SURFACE ENGINEERING: ADVANCED MATERIALS FOR INDUSTRIAL APPLICATIONS

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Abstract

The principles of surface engineering and the reasons for its emergence as a pervasive manufacturing technology are outlined. A breakdown of industrial activity in surface engineering in the UK and forces for change are discussed, together with their implications for the role of future research in advanced materials for industrial applications. Examples of current research studies are described involving plasma-assisted chemical vapor deposited SiO_2-GeO_2 thin-film waveguides in integrated optics and electroplated chromium piston rings or cylinder liners in internal combustion engines.

INTRODUCTION

Surface engineering may be defined as the design of engineering to improve their performance in service. This can be achieved by surface treatments, which can provide combinations of surface and bulk properties unobtainable in a single material. A ceramic on a metal, for example, can give extreme hardness at the surface, while maintaining an acceptable fracture toughness throughout the section. The surface treatments may involve coating, chemical modification or physical processing. Coating processes, such as electroplating processes, produce a discrete layer of a new material with a sharp interface at the substrate. Chemical modification techniques, such as nitriding, provide a diffuse layer of a foreign element with no definitive interface. Physical processes, such as grit blasting, change the surface profile but not the chemical composition.

The properties of the surface layers are often quite different from those of the bulk material, because they are frequently formed under non-equilibrium conditions. Many surface treatments involve rapid cooling or low homologous temperatures resulting in the creation of metastable structures such as new amorphous or crystalline phases and extended solid solubilities, often with high levels of residual stress. Surface-sensitive properties are of particular interest since they are most readily affected by surface treatments and include friction, wear, corrosion, oxidation and opto-electronic behaviour.

The importance of surface treatments lies in their ability to improve performance, create new products and conserve scarce materials by substitution. Respective examples are carburizing gears to extend component lifetimes, vacuum-evaporated cobalt-nickel thin films on PET as video tapes and electroless nickel-phosphorus coatings on plain carbon steel to replace certain chromium stainless steel parts. Surface engineering is driven by the engineering application and is primarily an applied science. Surface engineering thus involves a detailed knowledge of the end application, its function and requirements, the property evaluation and quality control of the working surfaces, characterization of the surface structure and an understanding of the capabilities of the available surface treatment processes.

This paper is concerned with the use of advanced materials and the role of research in the surface engineering industry. Research in surface engineering requires funding for labour, equipment and consumables. In the UK, this funding is mainly obtainable from government bodies, the Commission of the European Communities and industrial companies, but the underlying primary motivation of all three in this instance is to improve the competitive position of UK industry. The majority of research in surface engineering therefore has to be justified on the grounds of tangible industrial benefits. The direction of research is thus closely linked to the current status of the industry, the products required by the users, the forces for change and their effect on the future needs of industrial companies.

PRODUCT APPLICATIONS

The surface treatment industry is essentially market-led and provides the products required by its customers, who aim to satisfy the applications of the users. Surface engineering is an important, pervasive technology used by almost every part of manufacturing industry with the result that its product applications are extremely diverse. The use of surface treatments has grown steadily over the last two decades. Some of this growth is due to the development of new techniques, such as plasma-assisted chemical vapour deposition and ion implantation. However, the less capital-intensive newer techniques, such as powder polymer coating (e.g. electrostatic spray, fluidized bed) and electroless deposition have to date made much more impact in economic terms; for example, the replacement of cadmium by epoxy resin coating in suitable cases and the switch from anodizing aluminum to coating with polymers. The role of electroless nickel coating has been partly cannibalistic in the sense that they have replaced chromium plating in some cases, but in others have found new applications due to the superior throwing power and unique properties.

An example of the commercial benefit of surface engineering can be found in high-speed twist drills [1]. Steel drills have traditionally been surface treated by a steam tempering process to produce the familiar blue oxide finish. A collaborative research program (SKF, Dormer, MultiArc) has now develop a plasma-assisted physical vapour deposition process for coating the drills with titanium nitride. The use of this coating initially enabled the drill to produce twice as many holes before replacement compared with the conventional drill. However, the greater cutting ability of the drill led to choking of the flutes by swarf. Subsequent re-design of the shape and helical angle of the flutes aided swarf clearance considerably and the resultant TiN-coated drill exhibited a tenfold improvement in life compared with the conventional product. Cost savings accruing from a longer drill life or faster speeds for the same drill life are typically 30% per hole drilled.

There are numerous examples in other industrial sectors. Yttria-stabilized zirconia coatings produced by plasma spraying provide higher aircraft engine efficiencies by acting as thermal barrier layers on critical components such as turbine blades. Other industries include automotive (bearings, shafts, cams, tappets, etc.), chemical plant (catalyst support beds, pumps, valve seals), textile machinery (rollers, bearings, thread guides) and machine tool (cutting, boring, drilling, slideways).

