E. Sugars

Fulmer Newsletter

contract research and engineering in materials and process technology

No.51 September 1983

CVD COATING

A REVIEW OF FULMER TECHNOLOGY

CHEMICAL VAPOUR DEPOSITION (CVD) IS AN IMPORTANT MEMBER OF THE TECHNOLOGIES USED IN THE PRODUCTION OF METAL AND OTHER INORGANIC COATINGS. EXPERIENCE HAS SHOWN THAT FOR MANY SPECIAL APPLICATIONS, CVD COATINGS, BECAUSE OF THEIR UNIQUE PROPERTIES, ARE ABLE TO PROVIDE BENEFITS NOT OTHERWISE READILY ACHIEVABLE BY THE OTHER COATING METHODS. THIS ARISES FROM THE NATURE OF THE CVD PROCESS WHICH INVOLVES DEPOSITION ON AN ATOMIC SCALE AND THE USE OF SUBSTANTIALLY ELEVATED TEMPERATURES, BOTH OF WHICH CONTRIBUTE TO THE FORMATION OF VERY COHERENT DEPOSITS OF EXTREMELY LOW PERMEABILITY. ADDITIONALLY, RATES OF DEPOSITION OF CVD COATINGS ARE OFTEN SUFFICIENTLY HIGH TO PERMIT THE GROWTH OF RELATIVELY THICK COATINGS AS INTERMEDIATES IN THE FABRICATION OF FREE-STANDING SHAPES.

CVD AT FULMER

It is now approximately 25 years since Fulmer became involved in the deposition of metals and compounds by CVD. Since that time it has maintained a continuing research activity in the subject which has produced established methods for the preparation of numerous CVD coatings. In a number of instances Fulmer has also undertaken major development programmes, which have been successful in establishing conditions for large-scale pilot plant production.

A summary of our activities in CVD was last published in the Fulmer Newsletter Number 39 (March 1975). This proved to be a very popular publication. An update is now desirable to take account of recent activities.

CVD Tungsten Shapes

THEORETICAL CONSIDERATIONS

THE CVD REACTION AND THERMODYNAMIC FEASIBILITY

Chemical vapour deposition may be defined as the deposition of solid material from the vapour phase brought about by a thermally induced chemical reaction.

The temperatures required for deposition vary considerably according to the chemical reaction involved. It may only be slightly above room temperature as for example in the case of nickel deposition from nickel carbonyl, $Ni(CO)$, or it may be above 2000°C for the deposition of pyrolytic graphite by the thermal decomposition of hydrocarbons. Assessment of the usefulness of a particular reaction may be obtained by calculating the thermodynamic feasibility of the reaction at a number of temperatures. Tabulated data on the heats of formation and entropies of the reactants and products are used to derive free energies, and from these the corresponding equilibrium constants are obtained. Reactions with equilibrium constants considerably greater than unity are highly feasible whereas those with constants appreciably smaller can be expected to be very much less favourable. Even in the latter case, useful deposition may be achieved although process efficiency in terms of degree of conversion of reactants may be very low. For endothermic reactions, equilibrium constants increase with increasing temperature, thus creating more favourable deposition conditions. Reactions which are substantially exothermic are theoretically feasible at all temperatures and are therefore only limited by kinetic considerations which can usually be overcome at moderately elevated temperatures.

PRACTICAL CONSIDERATIONS

RANGE OF COATINGS PRODUCED BY CVD

The CVD method may be used to produce a wide range of coatings of single elements and inorganic compounds, although so far most work on compounds has been limited to binary compounds. The method is in principle very simple, but considerable optimisation of the process conditions is frequently necessary to produce the highest quality coatings. An essential requirement of the CVD process is the availability of suitable vapour sources, the selection of which is important both in terms of process costs and deposition temperature. Additionally, selection can markedly influence the morphology of the coatings, and this can be very important in the development of coatings with very special properties, such as a high electrical work function.

Examples of vapour sources are metal halides, in particular fluorides and chlorides, metal carbonyls, metal organics and hydrides. Halides are widely employed as for example in the production of titanium carbide and nitride coatings. There is now however considerable interest in the wider use of metal organic precursor vapours for the preparation of electronic coatings at lower temperatures than would be possible from halide vapours.

