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Applications of Energy-Assistance to the formation of novel surface coatings

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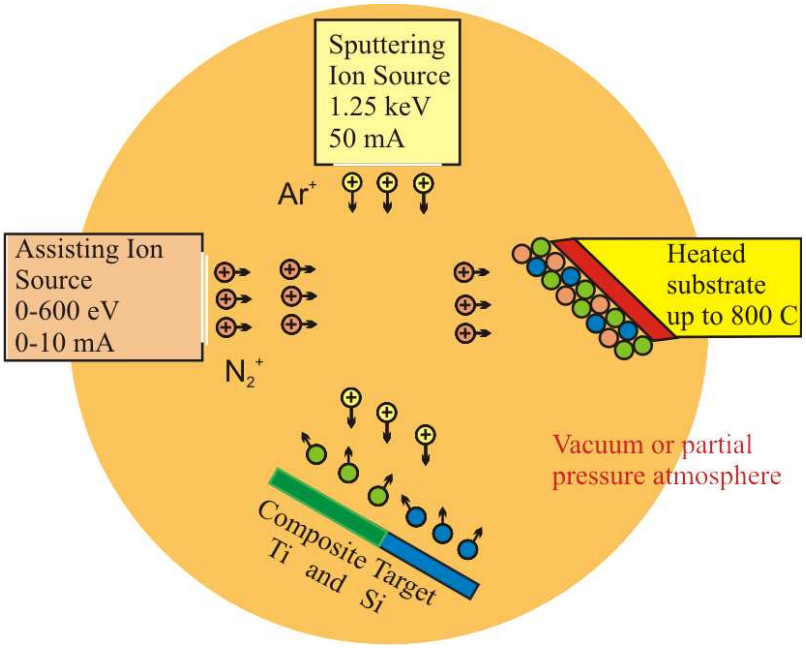
In the area of manufacturing, surface coating of materials is a widely-used process representing a multi-billion pound per annum industry. the choice of a suitable coating allows the design engineer to choose a material for its optimum bulk properties but, at the same time, tailor the surface properties for a specific application. For example, components made of iron have good mechanical strength but, because the iron surface forms an oxide, a suitable coating (usually chromium-based) is used to protect the product. Over the last decade interest has surged in the potential use of more exotic coatings with controlled micro- and nano-structure. Professor John Colligon and Dr Vladimir Vishnyakov have developed techniques for production of such coatings.

Coatings which have an appropriate microstructure not only protect the component, but also, can offer better wear, hardness, corrosion-resistance and temperature-stability than previously attainable. Attention has been directed therefore to study the influence of deposition parameters on film morphology and microstructure. It is known that energetic bombardment of a material during deposition onto a substrate completely changes the nucleation and growth process of the resulting coating. This so-named Energy-Assisted Deposition (EAD) provides additional energy as a result of collisions with the atoms being deposited which leads to changes in microstructure, phase and composition of the coating formed. The added energy is often provided by bombardment of the growing film by an energetic ion beam. The ion bombardment can also be provided by depositing in a plasma system with the substrate at a negative voltage to attract positive ions. A schematic diagram of a typical energy-assist system is given in Fig 1.



One of the first recorded suggestions of the effects of energy-assistance on film properties is seen in a UK patent filed by Berghaus in 1938 on “Improvements in and relating to the coating of articles by means of thermally vaporised material” (1). The main practical demonstration of this process was first reported in the 1960’s by Mattox, who referred to it as “Ion Plating” (2). It was immediately clear that the density of coatings and their adhesion to a substrate using energy-assistance was vastly improved. Electron microscopy studies showed that the fundamental growth process, and hence film morphology, could be controlled simply by increasing the bias on the substrate being coated, i.e. by varying the degree of added energy.

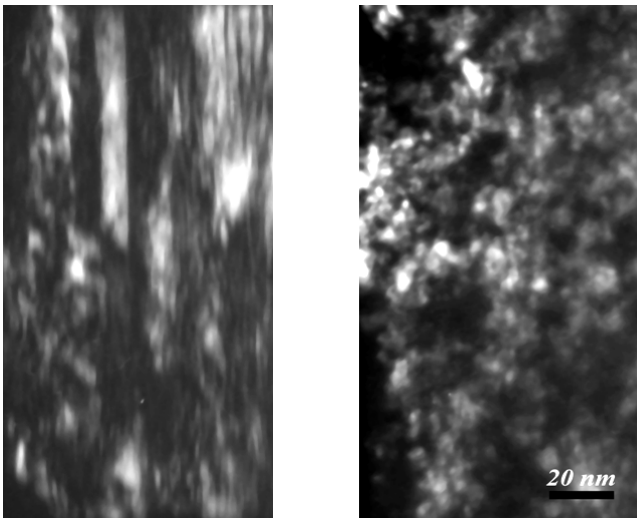
The effects of such additional energy on film morphology were already clear in the 1970’s from the work of Movchan and Demchisin who showed that the morphology of coatings formed was related to the ratio Ts/Tm (substrate temperature over coating material melting temperature,). The additional energy, albeit small in their work, was thus already showing its value but there was a limit to how much additional energy could be added using temperature alone. Several more-refined versions of the original model have since been presented by Thornton and, recently, by Musil.