Manufacturing industry is moving away from the use of surface treatment as a mean of compensating for poor material properties towards the incorporation of surface treatment specifications at the design stage, particularly in cases where cost-effective benefits are identified. Coating technologies are being increasingly adopted industry to improve its competitive position by adding value to components through their superior performance.

SURFACE ENGINEERING INDUSTRY IN THE UK

(a) <u>Market Value</u>

Production in the UK surface engineering industry expressed in terms of value added, or the value of output net of inputs, is estimated in table 1 and figure 1. The figures are very approximate partly because Government statistical data only relates to companies having more than 50 employees, which excludes a considerable proportion of the UK surface engineering base. The figures apply to the so-called functional coatings (non-decorative with specific property requirements such as wear, corrosion or oxidation, although the division between functional and decorative coatings is somewhat arbitrary) and excludes paints. The paint industry in the UK is valued at approximately 1200 US$ and is dominated by large companies such as ICI. The total value of the functional coatings business is approximately 2.5 billion US$ per year, which is about 1% of the total UK manufacturing activity. However, surface engineering is often only one unit process in a chain of processes making up the integrated manufacturing route of an engineering product, the surface engineering content of which is typically 5-10% of the sale price [2]. The true value of surface engineering can be estimated in terms of the value of the intermediate products sold that are critically dependent on surface engineering processes. These intermediate products are primarily components supplied to larger assemblies as, for example, zinc-plated carburettors for automobiles. The sale of intermediate products that are critically dependent on surface engineering processes in the UK has been estimated [2] at 20 billion US$ per year or the order of 10% of the total UK manufacturing output. However, the value placed on such intermediate products can only be very approximate.

TABLE 1. Estimated value of the UK surface engineering industry

Technology	Value US$(million)	% share
Electroplating	1000	40
Surface heat treatment	600	23
Galvannizing	300	12
Powder coating	200	8
Phosphating, chromating	200	8
Thermal spraying	70	3
Anodizing	45	2
Other (enamelling, etc.)	40	2
New technology	40	2
TOTAL	2495	100

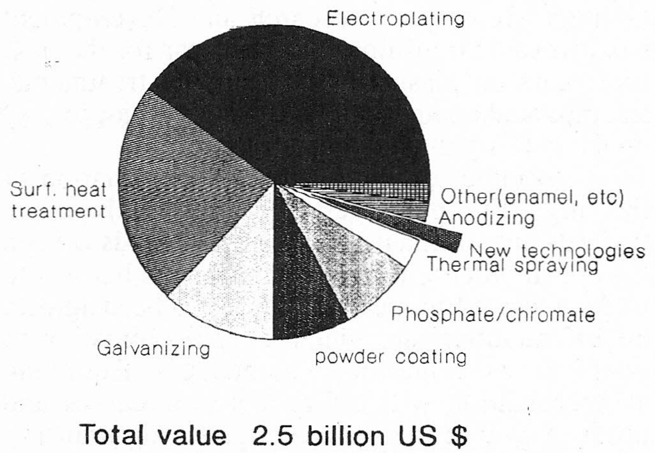


FIGURE 1. Estimated value of the UK surface engineering industry.

The overall growth of the surface engineering sector between 1986 and 1989 was about 10% per year but has now slowed to 5% per year. A breakdown of the new technologies is given in table 2 and figure 2; these processes contribute only 2% to the total sector but their growth rate has been almost double that of the established sector. The new technologies are particularly strong in specialized sectors such as machine tools and aerospace but there is little evidence to date that they are replacing the established processes for traditional product applications to any significant extent.

TABLE 2. Estimated value of new surface engineering technologies in the UK

Technology	Value US$(million)	% share
Physical vapour deposition	10	36
Chemical vapour deposition	6	22
Plasma nitriding	5	18
Plasma spraying	5	18
Ion implantation	0.5	2
Laser/electron beam	0.5	2
Other (e.g. friction)	0.5	2
TOTAL	27.5	100

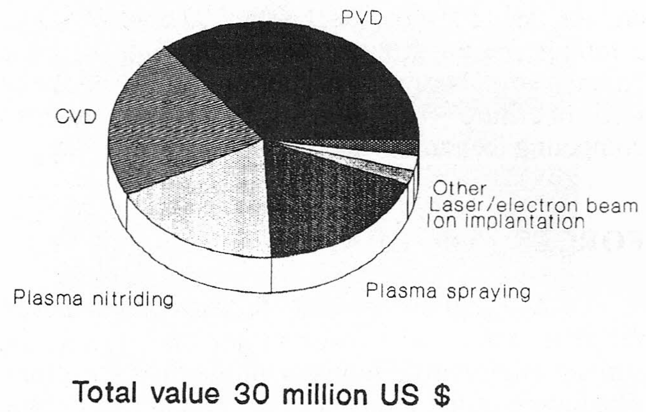


FIGURE 2. Estimated value of new surface engineering technologies in the UK.

