

pattern. The co-ordinates α and δ are then read off directly. If the centre of the pattern needs to be established then, from the geometry of the projection, it must lie at the intersection of the major axes of the ellipses which the Kossel cones form on the film. When the chart is oriented correctly on a line, therefore, the central axis of the chart will lie along the major axis of that ellipse. The cone angle of the line can also be used for indexing the corresponding plane if the crystal is known and with low symmetry crystals the extra information from the angular co-ordinates of the plane normal is invaluable for indexing purposes. The accuracy of orientation determination is not very sensitive to the cone angle and $\pm 1^\circ$ can be tolerated in the fit. The fitting procedure is easiest between the range of Bragg angles from 25° to 60° and hence with charts constructed at 2° intervals the number of charts required for the orientation determination of all crystals types would be less than 20. In particular, since the source-to-film distance is fixed in this proposed design only one set of charts would be needed to index and orientate accurately all crystals. In practice the orientation of a known crystal can be established from the original pattern in approximately 5 min.

This proposed design of camera takes full advantage of the fact that the generation of a Kossel pattern is independent of the electron beam direction and utilizes the capability of modern interpretation procedures to deal with patterns where the centre and the source-to-film distance are not known in advance. The position of the film, off the electron beam axis, should not interfere with other uses of the system and the camera could therefore be a permanent attachment to an electron probe microanalyser or scanning electron microscope. The design could serve equally well as the basis of a relatively low cost instrument which would be used primarily for the generation of back-reflection and transmission Kossel patterns.

The Kossel technique provides a comprehensive diffraction system and in the opinion of the authors, the widespread use of such a system is justified by the value of the results obtained by its application. A full description of the practical procedures to be followed in order to obtain good Kossel patterns is being prepared for publication [11].

References

1. P. C. ROWLANDS, E. O. FEARON, and M. BEVIS, *J. Mater. Sci.* **5** (1970) 769.
2. M. UMEMO and G. SHINODA, *ibid* **3** (1968) 120.
3. N. SWINDELLS and J. BURKE, "The Mechanism of Phase Transformations in Crystalline Solids" (Institute of Metals, London, 1969) p. 92.
4. D. L. VIETH and H. YAKOWITZ, *Rev. Sci. Instrum.* **39** (1968) 1929.
5. H. HÄLBIG, P. L. RYDER, and W. PITSCH, "X-ray Optics and Microanalysis", Proc. 5th Int. Congress, Tübingen 1968 (Springer-Verlag, Berlin, 1969) p. 388.
6. M. BEVIS, E. O. FEARON, and P. C. ROWLANDS, *Phys. Stat. Sol. (a)* **1** (1970) 653.
7. N. HARRIS and A. J. KIRKHAM, *J. Appl. Cryst.* **4** (1971) 232.
8. P. ROWLANDS and M. BEVIS, *Phys. Stat. Sol.* **26** (1968) K25.
9. N. SWINDELLS and M. BEVIS (1972).
10. N. SWINDELLS, "X-ray Optics and Microanalysis", Proc. 5th Int. Congress, Tübingen 1968 (Springer-Verlag, Berlin, 1969) p. 383.
11. N. SWINDELLS and N. HARRIS, submitted to *J. Appl. Cryst.*
12. P. C. ROWLANDS, Ph.D. Thesis, University of Liverpool, 1970.

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Friction changes in ion-implanted steel

We wish to report a change in the frictional properties of an En steel implanted with various metallic and non-metallic ions using a 500 kV accelerator at AERE, Harwell. To our knowledge, this is the first reported case of a significant mechanical effect brought about by the ion

implantation of various elements into an industrial steel.

Ion implantation may be described as the projection and deposition of atoms by the bombardment of a solid substrate. In conventional implantation equipment a beam of ions is accelerated across a high potential to strike a solid target at the end of a vacuum tube. Pene-

TABLE I [Ref. 2] Composition of En 352 (at. %)

C	Si	Mn	S	P	Ni	Cr	Mo
0.20 max	0.35 max	0.50 to 1.00	0.050 max	0.050 max	0.85 to 1.25	0.60 to 1.00	0.10 max

tration of the projected ions into the target occurs because the ions arrive at high energy. Statistical fluctuations in the energy loss processes lead to a distribution in depth of the implanted species. For amorphous target materials it is possible to calculate the depth of penetration with some accuracy, and the concentration of embedded material can be arranged to peak at a chosen depth. Ion implantation is now well established in the semiconductor device industry where it enables doped junctions to be formed in a single operation. In the work reported here we have utilized ion implantation to incorporate solid lubricants within the surface of a metal. This is not a coating: the foreign atoms form an integral part of the material.