During film growth the atoms arrive at the surface randomly and in predominant number of cases they do not land in energy-favourable surface positions. This means that the atoms would need to migrate across the surface to find the energy minimum position where they remain. In order to be able to move by diffusion, across the surface, the atoms need energy, which is usually supplied by thermal means. As mentioned earlier, there is a limit to how far we can heat the film and, in many cases, the substrate cannot be heated; even if it can, heating is not an economically-feasible proposition. Ion bombardment provides an ideal

solution, in terms of added energy, to aid surface movement of deposited atoms without significantly increasing the temperature of the coating and substrate. In addition, during the initial stages of ion-assistance, some substrate atoms (which would otherwise be ejected as sputtered atoms) can be knocked into the coating material and some film atoms are driven back into the substrate to form an ion-beam-mixed layer, thereby improving the adhesion of the coating. Considerable work has been done on energy-assistance effects using ion beams by Weissmantel, Harper and Martin in the period 1979 – 1986 which allowed some general guidelines concerning the optimum ion energy for improvement in coatings (about 30eV) and optimum added energy per depositing atom (in the range 10-100eV per atom) to be established.

The effect on film morphology is clearly shown in Fig. 2 from work by the present authors where the side view of a slice of deposited Titanium Nitride is shown. The imaging conditions are set such that the crystals of certain orientation appear lit. The left hand picture shows the coating deposited without ion bombardment. Here deposited atoms have limited energy and can only migrate short distances on the surface to form islands of TiN which then grow to form columns. The right hand picture shows the same view of TiN deposited during simultaneous bombardment with Nitrogen ions accelerated to 200 Volts where one N ion reaches the surface for every 2 Ti atoms. There is clear evidence that the extra energy has promoted interdiffusion of atoms between the original columns leading to a much more crystalline and denser coating. The removal of gaps between columns makes this energy-assisted coating far better for corrosion protection.

Dark field images of TiN films grown at 473K



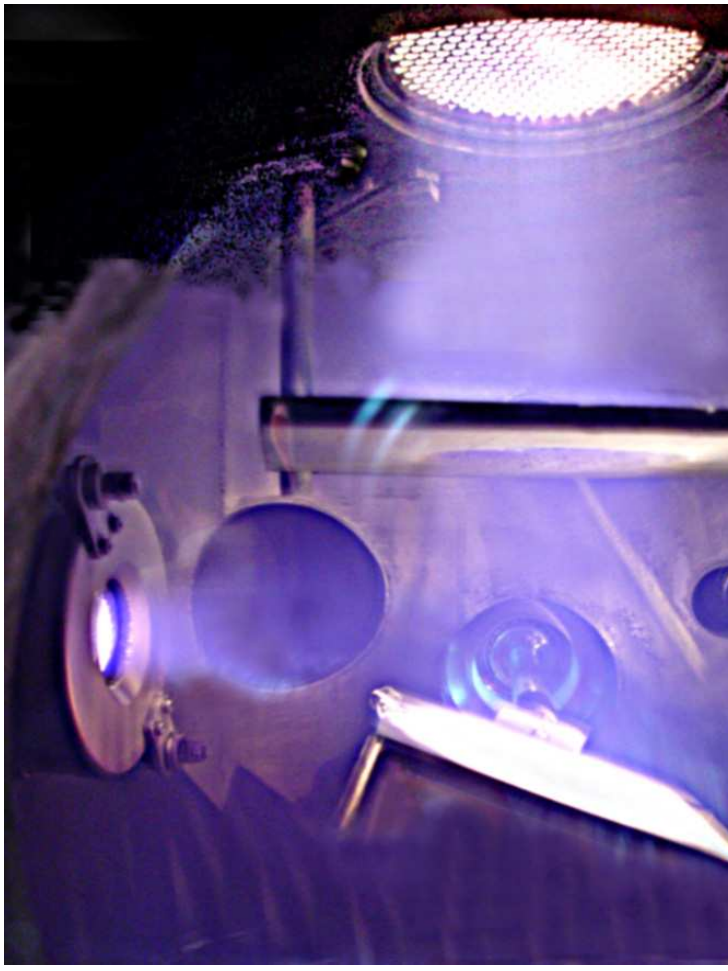
Non-ion assisted **200 eV N ion assist. ion/atom ratio 0.5**

To demonstrate the effects of Energy-Assisted Deposition (EAD) on coating structure and performance and some of our experience in solving problems using this coating method we now present results of two EPSRC-funded programmes awarded to our Surface Coatings and

Characterisation section (which has recently joined the Electron Microscopy and Materials Group at Huddersfield University).