(b) Structure

Electroplating has remained the most important process within the industry for many years. It consists [3] of a limited number (~10) of medium-sized chemical supply companies and a much larger (~1000) of small processing companies with a workforce per company of typically 20-30. The total number of employees in the surface engineering sector is approximately 20,000. The business tends to consist of work that is subcontracted from other (often much bigger) companies. For example, about 1000 small electroplating firms serve the UK automotive industry and a similar number of small subcontractors service the UK aerospace industry. The electroplating industry is generally a high turnover, low profit margin and small order-book business where customers tend to demand short lead times. Investment is inhibited by a lack of financial resources and a reluctance to write off existing facilities.

The surface engineering industry is very approximately evenly split between subcontracting by mostly small companies and in-house processing by often much larger companies. The large companies have tended to subcontract work to an increasing extent over the last five years because this provides production flexibility, obviates investment and offsets risks. However, there are now some indications that this trend may be reversed due to concern of the larger companies in the commercial viability of some of the contractors, the dangers of single-source supply and the need for closer technological control. Over a longer period, however, it is possible that the balance of subcontracting to in-house processing will oscillate from one to the other due to competing technological and economic factors.

FORCES FOR CHANGE

A number of new factors have arisen recently which will force major changes in the surface engineering industry in the next ten years. The nature of the industry at the end of this decade vary much on how it deals with the opportunities and threats brought about by these external pressures.

New environmental legislation to control health and safety of the workers, effluent and waste disposal, and protection of the environment outside the factory is causing many processing companies to examine the viability of their existing technology base. The pressure comes from national and particularly supra-national bodies, such as the European Community and the Montreal protocol on CFCs. For example, the use of hexavalent chromium salts and nickel sulphate is now restricted under health and safety regulations. These chemicals are used widely to produce coatings in the electroplating industry and substitution is proving difficult. Some of the possible alternatives such as those based on nickel chloride and sulphamate may themselves become further restricted in the future. Charges for the disposal of trade effluent to sewer and of waste sludges to landfill are expected to rise substantially in the next few years, particularly if the proposed EC directives become operative. Further concern centres around the anticipated rise in cost of a major raw material, water, stimulated partly by the privatization of water authorities in the UK. More stringent restrictions on air emissions from ovens, heat treatment furnaces, spraying booths, etc. will also result in increased production costs.

The principal industrial competitors of the UK are Germany, France, Japan and the USA. International competition will be enhanced after December 1992 with the creation of the single European market, which will facilitate free trade throughout the member states. The principal competitors are investing significantly in the surface engineering industry and the requisite exploitation infrastructure. For example, the German Ministry of Research and Development has invested 90 million US$ per year for the next five years on plasma-related surface treatments. International competition will have a major impact on the industry in the coming decade.

Another consequence of the formation of the single European market in 1992 is the move towards the rationalization of standards within Europe in order to remove the technical barriers to trade. Once a European Standard has been agreed, all EC members are under a legal obligation to adopt it as a national standard. European standardization will affect many processes and products within the surface engineering industry. In the extreme, the processing in some companies may be inadequate and they may lack the resources to upgrade in order to manufacture their products to the new standards.

RESEARCH

The research activity in industry is generally confined to the larger companies involved in chemical supply (e.g. electroless nickel formulations, phosphates), process equipment manufacture (e.g. advanced thermal spraying, chemical vapour deposition) and the user companies (e.g. automotive, aerospace, electronic, machine tool). These companies often have their own research departments but also interact with the rest of the UK science base. The surface engineering science base in the UK is significant and resides in industrial research centres, government research establishments, universities and contract research companies.

The research in the science base is critically dependent upon funding from industry, government bodies (Science and Engineering Research Council, Department of Trade and Industry, Ministry of Defense) and the European Community (e.g. BRITE-EURAM). However, all these funding sources in this context are directed at improving the competitive position of UK manufacturing companies. Surface engineering research in the UK is thus driven by the needs of industry.

Up to the present time, the subcontracting companies have interacted comparatively little with the UK science base and generally respond only to the demands of their current customers. However, future threats and opportunities, together with the possibility of company mergers into larger units ,might possibly lead to a change in their approach to research.

EXAMPLES OF RESEARCH STUDIES

The final section in this paper provides two examples of current research studies in surface engineering.

