Metal-Metal Nanocomposite Coatings with Enhanced Mechanical Properties

(Adrian Leyland and Allan Matthews)

Project Background

The EPSRC Individual Grant Review Form (which this report accompanied) pertained to expenditure incurred at Sheffield University during the period 01/10/03 to 31/07/04. However, project GR/N03495 was originally issued at Hull University, with a value of £160,870, for an intended 36 month period (01/06/00 to 31/05/03). The project was subsequently extended by three months at Hull to 31/08/03 (within the same agreed budget), to accommodate a 36-month PhD studentship appointment (Mr. C. Tsotsos) made on 01/09/00. A move by both investigators from Hull to Sheffield University in January 2003 instigated a project transfer, which in effect occurred on 01/06/03, shortly after the original end date (once Hull's final expenditure statement was lodged with EPSRC). There was however some further overlap, mainly to allow the PhD student at Hull to complete. Having gained his PhD award, the student subsequently transferred to Sheffield (as a PDRA) on the balance of funds available (£12,284), from 01/10/03 until the new project end date of 31/07/04. Since the large majority of expenditure on GR/N03495 occurred at Hull, this report reflects the research work performed at both Sheffield and Hull, between June 2000 and June 2004 (when the PDRA appointment at Sheffield ceased). Furthermore, it should be noted that, subsequent to the award of GR/N03495 at Hull, Dr. M.A. Baker of Surrey University obtained funding under Fast Stream award GR/R07981, to characterise, primarily by XPS and TEM, some of the coatings produced in this project. Both parties gained mutually-beneficial collaboration from this parallel funding provision (between 16/07/01 and 15/01/03) and, in discussing our project outcomes below, we acknowledge the input of the Surrey team in developing an improved understanding of the structure-property relationships in our metal nanocomposite coatings.

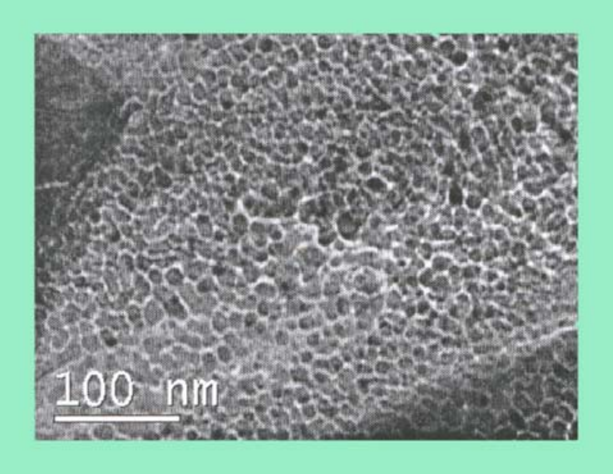


Figure 1 TEM bright-field plan-view of CrCu(N) coating nanostructure

Scientific Context

Conventional wisdom has for some years dictated that high hardness is the main material requirement when designing surfaces to resist wear. On this basis, ceramic coatings are an obvious choice to improve the wear behaviour of engineering materials, since many ceramics possess both high hardness and chemical inertness. Furthermore, such coatings (when applied to easily-machined metallic substrates) in principle circumvent the shortcomings of bulk ceramic materials, such as low fracture toughness, poor machinability and inadequate tensile strength & ductility. This epitomises how Surface Engineering has developed as a new technological discipline over the last 25 years in which, ideally, a bulk material (the 'substrate') and a coating are combined in a way that provides a cost-effective performance enhancement of which neither would be capable alone. The recognition of Surface Engineering as a field in its own right has arisen largely through the emergence of plasma-assisted vacuum coating processes, such as physical vapour deposition (PVD) – allowing wear-resistant ceramic thin films such as titanium nitride (TiN) to be deposited on a wide range of industrial tooling. The result of such developments has been a step-change in industrial productivity and manufactured product quality. So-called 2nd- and 3rd-generation ceramic coatings have recently been developed (with, in many cases, nanolayered or nanocomposite structures), to further extend tool performance – the objective being to increase coating hardness further, or extend the hardness capabilities to higher temperatures.