In principle, ion implantation is a technology which offers the opportunity of implanting any element or combination of elements into any solid substrate. Since penetration of the ions is a result solely of their energy, an implanted region will be produced regardless of solubility considerations. With the deliberate object of depositing solid lubricants, we have confined our implanted species to some of the elements which either singly or in combination with other elements are known to improve wear performance.

En 352 is a case-hardening steel which contains several alloying elements to a combined total

of about 4 at. % (Table I). The specimens used in this work were polished discs which were implanted to doses of the order of 10^{16} ions cm^{-2} . The implanted areas were often distinguishable as a darkened band on the surface of the specimen. Precision friction measuring apparatus [1] was used to detect and record the mechanical response of a small sphere sliding slowly across the surface of the specimen under a known load. For brittle materials such as glass this type of "sliding Hertzian" loading results in a continuous succession of small crescent-shaped cracks in the wake of the indenter since the material fails under the combined action of shear and tensile Hertzian stresses. For calculation of fracture parameters, it is important to know very accurately the frictional force acting on the sphere in a direction parallel to the direction of sliding. This instrument (Fig. 1) is, therefore, ideally suited to the detection of small changes in friction.

A 4 mm diameter tungsten carbide ball was loaded to 2 kg and tracked smoothly across the steel surface. For many of the implanted metallic ions the frictional force was observed to undergo a large change as the ball was tracked over the ion implanted region (Fig. 2). To date, species such as Mo^+ , Sn^+ , Pb^+ , In^+ , Ag^+ , S^+ and Kr^+ have been implanted; no effect was observed over a Kr^+ -implanted zone,

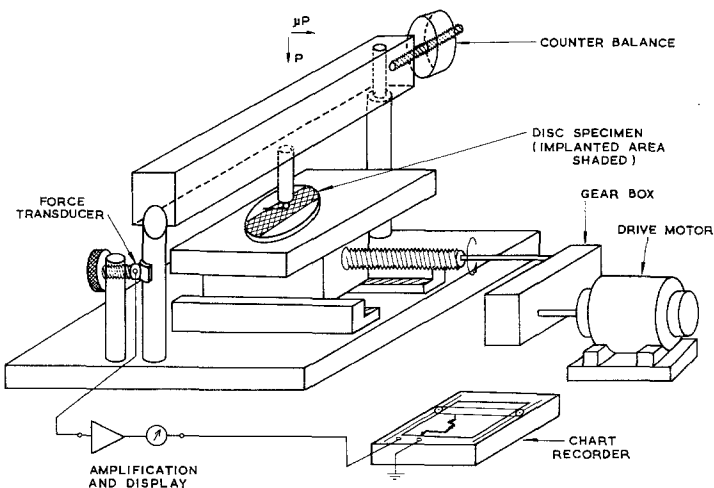


Figure 1 Schematic diagram of friction measurement apparatus.

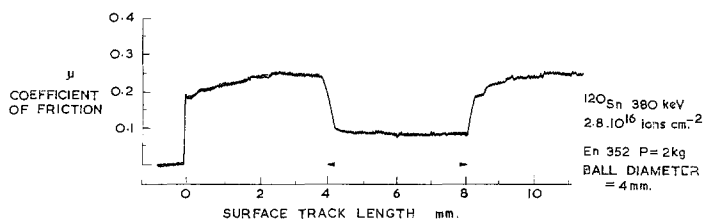


Figure 2 Frictional change for Sn⁺ 380 keV, 2.8×10^{16} ions cm⁻². The markers show the extent of the ion implanted region.

but decreases or increases of up to over 40% were observed in the frictional force with the other species, compared with the unimplanted material.

Fig. 3 shows the effect of repeated sliding over a single wear groove. The implantation of 6.3×10^{16} ions cm⁻² of Pb⁺ produced a succession of very large stick-slip events when traversed by the ball. Rapid changes in friction appear as a broadened trace on the chart recorder. Retracking several times over the same groove reduced the amplitude of stick-slip, and also inhibited the gradual increase in friction which normally occurs as the untreated

steel is traversed (Fig. 3). The reason for an increase in friction after repeated traversals on unimplanted steel may be due to the ploughing in of hard oxide particles formed at hot spots during sliding contact. The mechanism for the lubricating effect of lead after "running-in" (Fig. 3) will be speculative until more detailed examination of the chemisorbed species has been completed. Low shear strength metals such as lead and silver are favoured as solid lubricants for vacuum environments. In air, however, we see that the Pb⁺-implanted area does not change in μ and it is therefore likely that the *oxide* is softer over this region and is acting as a lubricant. The lubricating effectiveness of lead in air may be governed by the presence of un-oxidized Pb atoms which can diffuse to the surface. The wear resistance of ion-implanted lubricants under very many repeated wear cycles and conditions of high speed is yet to be established, however. Micro-beam back-scattering experiments on specimens wear-tested by the method described in this paper show that transfer of lubricant ions along the wear groove outside the implanted region occurs for some ions [3]. For example, the distribution of Ag and Sn becomes more diffuse as wear proceeds. This observation correlates with friction data showing that in air Ag and Sn lose their lubricating effectiveness very rapidly.

