proc.Roy.Soc., 1946, A.187, 430.
- Claypoole, Trans.A.S.M.E., 1939, 61, 323.
Trans.A.S.M.E., 1943, 65, 317.
- Clayton, Proc.Inst.Mech.Eng., 1945, 153, 332.
- Davis and Holmes, J.Inst.Metals, 1950, 77, 185.
- Dow, Phys.Rev., 1929, 33, 282.
- Dykes, J.Appl.Mech., 1946, 13, (2), A-148.
- Ernst and Merchant, Conf. Friction and Surface Finish, M.I.T., 1940, 73.

- Ewing, *Not.Proc.Roy.Inst.*, 1892, 13, 387.
- Finch, *Proc.Phys.Soc.*, 1950, B.63, 465.
Nature, 1936, 137, 516.
- Fink, *Metallwirtschaft*, 1934, 13, 633.
- Forrester, *Proc.Roy.Soc.*, 1946, A.187, 430.
- Gregory, *Nature*, 1946, 157, 442.
- Gwathmey et al., N.A.C.A. Tech.Note 1461 (1948).
- Hardy, *Trans.Roy.Soc.*, 1932, A.230, 1.
- Heaton et al., *Nature*, 1942, 150, 520.
- Holm, *Wiss.Veroff.Siemens Werk.*, 1938, 17/4, 38.
1936, 15/1, 122.
- Hughes and Whittingham, *Trans.Farad.Soc.*, 1942, 38, 9.
- Jacobs, *Ann.der Phys.*, 1912, 38, 126.
- Landsberg, *Ann.der Phys.*, 1864, 121, 283.
- Palmer, A.S.T.M. Symposium on Wear of Metals, 1937.
- Parker and Hatch, *Proc.Phys.Soc.*, 1950, 63, 185.
- Rideal, *Trans.Faraday Soc.*, 1947, 63, 435.
- Rosenberg and Jordan, *Trans.A.S.M.E.*, 1935, 23, 577.
- Sackmann et al., *J.Appl.Phys.*, 1944, 15, 459.
- Schnurmann and Warlow-Davies, *Proc.Phys.Soc.*, 1942, 54, 14.
- Shaw and Leaver, *Phil.Mag.*, 1930, 10, 809.
- Strang and Lewis, *J.Appl.Phys.*, 1949, 20, 1164.
- Strough and Rapp, *Phys.Rev.*, 1941, 52, 65A.

- Tingle, Trans. Faraday Soc., 1950, 46, 92.
- Tomlinson, Phil.Mag., 1929, 7, 905.
Proc.Roy.Soc., 1927, A.115, 472.
- Tylecote, Trans.Inst.Welding, 1945, 8, 163.
- Van Duzee and Thomas, Trans.Electrochem.Soc., 1940, 87, 341
- Viewig, Pet., 1924, 20, 899.
- Wagner, Z.Phys.Chem., 1938, B.40, 455.
- Whitehead, Proc.Roy.Soc., 1950, A.201, 109.