However, in many prospective applications other than cutting tools, where different wear regimes are often encountered concurrently and the substrate stiffness and strength may be comparatively low, ultrahard ceramic films (which tend also to exhibit high stiffness) are rarely the ideal solution. To achieve weight savings, retain a high specific strength and, at the same time, meet stringent legislative requirements, industry is looking increasingly to use composites and light-alloy materials in their products. The range of applications for such materials is growing, but is nevertheless constrained by their poor wear characteristics. Vapour-deposited thin films present a potential solution, but hard, stiff ceramic films are fundamentally mismatched to these soft, low elastic modulus materials. As has been demonstrated previously, by bearing designers and polymer tribologists, a bulk materials approach to wear which utilises both the hardness (H) and the elastic modulus (E) of the material (ie. an H/E ratio parameter), gives more consistent and predictable results in ranking wear performance across a diverse range of engineering materials. In this respect, a high H/E ratio is desirable, since this implies a longer 'elastic strain to failure' (ie. improved resilience) for the material. Unfortunately this approach was, until recently, neglected by many materials tribologists – and almost completely ignored by the tribological coatings community.

Our experiences prior to this project, in comparing metallic and ceramic PVD coatings, made us aware that in many tribological contact situations other than pure sliding (such as impact, abrasion, erosion and fatigue), the hardest coatings rarely perform best – and it is often metallic films which (if sufficiently hard) give superior results, due primarily to a combination of resilience and toughness more closely matched to the substrate material properties and requirements. (In essence, such coatings tend inherently to be more 'damage tolerant'.) The main drive for this research project was therefore to explore the concept of metallic nanostructured films (Figure 1), where the hardness could – in principle (through grain refinement and appropriate alloying) – be raised to the levels exhibited by ceramics, whilst retaining the elastic properties of the metal constituents (to minimise coating/substrate 'strain mismatch' under load).

In formulating such ideas, we realised firstly that few, if any, academic researchers worldwide in the field of coatings tribology were paying significant attention to the requirements of the substrate material. Secondly, in the increasingly scientifically important area of nanostructured wear-resistant vapour-deposited films, the main objective of many researchers seemed almost invariably to be able to report extreme high hardness values, often without considering how such data might be reliably obtained, whether the empirical equations used remained valid (or whether indeed such high values were in fact important or necessary). Thirdly, in trying to understand failure mechanisms, many researchers were attempting to relate ceramic coating behaviour to a bulk fracture mechanics approach, when (for example) the basic assumption of a pre-existing crack or flaw, which would tend to grow rapidly above some ‘critical stress intensity factor’ (that a high elastic modulus would suppress), is probably not relevant to a dense, columnar, ceramic thin film on a (comparatively) low modulus metal substrate.

These considerations led to our first outcome from this project, in that we submitted a paper to the journal *Wear* (published in November 2000), in which we reviewed these (and related) issues and the current approaches used by others at that time [1]. We suggested an alternative approach to PVD coating deposition for tribology applications based more on resilience (ie. the ratio of H to E) and toughness – in the ‘engineering’ sense, of a coating/substrate system with the ability to accommodate substrate (or even coating) plastic deformation, where necessary – rather than just on hardness alone. In the few years following publication, other researchers have recognised increasingly the reasoning behind our approach, and that paper has now been cited more than 50 times (with over half of these occurring in 2004 alone). This is gratifying, in that our colleagues in the tribological coatings area – and indeed in the wider field of tribology – appreciate (and concur with) many key aspects of our approach to the subject. We have continued to develop and refine our methodology through the course of the project; this is reflected in our further publications on the subject [2-4, 6, 8, 15, 16] (and also in our Invited presentations [4a, 9a, 12a, 14a, 18a, 19a]).

Key Advances and Supporting Methodology

Mindful of the questions raised by the issues mentioned above, our first objective in the practical work programme of this project was to deposit chromium-copper PVD coatings (by unbalanced magnetron sputtering) [7, 10], since we expected the inherent low mutual solubility of these two elements to cause a short-range phase separation which would promote a nanocomposite structure of high hardness. Furthermore, both elemental materials are commonly available and are, in their own right, used routinely in traditional wear and corrosion resistant coatings (such as those produced by electroplating, for example); additionally, there remains an issue of hexavalent chromium residue disposal in hard chrome electroplating, which PVD alternatives would circumvent (eg. [5]). Also, the combination of chromium and copper would (we expected) tend to produce a coating with an elastic modulus similar to that of steel (ie. of the order of 200GPa), in line with our objective to more closely match coating/substrate elastic behaviour.