(a) Integrated optic waveguides

The recent development of optical fibres waveguides as a mean of transmitting information has now penetrated into virtually every area of information transmission, processing and storage. Optical fibres are also used to link computer peripherals, are likely to link processors, and are used as sensors. Planar waveguides play an important role in optical transmission as interconnections, beam splitters, mixers, wavelength multiplexers, etc. [4]. In its simplest form, a planar optical waveguide consists of a transparent thin film of refractive index n_1, slightly greater than of its substrate n_2. For shallow incident angles, Snell´s law of refraction cannot be satisfied, total internal reflection occurs and the interface acts as a perfect mirror ($\sin\theta > n_2/n_1$) (figure 3). Under this condition, the film operates as an optical waveguide: a ray of light is reflected from side to side along the film until it emerges at the far end. For example, figure 4 shows the transmission of light in a silica-germania thin film waveguide on a silica substrate.

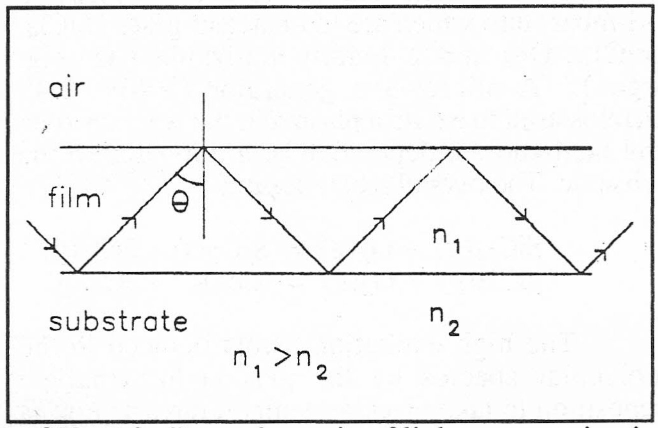


FIGURE 3. Ray schematic of light propagation in thin film optical waveguide.

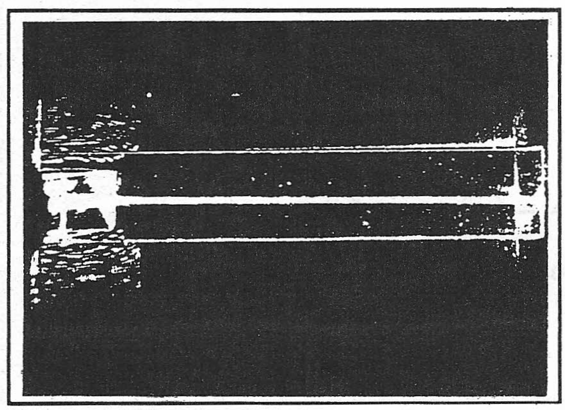


FIGURE 4. Transmission of light in SiO_2-GeO_2 planar waveguide on silica, showing coupling prism on left and guided light from left to right in centre of field. X1.6.

No consensus has been reached on a single ideal material fabrication technique for planar optic waveguides. Popular materials include lithium niobate, III-V semiconductors, glass and a variety of polymers. Typical fabrication techniques include diffusion, epitaxial, ion exchange and deposition. This research concerns the use of plasma-assisted chemical vapour deposition as a fabrication method, in which germania-doped silica is deposited as a glass layer on silica. A temperature of 1800°C is required in conventional chemical vapour deposition for this reaction and this work concerns the use of plasma-assistance to reduce the reaction temperature. The deposition apparatus is shown in figure 5 and consist of a heated reaction zone maintained at a low pressure (~1 mbar) into which are fed reactant gases ($SiCl_4$, $GeCl_4$, O_2) and a readily ionizable gas (e.g. argon). A microwave generator (500W, 2.45 GHz) is used to excite a plasma in the reaction zone and facilitate the deposition of a thin film on the substrate. The overall reactions are:

$$SiCl_4(g) + O_2(g) = SiO_2(s) + 2Cl_2(g)$$
$$GeCl_4(g) + O_2(g) = GeO_5 + 2Cl_2(g)$$

The high excitation levels induced in the molecular species by the plasma has enabled deposition to take place at temperatures as low as 25°C compared with 1800°C in the absence of plasma.

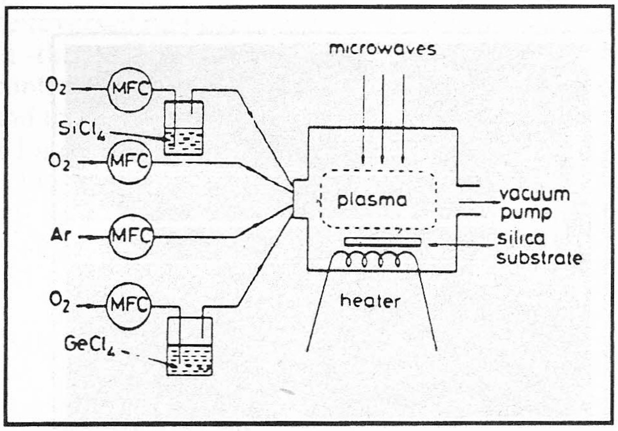


FIGURE 5. Schematic of PACVD apparatus for fabrication of planar waveguides. MFC = Mass Flow Controller.