RANGE OF CVD REACTIONS

Coatings of many metals have been achieved by the hydrogen reduction of the corresponding metal halide vapour. This has been found to be particularly useful for producing coatings of the refractory metals vanadium, niobium, tantalum, molybdenum, tungsten and rhenium. The method however is not very attractive for depositing titanium, zirconium or hafnium, whose more stable halides are extremely difficult to reduce to metal by hydrogen. Coatings of the non-metallic elements boron and silicon may also be obtained by hydrogen reduction of the corresponding chlorides or bromides although not by the more stable fluorides. Hydrogen reduction of halides in the presence of vapours of non-metallic elements, e.g. hydrocarbon, ammonia, water vapour, may be used to produce binary coatings of carbides, nitrides, oxides etc. Because of more favourable thermodynamics, such compounds can often be obtained more easily than the corresponding metal. This permits the production of many compounds of the group IV transition metals, e.g. titanium carbide.

Metals and compounds may also be deposited by thermal dissociation of vapour compounds, such as organo-metallics, carbonyls, hydrides and iodides. For example, tri-isobutyl aluminium vapour can be used to produce aluminium coatings at about 250°C. It may also be used to produce compounds, e.g. aluminium oxide, aluminium nitride. Molybdenum and tungsten carbonyls may under appropriate conditions of deposition be used to produce the corresponding carbides, whilst the thermal decomposition of silane may be used to produce silicon or in the presence of appropriate vapours, silicon nitride or silica coatings. Thermal decomposition of iodides requires substantially elevated temperatures of around 1200°C, but nevertheless is useful for certain metals, e.g. titanium, chromium.

Another important method of producing CVD coatings is that of vapour phase chemical transport. For many CVD coatings only very minimal interaction occurs between the deposit and the underlying substrate. However for one important class of coatings – diffusion coatings – this chemical interaction is an essential feature of the method, providing the driving force for coating formation. For example, although a gaseous mixture of aluminium chloride and hydrogen is not a suitable reaction for the formation of aluminium coatings even at substantially elevated temperature, it is capable of producing aluminium – containing coatings on iron or steel components, this being possible because of the existence of very stable iron-aluminium compounds. Usually this type of coating is produced by chemical transport in which aluminium is transported to the article to be coated from a particulate aluminium source through the agency of a halide activator, aluminium trifluoride. In a cosed system the activator is not consumed but acts as a catalyst for the vapour transport of aluminium. The method is particularly suitable for aluminizing, chrominizing, siliconizing and boronizing of iron, cobalt and nickel base alloys.

PROCESS CHARACTERISTICS

Rates of deposition in CVD vary from a few microns per hour to several hundred per hour, dependent upon the nature of the chemical reaction employed. For example, the rate for titanium carbide is several microns per hour, whereas for tungsten it can be as high as 500 microns per hour. Coating thicknesses varying from a few microns to several millimetres are possible, with coating times from a few minutes to, in some instances, several days. CVD operates in a pressure range (1 to 1000 millibars) which ensures good throwing power and minimum shadowing. Where even greater uniformity is required, pulsed pressure CVD is possible. Equipment design varies considerably depending upon application. Generally however the articles to be coated are treated in sealed or semi sealed chambers, and are usually heated resistively or directly by R.F.

COATING CHARACTERISTICS

A feature of all CVD coatings is the atom-by-atom build-up of material which in conjunction with the bulk properties produces a unique type of coating. CVD coatings can show structural variations depending upon the material being deposited and the process conditions. Orientated columnar growth with grain sizes 0.01 to 10 microns is found in many deposits. In anisotropic materials this can produce marked directional variations in the physical properties of a coating as for example in pyrolytic boron nitride plate where heat conduction in the plane of the plate is very much greater than through the plate. CVD coatings are usually of near theoretical density and lower permeability to gases and liquids, a factor of considerable importance where corrosion-resistance is involved; in fact CVD is used to in-fill other types of more porous coatings. CVD coatings are often obtained in a state of high purity, this arising both from the purity of the plating vapours and the refining action of the CVD process itself. The degree of bonding of a CVD coating to its substrate is dependent upon many factors, and the process parameters must be tailored to particular requirements and applications. Generally coatings produced at low temperature will be less well bonded than those produced at high temperatures; in such cases intermediate layers have been used successfully. However, many CVD coatings are produced for conversion into free-standing shapes, often by mechanical separation, and in these circumstances a poor bond is required. This can usually be achieved by proper choice of substrate.