Next, we incorporated nitrogen into the chromium metal (in supersaturation), to increase ‘lattice friction’ and raise hardness further. The outcome was metal coatings with, typically, a hardness of around 20GPa, but an elastic modulus near 200GPa (ie. similar to that of steel) and thus H/E ratios several times higher than those of many ceramic films. Through our collaborations with Surrey University, we also developed a model to describe how the nanostructure of such coatings varied with composition [10, 16a]. The earlier coatings – although promising – did not appear to possess the nanocomposite structure we predicted would give the best properties (ie. nitrogen supersaturated chromium nanograins surrounded by amorphous copper). Although we did not expect free copper to be seen in XRD analysis, XPS data should give an indication of the presence of Cu-Cu bonding – and this was generally not the case [7]. It appeared that most (if not all) of the copper was incorporated in the bcc chromium lattice – even at Cu concentrations as high as 35at.%. In our later work [10], we modified the deposition system to incorporate a radiant heater and a hot negatively-biased tungsten filament. This allowed us to control both the substrate temperature and current density in a wider range, and with less inter-dependency to other deposition parameters. Unlike Ref. 7, where the substrate temperature was barely 200°C, the subsequent work [9-12, 14, 17] was carried out in the 300 to 350°C temperature range (at approximately double the substrate current density), with exciting results. An underlying theme of the coating deposition work was equipment development. For example, as well as requiring more flexibility over deposition parameters than is possible in conventional magnetron sputtering systems, we needed to be able to explore different coating compositions quickly and effectively. To achieve this, we harnessed techniques that we were developing for TiAlBN ceramic nanocomposite coating investigations where, rather than (say) using single, composite sputter targets with fixed compositions (as other researchers were doing), we placed two elemental targets – ie. chromium and copper in this case – at 90° to each other, locating the substrate holder at 45° to each target (at a distance of ~25cm from the centre line of each. By careful selection of parameters,

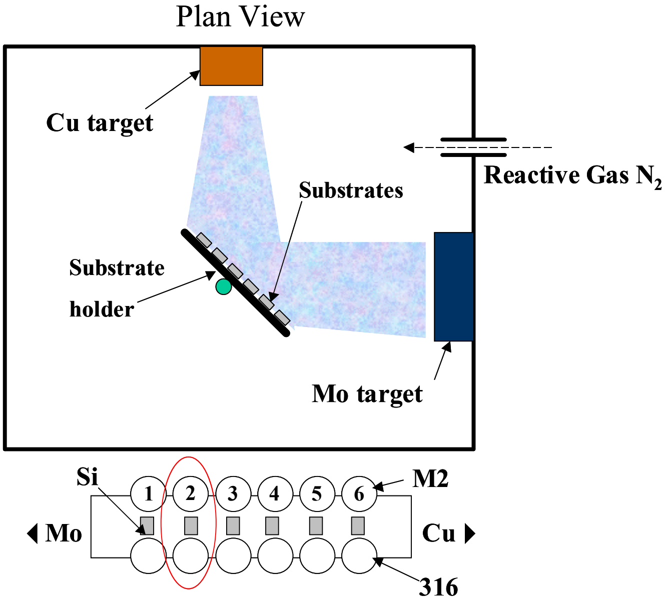
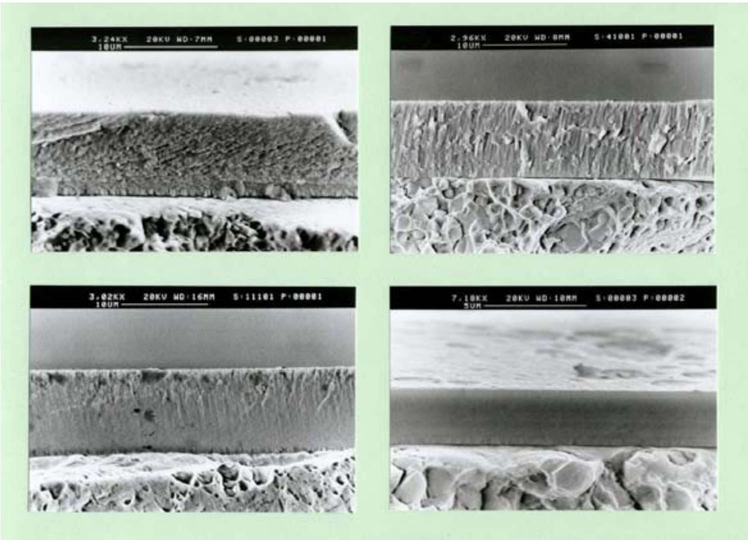