The quality requirements of the films centre around their mechanical and optical properties. The mechanical properties of the films (thickness ~ 5µm) were assessed by indentation fracture (figure 6) and the data in figure 7 indicate that the adhesion (interfacial crack length, C_i), integrity and residual stress (radial crack length, C_r) deteriorated rapidly at low deposition temperatures. Optical characterization showed that high quality performance was obtained in waveguides deposited at 1000°C in terms of a sharp step index profile (figure 8) and low attenuation (figure 9). A major deterioration in optical properties occurred at low deposition temperatures and the data in figure 10 shows that the attenuation is well above the maximum acceptable value of $1dBcm^{-1}$. The research has thus shown that GeO_2-SiO_2 planar waveguides can be produced by plasma-assisted chemical vapour deposition at temperatures well below those for conventional chemical vapour deposition but that an optimum reaction temperature is required for acceptable mechanical and optical properties.

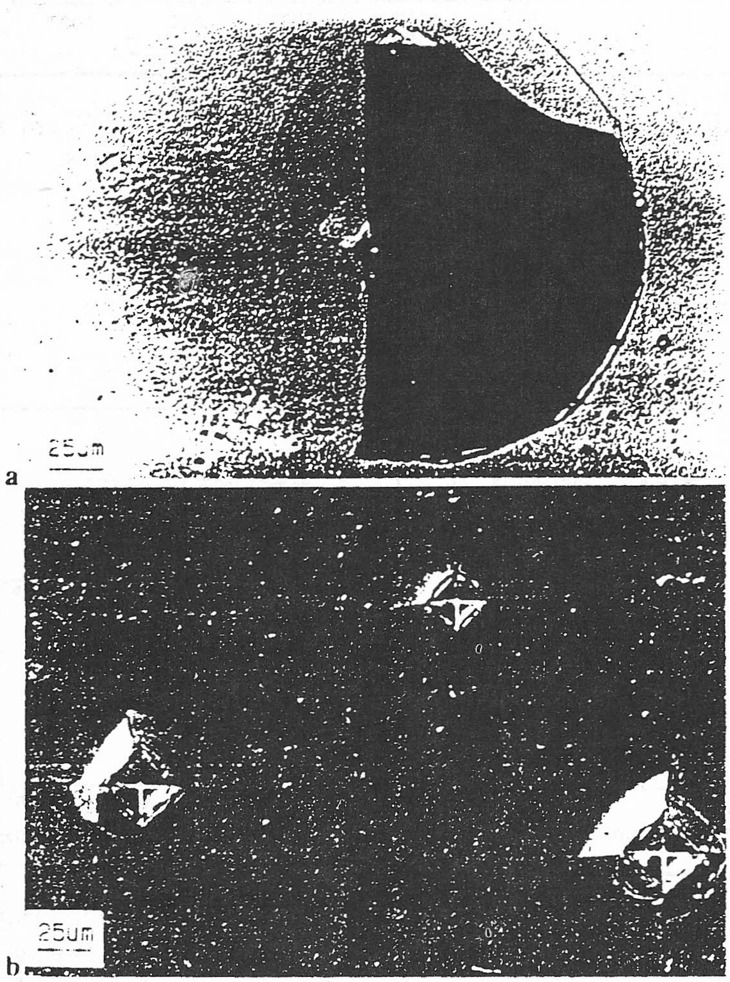
(b) Internal Combustion Engine

The piston-cylinder combination is a crucial arrangement in the internal combustion engine for the conversion of chemical energy to mechanical energy (figure 11). The contact between the piston rings and inside surface of an engine cylinder must be as light as possible in order to seal the annular gap with a lubricant. However, the piston should still be able to slide freely and not wear its piston rings nor the cylinder bore too rapidly. The dominant requirement with precision components is to provide low friction and wear throughout the life of the engine. Electroplating the piston rings or the cylinder liner with chromium may reduce friction and wear due to its high hardness (HV ~ 1000Kg mm^{-2}), but suffer from a relatively poor oil wettability. Under adverse conditions, the oil does not spread adequately over the cylinder walls leading to marginal lubrication, metal-to-metal contact and substantial wear. It study investigates the influence of surface topography on the wettability of electroplated chromium coatings [6].