CVD COATINGS AND FREE STANDING CVD COMPONENTS PRODUCED AT FULMER RESEARCH LABORATORIES

Coating Material	Plating Vapours and Deposition Temperature (°C)	Coating Material	Plating Vapours and Deposition Temperature (°C)
*Graphite	CH_4/H_2 2200 – 2400	*†Boron Nitride	BCl_3/NH_3 1750 – 1950
*Tungsten	WF_6/H_2 400 – 600		BF_3/NH_3 1750 – 1950
	WCl_6/H_2 900 – 1100	*Boron Carbide	$BCl_3/H_2/CH_4$ 1200 – 1400
*Rhenium	ReF_6/H_2 250 – 500	*Silicon Nitride	$SiF_4/H_2/NH_3$ 1200 – 1400
	$ReCl_5/H_2$ 950 – 1100		$SiCl_4/H_2/NH_3$ 1200 – 1400
	$ReOCl_3/H_2$ 950 – 1100	Silicon Dioxide	SiH_4/O_2 h.f. plasma
Tantalum	$TaCl_5/H_2$ 1000 – 1200	Aluminium Oxide	$AlCl_3/H_2/CO_2$ 1200 – 1400
	$Ta/Cl_2/H_2$ 1000 – 1200	*Zinc Sulphide	Zn/H_2S 500 – 700
*Aluminium	alkyl 240 – 270	(Gold)	Aerosol Spray R.T.
Tungsten Carbide (W_2C)	$WF_6/H_2/C_6H_6$ 400 – 550	Diffusion Coatings:	
Titanium Carbide	$TiCl_4/Ti/H_2/CH_4$ 600 – 1000	Aluminized Siliconized Boronized Chromized	Halide-activated Powder Packs 800 – 1100 With Pressure Pulsing
Titanium Nitride	$TiCl_4/Ti/H_2/N_2$ 800 – 1000		

* Also produced as free-standing shapes. † Routinely produced by Fulmer for sale in free-standing shapes.

All the coating materials itemized in the table have been studied in depth. Some of the more recent or important ones are further summarized in the text.

MAJOR CVD PROJECTS

DIFFUSION COATINGS BY PRESSURE PULSE METALLISING

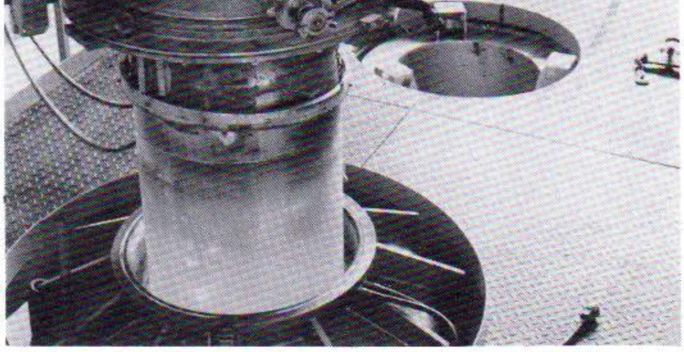
A recent major development undertaken by Fulmer in collaboration with the National Gas Turbine Establishment has led to a greatly improved technology for applying high temperature oxidation-resistant diffusion coatings to both the external and internal surfaces of gas turbine blades. The new technology is based upon a modification of the conventional pack cementation method of coating. Instead of submerging blades in the heated, halide-activated powder pack, the blades are mounted out of contact with the pack, usually above it, whilst the deposition chamber is subjected to a cyclical variation in pressure. The "throwing power" of the active vapours is substantially increased with the result that surfaces which hitherto were not readily accessible to the coating vapours, such as internal channels, can now be effectively coated. Excessive halide depletion due to pressure cycling is avoided by modification of pack constitution and composition. The process has been tested in a large development plant capable of aluminising up to one thousand blades at one time. The new process offers a number of advantages over the conventional pack process:

Improved coating uniformity
Improved coating of poorly accessible surfaces
Less build-up of cating at edges
No damage to components by powder pack
Reduced process cost

The process, which has been patented, is likely to find industrial application in many diffusion coating systems, and is currently being explored by Fulmer as a means of applying improved, wear resistant, boronised coatings. This is a two year multi-client exercise with an entry fee of £10,000. Only contributors will be granted a license for the process.

For further information contact:

Mr. C. Hayman, Fulmer Research Laboratories.