Figure 2 Schematic plan-view of typical sputter PVD chamber configuration

this allowed us to place up to 6 sample sets on the substrate holder at different positions between the targets to, for example, deposit CrCu(N) films with 6 different Cr/Cu ratios (at a given nitrogen gas flow rate) in a single deposition cycle – usually without significant changes in coating thickness (or substrate current density) from sample to sample. This 'combinatorial' approach allowed us to explore many more coating compositions and types than would otherwise have been possible. A schematic diagram of a typical deposition chamber layout for our work is shown in Figure 2. As well as depositing coatings using the unbalanced magnetron sputtering technique, we verified the possibility to deposit chromium-copper and chromium-copper-nitrogen films using a twin electron-beam PVD method, in which the two metal constituents were placed in separate crucibles and concurrently evaporated. (The evaluation of these films is continuing at the moment, and we intend to publish the results soon.) Such methods lend themselves to high-rate coating deposition and the capability to produce thick films with (for example) improved corrosion protection capability.

Figure 3 Cross-sectional morphology changes in MoCu(N) films with increasing N



Another task performed was the deposition of molybdenum-copper and molybdenum-copper-nitrogen films [9], again demonstrating how the coating structure changes with varying nitrogen gas flow rate, and the encouraging combinations of hardness / toughness which can be obtained. In this work we also demonstrated the capability to deposit relatively thick films – even by magnetron sputtering. As Figure 3 illustrates, it was possible (with careful grading of copper content above the coating/substrate interface) to produce adherent MoCu(N) coatings with thicknesses in excess of 10µm, at a typical deposition rate of 6-7µm/hr. Conventional ceramic PVD coatings suffer from high compressive stress which (although sometimes beneficial at 2-3µm thickness) tends to induce coating spallation above 6-8µm. Furthermore, it is difficult to reactively deposit PVD ceramic films with good stoichiometry and structure at rates much higher than 2-3µm/hr – even at a deposition temperature of 500°C. For our MoCu(N) coatings (deposited at ~325°C), the only limitation to achieving deposition rates higher than 10µm/hr was target overheating. This was however a 'self-imposed' limitation, in that we needed to change sputter targets frequently – and therefore did not use a brazed backing plate to aid target cooling. The target powers we used were consequently barely one-third of the theoretical system capability; metallic coating deposition rates of up to 20µm/hr thus appear to be realistically attainable from sputter PVD techniques, whilst at the same time achieving 'ceramic' hardness values in excess of 30GPa [9]. Such capabilities provide a challenge to corrosion-resistant electroless and electrodeposited hard coating methods that ceramic PVD nanocomposite films are not able to match.

We found in (particularly) our chromium-copper-nitrogen work that several of the coatings contained amorphous phase constituents, which led us to consider the theory and principles of bulk metallic glass (BMG) formation, promulgated initially by Hume-Rothery around 60 years ago, and developed by others in the intervening years. We decided to add both boron (as we originally intended) and titanium to this system, with the result that X-ray amorphous CrTiCu(B,N) films were produced over a wide range of chromium/copper composition ratios (see Figure 4), giving hardness values exceeding (in some cases) 30GPa [11]. (The addition of these elements was achieved by replacing the middle segment of a – three-segment – rectangular chromium target with a titanium diboride segment.) Remarkably, vacuum annealing of such films at temperatures up to 600°C provided an unexpected increase in hardness – approaching 40GPa [12, 14]. The coatings remained largely X-ray amorphous – although we believe that structural relaxation and partial nanocrystallisation occurred. Since many high-strength BMG compositions are based on zirconium, we also carried out some preliminary work to look at Zr-based metallic nanocomposite films with additions of (for example) yttrium and/or tin [11a, 15a, 17a]. The objective in this case was to take advantage of the sub-70GPa elastic moduli (and of course the low miscibility and high glass-forming ability) of such combinations of elements, to develop even lower modulus hard coatings more suitable for light-alloy applications. This work is continuing through PhD project Studentships at Sheffield (with EPSRC funding, and other support), and we hope to submit for publication some of the findings later this year.