Three types of chromium coatings were produced:(a) conventional, (b) nodular by means of a low electrolyte temperature during plating and (c) etched reversing the polarity at the end of plating (figure 12). A technique [7] was used to evaluate the rate of spreading of oil on a surface by means of a wettability exponent, W:

$$A = Ct^{W} \qquad (1)$$

for wich A is the area of spread of the oil after a time t while W and C are constants for the system. The wettability exponent of the conventional chromium of 0.139 was increased by the presence of nodules to a value of 0.253 and particularly by back-etching to a value of 0.351. The surface profiles of the nodular and etched chromium are shown schematically in figure 13 with their corresponding material ratio curves (figure 14). Whereas only 10% of the metal surface is exposed to bear the load after 1μm wear on the nodular surface, as much as 70% is exposed in the etched surface. The high material or bearing area of the etched surface is beneficial in reducing temperature build-up and contact pressures, but is also very effective in trapping oil in its deep valleys in an otherwise fairly flat surface. The oil retention volume V_0 as shown in figure 15, is the volume of valleys below the core roughness and is an indication of the oil retained by a cylinder bore surface after it has been scraped by a piston ring. The V_0 value is much larger for the etched surface than the nodular surface (figures 13 and 14) with the result that the etched surface will be more adequately fed with oil under sliding contact. Both the nodular surface and the etched surface thus provide improved wettability but the etched surface has the additional advantage of higher oil retention and a larger bearing area. This work shows the critical importance of surface topography in lubricated sliding contact and how it may be controlled during surface treatment.



a at 100°C; *b* at 1000°C

FIGURE 6. DIC micrographs in SiO_2-GeO_2 waveguides deposited at given temperatures.

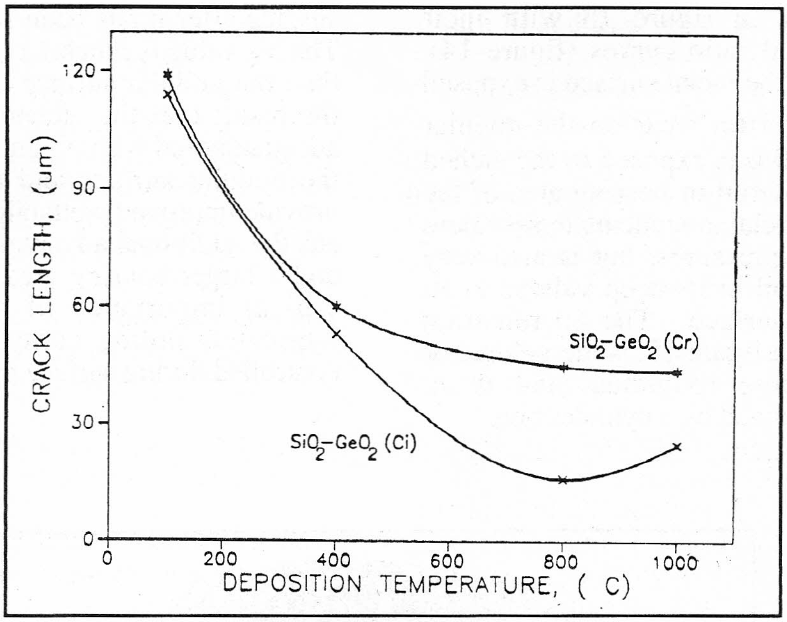


FIGURE 7. Effect of deposited on the interfacial C_i and C_r crack lengths in SiO_2-GeO_2 waveguides on silica substrates.

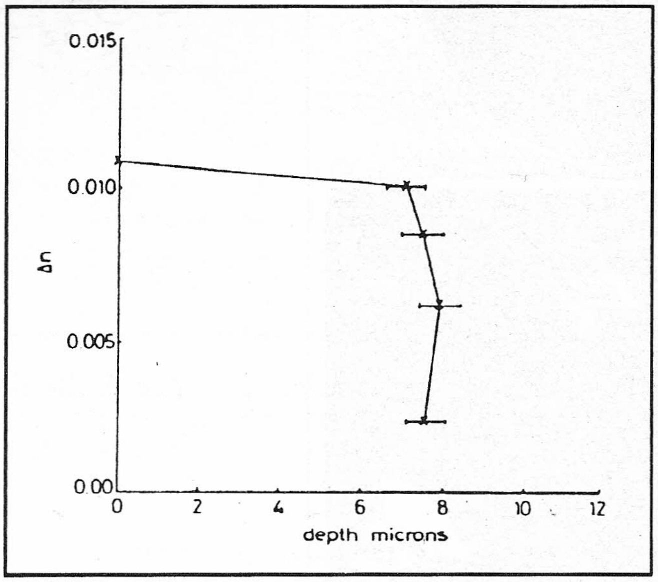


FIGURE 8. Refractive index profile for SiO_2-GeO_2 film deposited at 1100°C on silica: difference in refractive index between film and substrate (Dn) is plotted as a function of depth.