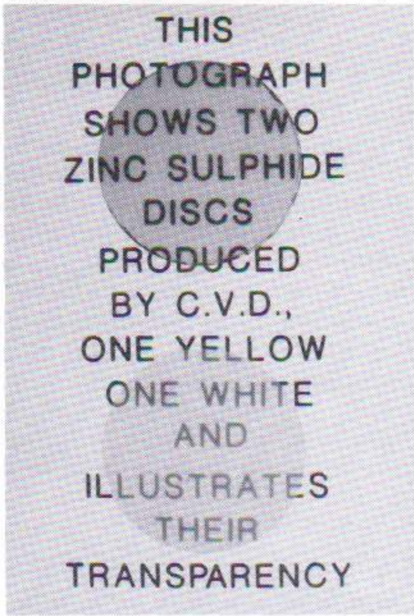


Retort of Pulse Aluminizing Plant

ZINC SULPHIDE WINDOWS

There is at present considerable interest in the growth of polycrystalline deposits of zinc sulphide and other chalcogenide compounds produced by chemical vapour deposition. Thick (10mm) deposits of these materials in the form of domes or flats are attractive as windows which transmit well in the infrared.

In a collaborative programme, in-depth studies have been made to establish basic parameters for the growth of CVD zinc sulphide of good I.R. window quality. The studies have defined conditions for the fabrication of two types of zinc sulphide plate – a somewhat brittle yellow type characterised by an I.R. absorption at 5 microns and a less brittle white material which does not display this absorption. Further studies are being made towards establishing a suitable technology for the production of zinc sulphide domes and flats.



CVD Zinc Sulphide

HIGH PURITY SILICA COATINGS

Recent studies have demonstrated the feasibility of applying silica coatings to industrial silica ware to produce a high purity surface suitable for the growth of electronic materials. The coatings were applied from a gaseous mixture of high purity silane and oxygen in the presence of an R.F. (27 MHz) plasma. Good quality glassy coatings of about 100μ thickness and of good compatibility with the substrate glass have been successfully produced.

GOLD COATING PROCESS

An aerosol spray technique for applying very thin (1000 A) coatings of gold to various substrate materials, has been developed. The process, although not strictly CVD, operates at ambient temperature and can be used to coat internal and external surfaces of large surface area (several square feet) with a conducting layer of pure gold in about one minute.

TUNGSTEN

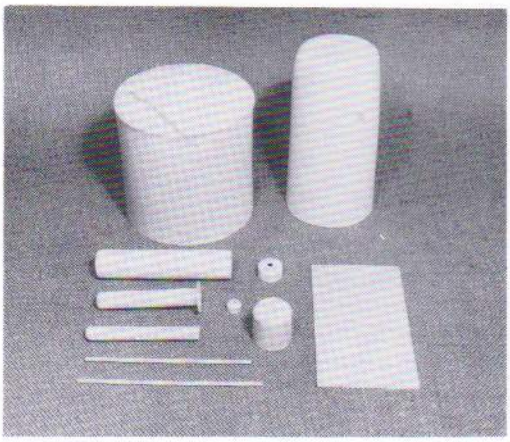
Tungsten (m.p. 3410°C) is very conveniently deposited from mixed tungsten hexafluoride/hydrogen vapours at temperatures above about 400°C. The process has been used to apply very thick coatings to rocket nozzle chokes. The CVD route has also proved attractive for the production of free-standing shapes, e.g. tungsten crucibles and tungsten tubes, in diameters ranging from 1 to 10mm.

PYROLYTIC BORON NITRIDE

Anisotropic pyrolytic boron nitride is a high temperature ceramic material produced at about 1900°C from a vapour mixture of boron halide and ammonia. It is usually deposited on to graphite moulds to form coatings of about 1 mm thickness. These are then released to produce free standing shapes, e.g. crucibles, tubes, plate. A production unit for the manufacture and sale of the materials was set up some years ago. Recently the unit has been relocated and extended and is now producing a range of products. Some of these are designed to individual customer's requirements.