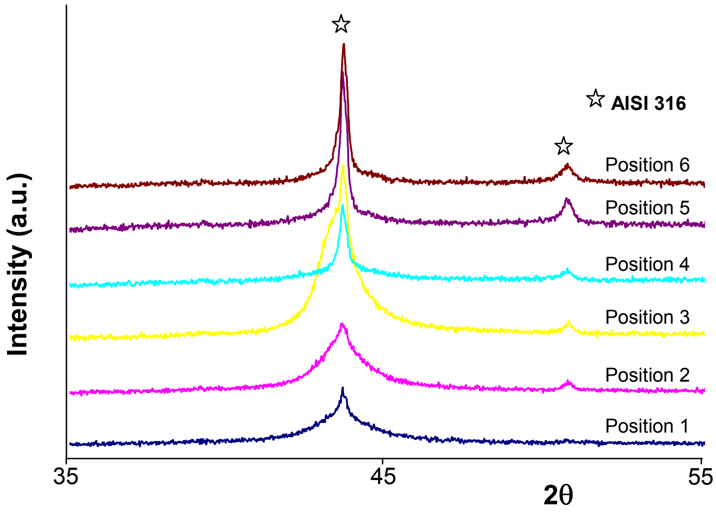


Figure 4 XRD patterns of CrTiCu(B,N) coatings showing uniformly amorphous structure with changing Cr / Cu ratio (position numbers relate to those indicated in Fig. 2)

NB: Together with our colleagues at Surrey, we applied a wide variety of investigative techniques to our coatings, including SEM, TEM (including EELS), XPS, AES, XRD; Knoop microhardness testing, Vickers and Berkovich nanoindentation hardness/modulus testing; pin-on-disk, reciprocating-sliding, ball-on-plate impact and micro-abrasion wear testing; etc. Limitations of space prevent full descriptions of all the electron microscopy, chemical and structural characterisation, mechanical and tribological testing & evaluation carried out; however, these aspects are covered in more detail by the papers mentioned in the publications list on page 6.

Project Plan Review

This project covered a difficult period in which the entire research group of the Investigators was relocated from Hull to Sheffield University. The possibility for disruption to the work programme was therefore considerable. Nevertheless, through careful planning and by ensuring an 'overlap' of activity in each location, the project proceeded smoothly (and to budget), without significant hindrance to the scientific research. Almost all intended objectives (and others besides) were fully accomplished. Measured against the objectives stated at the outset, the EB source material trials envisaged in objective 3 were perhaps somewhat less extensive than originally planned. Preliminary twin-EB studies using elemental chromium and copper source materials were however performed using, without charge, the equipment and facilities of Tecvac Ltd, Cambridge (acknowledged with thanks), confirming the potential to deposit Cr-Cu and Cr-Cu(N) nanostructured films by high-rate methods. Furthermore, additional work performed under this project funding (adding both boron and titanium to the Cr-Cu-N ternary system) led to our discovery of the capability to produce hard CrTiCu(B,N) glassy-metal coatings, which could be post-coat vacuum heat-treated to further increase hardness. Such a result is in complete contrast to the findings in most other nanocomposite coating research worldwide, where post-coat heat-treatment generally leads to relaxation of (high) compressive stresses, with a consequent substantial reduction in measured hardness. This leads to the exciting prospect of ‘ultrahard’ (ie. ≥40GPa ‘true’ hardness), low modulus films, with previously unattainable levels of resilience and toughness – which challenge conventional assumptions in regard to tribological coating material selection. With specific regard to novel PVD evaporant and sputter target materials, our work under this project has triggered new international collaborations with (for example) colleagues at Moscow State Institute for Steel and Alloys (under Royal Society funding), who possess both a unique capability in Self-Propagating High-Temperature Synthesis of complex-alloy coating source materials (which lend themselves to both sputter and electron-beam PVD coating methods), and a common interest in nanocomposite coatings development. We believe that our joint knowledge and expertise should soon lead to the commercial exploitation of the novel coating materials and concepts arising from the work reported here.

Research Impact and Benefits to Society

The project has achieved a significant improvement in the fundamental understanding of nanostructured coatings in general, and of the applications-related substrate/coating requirements in tribological thin films. Our findings are causing considerable interest in the research community – both amongst tribologists seeking to eliminate wear, and amongst materials scientists involved in bulk nanostructured and ‘glassy’ metals research, where existing approaches still exhibit difficulties in achieving fully-dense nanostructured materials, from which reliable property data can be extracted. PVD thin film technology allows fully-dense material compositions to be formulated which are difficult or impossible to synthesise by other methods but, conventionally, PVD coatings are too thin to provide a sufficient quantity of material from which bulk property data can be obtained. The prospect to produce much thicker PVD metallic films (eg. through EB evaporation), or to translate our expanding knowledge of source material preparation to other methods (such as electrolytic deposition and treatment methods), can be capitalised on by the bulk metallic glass and nanostructured materials research communities. The wider use of light alloys (e.g. in automotive and aerospace applications) necessitates the development of suitable, low modulus, wear-resistant thin films. At present, the industrial market for PVD processes in coatings tribology remains low, at less than 3% by value (and substantially less by volume) of the total Engineering Coatings market. The development of resilient and tough coatings (such as those investigated here) is becoming an increasingly key aspect in satisfying industrial requirements. Many further potential applications exist in other key technology areas (such as power generation plant, and biomedical materials & devices, for example).