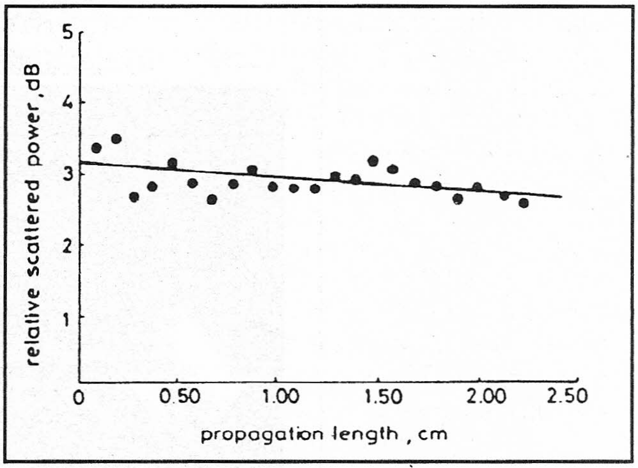


FIGURE 9. Attenuation measurements of four moded SiO_2-GeO_2 waveguide deposited at 1100°C on silica:gradient = -0.21 dB cm^{-1}

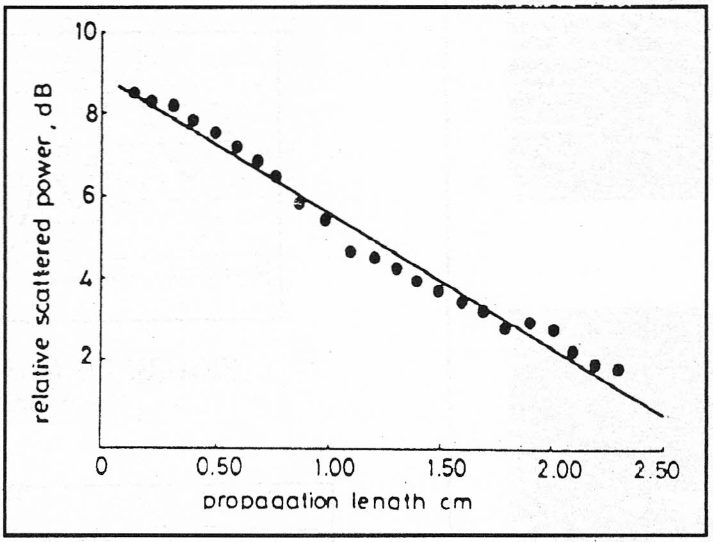


FIGURE 10. Attenuation measurements of six moded SiO_2-GeO_2 waveguide deposited at 100°C on silica: gradient.

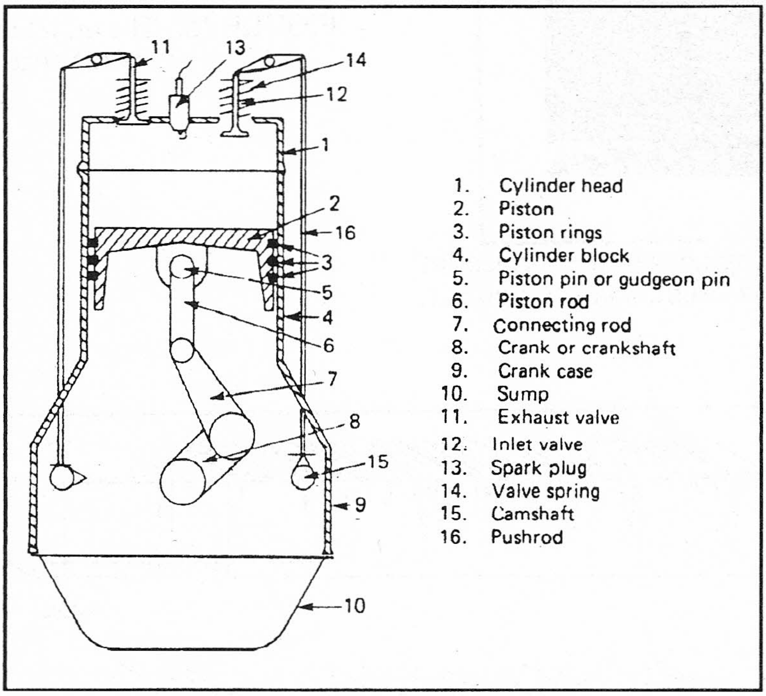


FIGURE 11. Schematic of the reciprocating internal combustion engine.