Properties

- Good strength at high temperature
- Excellent thermal shock resistance
- Good chemical stability
- Impermeable to gases and liquids
- Electrical insulator of high dielectric strength
- High purity
- Highly orientated hexagon layer structure
- Slightly flexible, readily machinable



Pyrolytic Boron Nitride Ware

Applications

- Containers for the growth of materials
- Sub-components of molecular beam cells
- Sub-components of molecular beam furnaces
- Helix support rods of travelling wave tubes

RHENIUM

Free-standing components in rhenium, particularly small rhenium nozzles and narrow bore tubes, are important in the construction of resistojet motors for use in aerospace applications. The use of rhenium is dictated by the need for a high melting metal, room temperature ductility and compatibility with hydrogen-containing vapours. The value of CVD rhenium can be related to the extreme difficulty of producing such shapes by conventional metallurgical techniques. In the Fulmer process, rhenium shapes are produced by the hydrogen reduction of rhenium chloride at about 1000°C, the halide vapour being generated by in situ chlorination of the metal. Deposition is made on to mandrels which can subsequently be removed by dissolution in acide.

ALUMINIUM

CVD aluminium coatings of high purity have been produced by the low temperature (250°C) thermal decomposition of tri-siobutyl aluminium and di-isobutyl aluminium hydride vapours. The coatings are also ductile and very impermeable to gases and liquids, and may be recommended for use on components which are required to operate for long times in corrosive environments, e.g. sea water.

TUNGSTEN CARBIDE

By a patented Fulmer process, a hard wear resistant coating of CVD tungsten carbide (W_2C) is applied to steel components at sufficiently low temperature to prevent thermal degradation of the steel. Deposition is achieved from a vapour mixture of tungsten hexafluoride, hydrogen and benzene at a temperature of about 500°C, which is approximately 500°C lower than that required for the deposition of titanium carbide. The coating, which is extremely hard (~2500 DPH) is applied over a very thin layer of electroless nickel, which is used to provide good bonding. The process can be used to provide relatively thin coatings of a few microns, or somewhat thicker coating~50 microns, which can subsequently be machined to a fine finish, as for example in gauging tools. So far the coating has performed best in low stress applications.

Further information on CVD Coatings: Mr. C. Hayman, Fulmer Research Laboratories.

PIEZOELECTRIC AND PYROELECTRIC POLYVINYLIDENE FLUORIDE (PVdF) FILMS

For some years there has been considerable interest in piezoelectric and pyroelectric polyvinylidene fluoride (PVdF) film for advanced electronic devices. Commercial introduction of such devices and R & D in this field has been hampered because of the limited availability of the film.

Yarsley Technical Centre, with its expertise in polymer films technology, undertook a project to develop processes for the manufacture of PVdF film and so create an indigenous U.K. source of the material available at a reasonable price. The project was sponsored by a consortium comprising major U.K. electronic companies, government departments and state-owned industry, all of which wished to use PVdF film.

As a result of this project, and following extensive trial manufacture, production facilities have been set up for the manufacture of piezoelectric and pyroelectric electroded PVdF films. Unpoled, unmetallised films are also available. These uniaxially oriented films exhibit excellent piezoelectric and pyroelectric properties and are physically robust. Ageing characteristics are believed to be superior to all commercial PVdF films previously available.

Applications

Polyvinylidene fluoride is a thermoplastic fluorocarbon resin which, when mechanically stretched and then polarised in an electric field, is rendered both piezoelectric and pyroelectric. The mechanism for piezoelectricity is thought to be a ferroelectric-like response based on net alignment, through polarisation, of the highly polar carbon-fluoride bonds in one of the crystalline forms of PVdF.

Since PVdF can be prepared as a flexible thin film which may be of large area, it can be used to construct novel types of transducer and other devices not previously possible using conventional single crystal and ceramic materials. It is also tough and chemically inert. Its high dielectric strengths and thus high input capability for electrical power results in maximum electrical power per unit volume approximately five times greater than PZT ceramics in pulsed applications. In receiving transducers, even greater advantages are possible (up to about 20 times, depending upon geometry and mode of operation).

These and other properties, including low mechanical and acoustic impedance, thermal stability and moisture resistance, give rise to a range of applications which includes the following:

Electroacoustic transducers (stereophonic equipment)
Underwater transducers
Microphones and headphones
Acoustic emission sensors (non-destructive testing)
Biomedical sensors
Infra-red sensors (fire alarms, intruder detection)
Impact measuring devices
Pressure sensing devices (e.g. safety systems)
Traffic sensing devices
Voltage-generating pressure switches
Strain gauges
Ultrasonic imaging
Thermal imaging and laser beam profiling
Accelerometers

Evaluation samples and further information on piezoelectric and pyroelectric PVdF films, which are now available on a commercial basis, can be obtained from

Further information: Mr. M.H. Elson
Yarsley Technical Centre (Ashtead)

IFWIM DATA AND REINFORCED PLASTICS

Yarsley Technical Centre has considerable experience of testing and developing reinforced plastics and products. More recently, Instrumental Falling Weight Impact Machine (IFWIM) test apparatus has been developed to assist in this work.