Further to our statement at the time of award, we therefore see the potential beneficiaries falling into three groups. Firstly, coating manufacturers and producers; secondly, coating end users and thirdly, in addition to our original perceptions, the wider academic and industrial research communities – as indicated in the preceding paragraph. Although our work has centred on PVD deposition techniques, we anticipate that some of the findings will be relevant to many other treatment processes (as discussed above, and in the final section below). The ability to reduce the substrate temperature during plasma-based deposition – and to deposit coatings at sufficiently high rates (preferably by ‘non-reactive’ methods) – are still particularly important issues, as this remains key to widening the range of applications for metallic nanocomposite coating technology, to include many of those currently served by traditional processes such as electroplating and thermal spraying – where a number of difficult environmental issues (eg. cadmium coating replacement) remain largely unresolved.

Explanation of Expenditure

The project was completed within budget. This was achieved despite conditions in which the original project had to be relocated from Hull to Sheffield in its critical final year, resulting in a need to transfer equipment and staff to the new location. There was a substantial period of overlap (which extended beyond the original project end date), and the necessary logistical arrangements were achieved through effective coordination between both Academic institutions and EPSRC. Technical and Secretarial staffing appointments (12 months and 2 months FTE, respectively) were made to plan; however some changes were made in regard to Research staff. Our original funding request was for one PGRA (Mr. M.C. Joseph) at 36 months FTE. However, at 01/06/00 Mr. Joseph remained employed on a RAIS extension to a previously awarded EPSRC/DTI LINK project, until February 2001. To circumvent this difficulty, we appointed (with EPSRC's approval) a PhD student (Mr. C. Tsotsos) from 01/09/00, having initiated the project on 01/06/00 by appointment of the Technician (Mr. J. Robson) to prepare coating and test equipment. To support Mr. Tsotsos in the initial stages of the project, we also appointed a PDRA (Dr. A.D. Wilson) for 6 months (September 2000 to February 2001) at 0.5 FTE. On completion of the LINK/RAIS project, Mr. Joseph was subsequently appointed to GR/N03495 at 24 months FTE from March 2001. Mr. Joseph thus remained on this project at Hull until February 2003; he then took up an industrial appointment – as did Dr. Wilson at around the same time. After the Investigators moved to Sheffield in January 2003, equipment remained at Hull for several months, whilst contractual procedures were dealt with. Mr. Tsotsos also remained at Hull to complete his PhD studies; he successfully defended his Thesis in October 2003 and transferred to Sheffield as a PDRA appointment for 9 months (October 2003 to June 2004) on the re-issued balance of project funds. After a further 3 months of Postdoctoral research at Sheffield, Dr. Tsotsos also took up an industrial appointment (October 2004). Despite the complexity of the situation, the outcome to the project was a total of approximately 70 months FTE Research input (36 months PhD studentship, 24 months PGRA and 10 months PDRA), against the original 36 months PGRA requested. The Investigators believe therefore that excellent value was gained from the project funds, and this is reflected in, for example, the high (and continuing) publications output, the industrial destinations of Research Staff and follow-on collaborations arising from the work.

Further Research & Dissemination Activities

As indicated above, our academic and industrial research collaborations arising from the work are extensive and continue to grow. Our collaboration with the team at Surrey University continues through another EPSRC project (£348,750 to Sheffield; GR/S05632) looking at low-temperature oxide film growth, and our joint participation in EU FP6 Coordination Action project CA-505549-1 (DESHNAF), which has the specific brief to discuss and disseminate information on current approaches to plasma-assisted deposition of hard nanostructured coatings, to both academics and industrialists, across Europe. Further joint bids with Surrey to EPSRC and the EU on the topics of evaluating the performance, properties and importantly the (difficult to obtain) short-range structural/ compositional characteristics of nanocomposite thin films, are planned for early-to-mid 2005.