It has been suggested to us that the peak friction values which occur at the edge of the implanted region are due to the presence of crater-like edges at the implantation boundary [4]. The build up of such a surface discontinuity will be principally dependent on the sputtering ratio of the implanted ions. For ions such as Pb⁺ and Kr⁺ (Fig. 5, top trace) the sputtering ratio is high, and it is significant that each of these species exhibits a "friction peak."

A characteristic of high adhesion regions

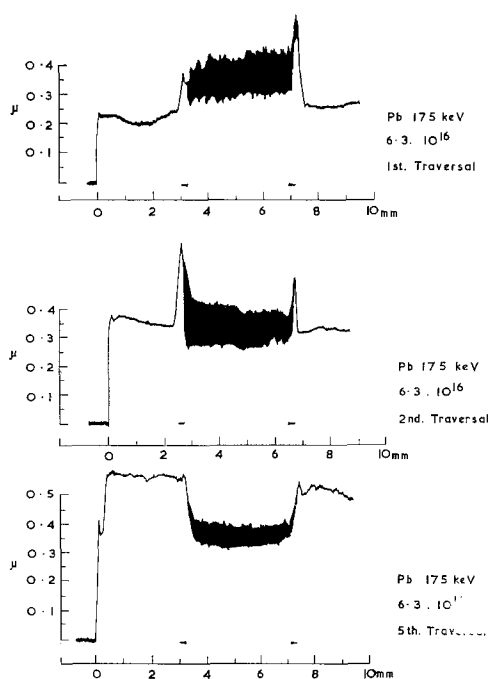


Figure 3 Coefficient of friction for Pb⁺ 175 keV, 6.3×10^{16} ions cm⁻², after retracking in air.

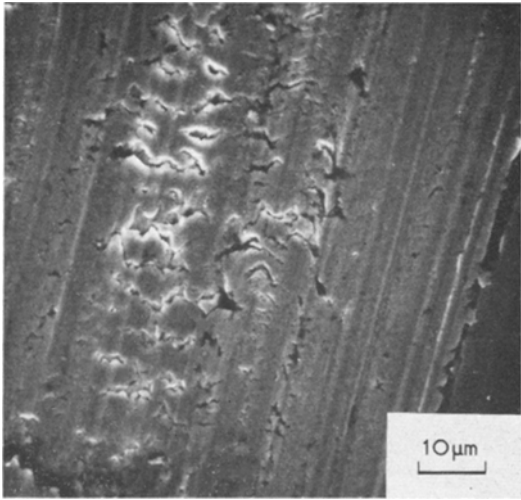


Figure 4 Scanning electron micrograph of wear groove for single traverse experiment over Pb⁺ implanted region.

(e.g., Pb⁺ ions, wear-tested in air) was the appearance of small tear marks approximately perpendicular to the direction of sliding (Fig. 4).

It seems clear throughout our experiments that the frictional effect is associated with the particular foreign species introduced and is not a result of damage or surface contamination. It is remarkable that the extremely small depths of penetration which conventional ion implantation can produce (~1000 Å) are sufficient to cause substantial changes in the friction behaviour.

In further experiments in which, for example, 2.8×10^{16} ions cm⁻² of Mo⁺ was followed by 5.6×10^{16} ions cm⁻² of S⁺, it was found that the combination of Mo + 2S gave a greater decrease in frictional force than Mo or S alone. Recent work has examined the lubricating effectiveness of compounds which contain highly polarized S atoms [5], and it is along these lines that we consider theoretical justification exists for the introduction of various atomic species as intrinsic extreme-pressure additives or solid lubricants. Further experiments are in progress to evaluate ion-implanted solid lubricants under vacuum and air-testing conditions (both dry and lubricated), and the results from these experiments will be published shortly.

The depth distribution of implanted ions may be calculated from the recoil energy spectrum of very light ions (He⁺) projected at normal incidence onto the implanted area

(Rutherford back-scattering [6]). Current experiments of this type are intended to reveal the distribution of the dopant species before and after wear testing, and to determine the optimum conditions for a post-irradiative anneal such that micro-reservoirs of solid lubricant may be precipitated at discrete intervals within the solid surface. This form of dispersed lubricant is considered highly desirable for many dry lubrication applications [7].