IFWIM testing produces results that are sensitive to many material variables. Consequently much interest has been shown by the reinforced plastics industry in the use of IFWIM testing for both the development of materials or products and for quality control. But the sensitivity of the test can also lead to much subjective interpretation when using the data for practical applications.

Yarsley believe that the reinforced plastics industry is not making the fullest possible use and scope of IFWIM testing, specifically, a) the results are capable of greater quantification than is currently carried out; b) there is no published information on the testing of different materials under similar conditions which would allow a broad understanding of how commonly-used reinforced plastics perform under instrumented impact testing; c) it is necessary to compare instrumented impact test results with other test methods, especially acoustic and vibrational NDT techniques.

Yarsley is therefore proposing a programme of work to meet the above objectives.

It should be emphasised that the objective of such work is to enable instrumented impact testing to be introduced more rapidly in to R & D and QC departments in the reinforced plastics industry. The understanding of the fundamental fracture-behaviour in these situations is considered to be a separate matter for which a longer time-scale is required.

Further information:
Mr. R.N. Trubshaw
Yarsley Technical Centre,
(Redhill)

SCRUB-RESISTANT INTUMESCENT PAINT FOR GRP BOATS

Ideally intumescent paint should not differ from a good quality conventional paint, to provide the protective, serviceable, and aesthetic properties on the surface. In addition, it must swell up in the fire, to produce an effective insulating multi-cellular layer of an adequate non-flammable foam, thus providing fire protection to the substrate and increase the chances of containing the fire. Unfortunately, most conventional intumescent systems contain water-soluble/sensitive materials which make them lose their intumescent properties after weathering or scrubbing.

Special Requirements for GRP Boats

The Navy has special requirements for GRP M.C.M.V.'s which limits the type of vehicle/solvents which can be used in formulating the paint. Additionally it has set performance requirements which cannot be easily achieved with conventional formulations.

Development of Scrub-Resistant Paint

The Yarsley Technical Centre has been working on this development for some years now. The first approach was to microencapsulate water-sensitive ingredients of the intumescent system. This technique, developed at YTC effected some improvement, but not sufficient to warrant a change-over from the usual formulation.

The present programme is aimed at developing new materials, multi-functional additives, which would act as intumescent agents as well as resin/vehicles. This involves a more fundamental study of the mechanism of intumescence and the properties of materials.

Further Information: Mr. W. Mikucki, Yarsley Technical Centre (Ashstead).

SEMINARS

Project Planning and Control for Research Managers

2E 500/116 6 - 7 Oct. 1983
2E 500/117 1 - 2 Dec. 1983

The seminar fee is £250 (+ VAT for UK participants) inclusive of accommodation and meals.

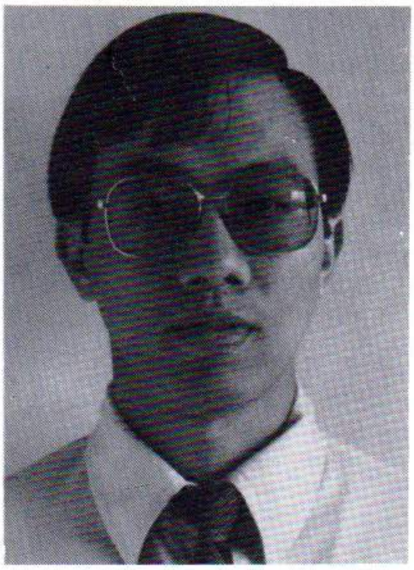
Further information from:
D.G.S. Davies, Fulmer Research Institute Ltd.

NEE LAM LOH

Nee Lam Loh has been appointed as Technical Manager Designate of the Metallurgy Division of Fulmer Research and Development (Singapore) Pte Ltd. to succeed Dennis Baxter who returned to the U.K. in August.

Dr. Loh received an honours degree in Engineering Science and Industrial Management, and then spent three years doing research at Liverpool University on the Plasma Nitriding of 722 M27 steel.

For the last two years he has been engaged in material consultancy and failure analysis as an Executive Metallurgist with the Singapore Institute of Scientific and Industrial Research.



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