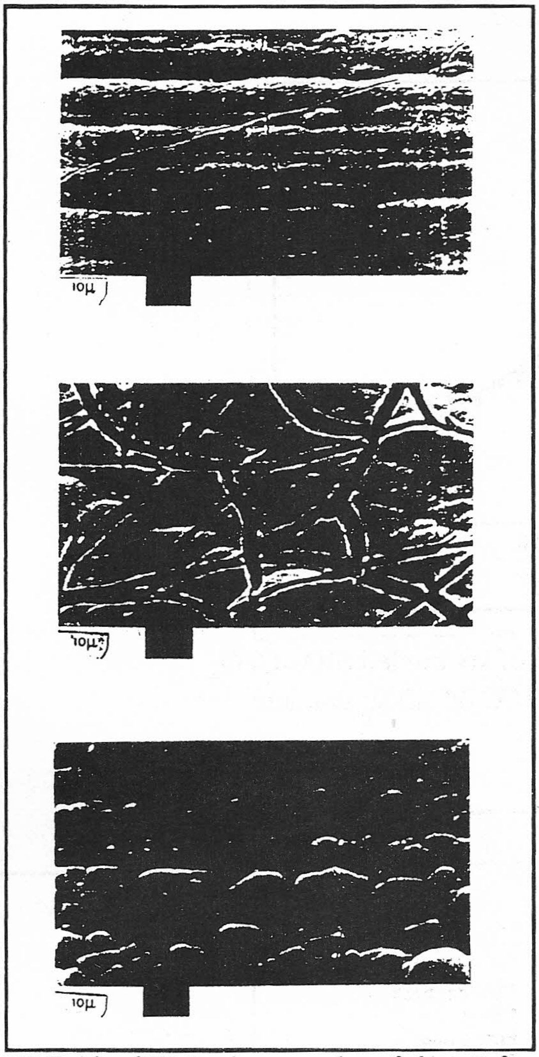


FIGURE 12. SEM micrographs of the surfaces of chromium plating: (a) conventional, (b) nodular, (c) back-etched.

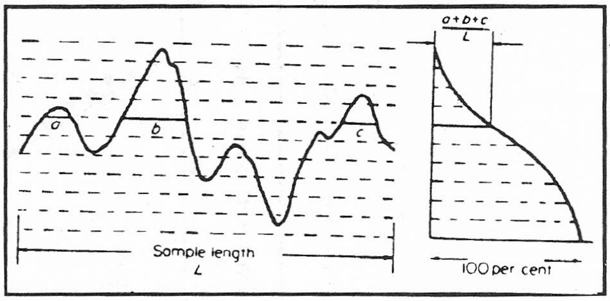


FIGURE 14. Derivation of material ratio (or bearing area) curve.

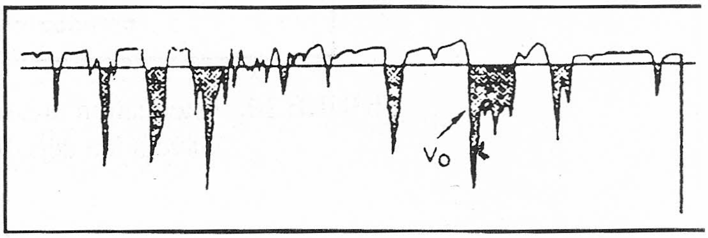


FIGURE 15. The oil retention volume, V_0, shown by the shaded area.

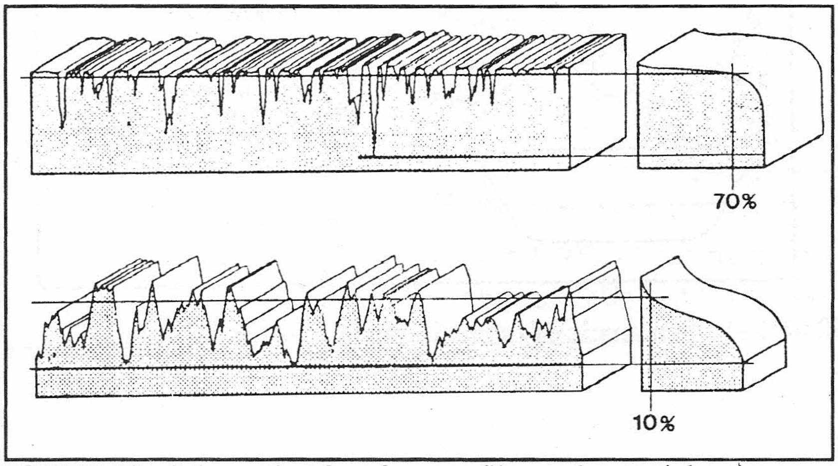


FIGURE 13. Schematic of surface profiles and material ratio curves for etched (top) and nodular chromium surfaces.

REFERENCES

1. R. Goodwin, "The Hole Story" in "A Cutting Edge for the 1990s", Institute of Metal, London, 1990.

2. D.A.J. Vaughan, "Future of Surface Engineering in the UK", Centre for Exploitation of Science and Technology, London, 1991.

3. D. T. Gawne, Trans. Inst. Met. Fin. **67** (1989) 15.

4. D.T. Gawne, N. Nourshargh, I. Kandasamy and E.M. Starr, Surface Engineering, **6** (1990) 107.

5. F.G. Arieta and D.T. Gawne, Brunel University. To be published.

6. F.G. Arieta and D.T. Gawne, J. Mater. Sci., **21** (1986) 1973.