Many of the concepts underlying our fundamentally new approach to tribological coating design are now incorporated into more widely-disseminated training courses and literature; for example, the IGDS modular MSc on 'Surface Design and Engineering' for graduate engineers in industry, and our textbook chapters (published by IMechE and Kluwer [16, 17]) discussing the topic. As well as transfer of information to UK industry through the subsequent employment of our project research staff, we are also engaging more widely with UK industry through other schemes, such as Knowledge Transfer Partnerships. We already participate in two KTP projects on metallic composite piston ring coatings (jointly with the Mechanical Engineering Department at Sheffield) and on processing efficiency & alternative approaches in the heat treatment of metals (jointly with the Chemical and Process Engineering Department), and we await the outcome of a new KTP proposal with Black & Decker / DeWalt UK (submitted January 2005), on abrasion-resistant materials/coatings for drilling of steel-reinforced masonry. All three projects mentioned (and the industrial/academic partners involved) will benefit to a substantial degree from the knowledge gained in the EPSRC-supported work reported here.

As mentioned above, another outcome arising from this work is our increasingly close collaboration with the Moscow State Institute of Steel and Alloys (MISA) – initially through Royal Society FSU Joint Project funding (awarded in 2003). The institute is a leading Russian Technological University with research activities closely aligned to industrial exploitation requirements. Colleagues in the Scientific-Educational Centre of SHS at MISA have research interests in ion-assisted sputter deposition of nanocomposite tribological films (similar to our group), but are also expert in the development of novel alloy and composite materials produced by SHS. Furthermore, they have developed a new 'electro-spark coating' technique, using an expendable electrode (which can comprise novel SHS-produced material) to deposit metallic composite coatings in an atmospheric spark discharge regime somewhat analogous to that of electro-discharge machining. The equipment is portable, and can be attached to a conventional machining centre to facilitate workpiece manipulation. The process is a potential low-cost, environmentally-friendly alternative to thermal spraying (yet with some of the superior adhesion characteristics of weld hardfacing).

MISA's SHS materials are already exploited industrially, and they are keen to collaborate with us to develop new coating source materials for wear-resistant metallic nanocomposite (and biocompatible cermet) thin film deposition, which could also be exploited commercially. Additionally, such materials (particularly the metallic ones) would lend themselves to thick nanostructured coating deposition by the electro-spark technique (where we expect the coating solidification rate is sufficiently high to retain the required properties). There is thus considerable scope to exploit a new, thick nanocomposite metallic film processing method – and meet one of our main long-term objectives in the research work reported here, namely to develop commercially-viable metallic nanocomposite coating deposition techniques, as alternatives to the existing (less environmentally-friendly) thick, metallic tribological coating methods currently used by industry (eg. electroplating and thermal spraying). In respect of these 'traditional' methods however, it should pragmatically be pointed out that the SHS technique could also be adapted easily to the production of metallic nanocomposite source materials in suitable plating electrode or wire/powder spraying material forms. A further dissemination outcome, currently under discussion, is the prospect of bilateral student exchange programmes (both postgraduate research and undergraduate teaching) between Sheffield University and MISA, to facilitate knowledge sharing – both in the field of nanocomposite coatings development, and in wider aspects of Materials Science & Engineering.

Finally, we can point to 25 presentations (many 'Invited') made on our work in this project at international conferences, workshops and seminars during the project period, with more planned (see Appendix A). Venues have included Europe & Scandinavia, the USA and the Far East. Overall, the follow-on research and information dissemination activities arising from the project results are significant, wide-ranging and continue to expand.