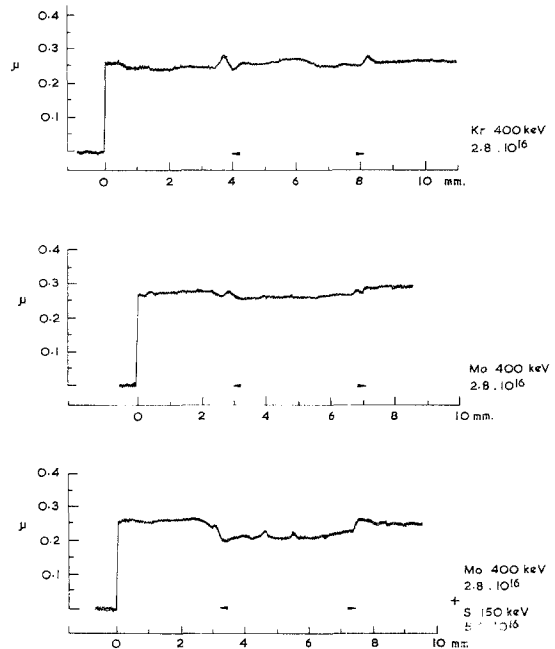


Figure 5 Friction traces for Kr, Mo and Mo + 2S implanted regions.

We consider the excellent thermal contact between the lubricated surface and its substrate to be an important advantage of this process over conventional coating of solid lubricants, which are often applied with a binder on top of an oxide film. One of the most important requirements, particularly at high speeds and heavy load conditions, is the removal of heat generated during friction. Increased thermal conduction from areas of thinly deposited lubricant may contribute towards the superior performance of very thin coatings as compared to thick ones.

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References

1. T. R. WILSHAW and R. ROTHWELL, *Nature, Physical Science (Lond.)* **229** (1971) 156.
2. J. WOOLMAN and R. A. MOTTRAM, "The Mechanical and Physical Properties of the British Standard En Steels" (B.S. 970-1955), Vol. 3 (Pergamon Press, Oxford, 1969) 482.
3. N. E. W. HARTLEY and J. F. TURNER, unpublished research.
4. C. MALONEY, private communication.
5. R. HOLINSKI and J. GÄNSHEIMER, *Wear* **19** (1972) 329.

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6. M.-A. NICOLET, J. W. MAYER, and I. V. MITCHELL, *Science* **177** (1972) 841.
7. M. J. DEVINE, E. R. LAMSON, J. P. CERINI, and R. J. MCCARTNEY, *Lubrication Engng.* **21** (1965) 16.

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The microhardness of composite materials

The Vickers and Knoop indenters are the two most commonly used for determining the hardness of materials. The essential difference between them is that the strain field under the Vickers indenter is spherically symmetrical [1], whereas that under the Knoop indenter is not. The latter has a shape anisotropy which makes the strain under it non-symmetrical even in a fully isotropic medium. Recent studies of Knoop hardness anisotropy in single crystals [2-4] have given a clearer insight into the deformation mechanism under the indenter. Discussion has been in terms of shear stresses developed from compressive [5] or tensile [2, 6] forces parallel or normal to the indenter facets, respectively. This means that the principal strains are in directions approximately perpendicular to the long axis of the Knoop indenter. In single crystals, the hardness is a reflection of the stresses developed on active slip planes, when these are small the material does not deform appreciably and so appears hard.

In the case of a highly anisotropic material such as a unidirectional composite, the degree of material anisotropy plays a dominant role in the deformation pattern produced by the indenter. Nonetheless the hardness of the material again reflects its response to the strain field applied by the indenter, as in the case of single crystals.

In order to examine such effects in highly anisotropic materials, we have made Vickers and Knoop indentations at loads ranging from 100 to 500 g in copper-Cu₅Zr and copper-CuZrSi unidirectionally solidified lamellar eutectics (42 and 90.8 vol % copper, respectively) and a 60 vol % carbon fibre-reinforced plastic (CFRP). Studies have been made of the dependence of hardness on relative orientation between the indenter and the fibre (or lamellar) direction. In Fig. 1 is shown the variation in hardness of a copper-Cu₅Zr eutectic as a function of indenter orientation, taking the condition as 0° when the long diagonal of the Knoop indenter or either diagonal of the Vickers is parallel to the lamellae and 90° when it is perpendicular to them. The arithmetic means of sets of ten indentations were taken at each angle and the root mean square error σ calculated. The error bars represent $\pm 3\sigma$. In the case of Vickers indentations, the diagonals are of unequal length (Fig. 2a) because the material is anisotropic. Therefore, we have calculated Vickers hardness values from the individual diagonals rather than averaging pairs as is usual. The exception to this separate treatment occurs at 45° when the diagonals are in an equivalent symmetrical position. In both cases, the fitted curves are sinusoidal but if the Vickers hardness values were to be derived from the mean of the diagonal lengths then no orientation dependence would be observed.

It was clearly shown in all samples that the