Refereed Journal Publications

1. "*On the significance of the H/E ratio in wear control : A nanocomposite approach to optimised tribological behaviour.*" A.Leyland & A.Matthews *Wear* 246 (2000) 1.
2. "*Developments in PVD tribological coatings.*" A.Matthews & A.Leyland *Proc. 5th ASM Heat Treatment & Surf.Eng.Conf. in Europe* (2000) 235. ISBN 087170-695-4 (Gothenburg, Sweden, June 2000)
3. "*Entwicklungen bei PVD-Verschleißschutzschichten.*" A.Matthews & A.Leyland *Härterei-Technische Mitteilungen* 56/1 (2001) 5.
4. "*Developments in PVD tribological coatings.*" A.Matthews & A.Leyland *Heat Treatment of Metals* 28/3 (2001) 63.
5. "*Structure and corrosion properties of PVD Cr-N coatings.*" C.Liu, Q.Bi, H.Ziegele, A.Leyland & A.Matthews *J.Vac.Sci.Technol.A* 20/3 (2002) 772.
6. "Plasma *immersion ion implantation as a technique in duplex & hybrid processing.*" A.Matthews, A.Leyland & A.Wilson *Vacuum* 68/1 (2003) 57.
7. "*The nanostructure and mechanical properties of PVD CrCu(N) coatings.*" M.A.Baker, P.J.Kench, M.C.Joseph, C.Tsotsos, A.Leyland & A.Matthews *Surf.Coat.Technol.* 162 (2003) 222.
8. "*Design criteria for wear-resistant nanostructured and glassy-metal coatings.*" A.Leyland & A.Matthews *Surf.Coat.Technol.* 177-178 (2004) 317.
9. "*Characterisation and tribological evaluation of nitrogen-doped molybdenum-copper PVD metallic nanocomposite films.*" M.C.Joseph, C.Tsotsos, M.A.Baker, P.J.Kench, C.Rebholz, A.Matthews & A.Leyland *Surf.Coat.Technol.* 190 (2005) 345.
10. "*Evaluating the nanostructure of PVD CrCu(N) coatings.*" M.A.Baker, P.J.Kench, C.Tsotsos, P.N.Gibson, A.Leyland & A.Matthews - accepted *J.Vac.Sci.Technol.A* (2005).
11. "*Mechanical and tribological properties of CrTiCu(B,N) PVD glassy-metal coatings deposited by reactive magnetron sputtering.*" C.Tsotsos, K.Kanakis, A.Davison, A.Matthews, A.Leyland & M.A.Baker Proc. PSE2004 - accepted *Surf.Coat.Technol.* (2005).
12. "*Investigation of the nanostructure and post-coat thermal treatment of wear resistant PVD CrTiCu(B,N) coatings.*" M.Monclus, M.A.Baker, C.Tsotsos, A.Leyland & A.Matthews Proc. PSE2004 - accepted *Surf.Coat.Technol.* (2005).
13. "*Hard tribological Ti-B-N, Ti-Cr-B-N, Ti-Si-B-N and Ti-Al-Si-B-N coatings.*" D.V.Shtansky, A.N.Sheveiko, M.I.Petrzhik, F.V.Kiryukhanntsev-Korneev, E.A.Levashov, A.Leyland, A.L.Yerokhin and A.Matthews - submitted *Surf.Coat.Technol.* (2005).
14. "*Hardness and nanostructure of vacuum annealed CrTiCu(B,N) glassy-metal PVD coatings.*" C.Tsotsos, K.Kanakis, A.Leyland & A.Matthews - in preparation (2005).

Book Chapters

15. Hard tribological coatings: Developments and applications. A.Matthews & A.Leyland in: *"Total tribology: Towards an integrated approach"* (Chapter 5) I.Mech.E *'Tribology in Practice'* Series. I.Sherrington, W.B.Rowe & R.J.K.Wood (eds.) *pub.* PEP Ltd, Bury St Edmunds, UK (2002), pp 39-63. ISBN 1-86058-393-8
16. Optimisation of nanostructured tribological coatings: A.Leyland & A.Matthews in: "*Hard Nanostructured Coatings*" (Chapter 14) J.T.M.deHosson & A.Cavaleiro (eds.) - *in press* Kluwer (2005).

PhD Thesis

17. "*Development of PVD metallic nanocomposite and glassy-metal coatings.*" C.Tsotsos The University of Hull (October 2003).

Conference Presentations

Appendix A

1a. “*Mechanical properties and impact wear resistance of metallic nanocomposite coatings based on chromium.*”
A.Leyland, C.Tsotsos, A.D.Wilson, M.C.Joseph, A.L.Yerokhin, X.Nie, S.J.Dowey, M.A.Baker, A.Morley and A.Matthews
Proc. ICMCTF, San Diego, USA (April 2001).

2a. “*Mechanical and tribological wear properties of nanograined magnetron-sputtered metallic coatings based on chromium.*”
A.D.Wilson, C.Tsotsos, A.Leyland and A.Matthews Proc. ICMCTF, San Diego, USA (April 2001).

3a. “*Evaluation of galling and seizure resistance of PAPVD TiAlBN and TiAlN hard coatings.*”
M.C.Joseph, A.D.Wilson, A.Leyland, A.Matthews & J.Housden Proc. ICMCTF, San Diego, USA (April 2001).

4a. “*Directions for tribological coating development.*” A.Matthews and A.Leyland
Invited Paper: 2001 MRS Fall Meeting, Boston, USA (November 2001).

5a. “*Structure and mechanical properties of Cr-Cu-based nanocomposite coatings deposited by magnetron sputtering.*”
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