The first study “A fundamental study of hard nanocomposite coatings” (EPSRC Grant GR/R66364/01) applied the EAD process to change the grain size of TiSiN coatings. According to the Hall-Petch relation, alloys with smaller grains exhibit higher strength so it would be expected that the hardness would also increase for lower grain sizes.

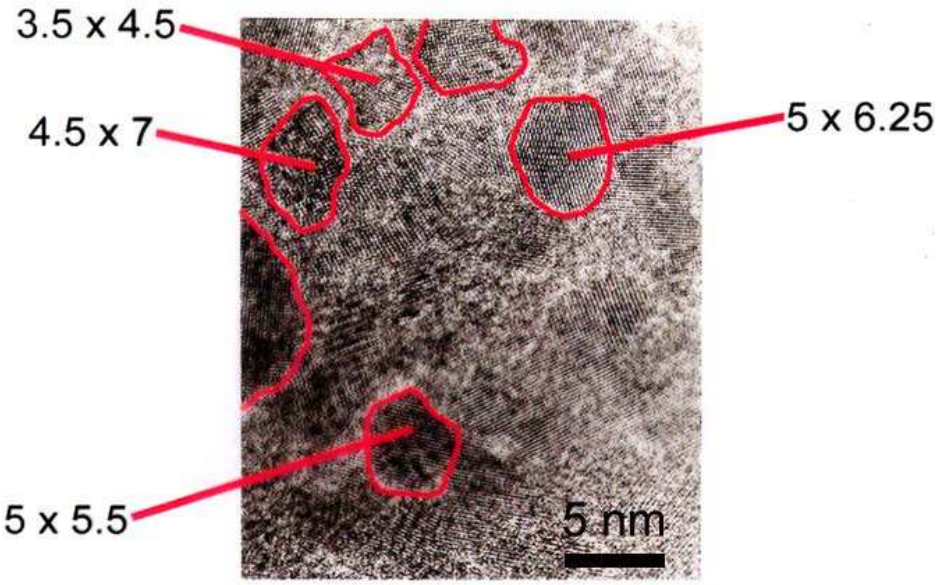
A dual ion beam system was designed specifically to explore the effects of varying parameters such as composition and added energy per atom to the growing film. Once the relation between film properties and parameters is known then a system capable of coating larger areas can be designed relatively easily. The experimental system we developed is shown schematically in Fig 3.



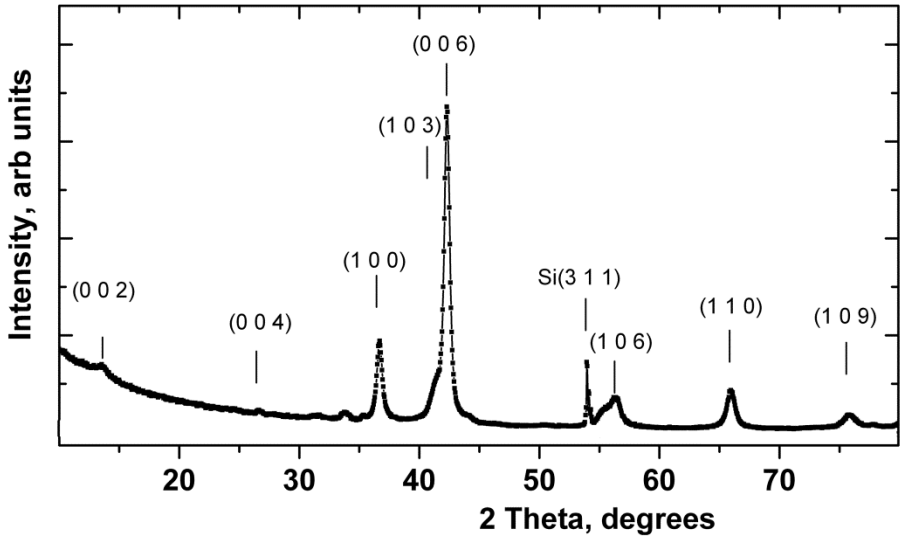
assisted
n system

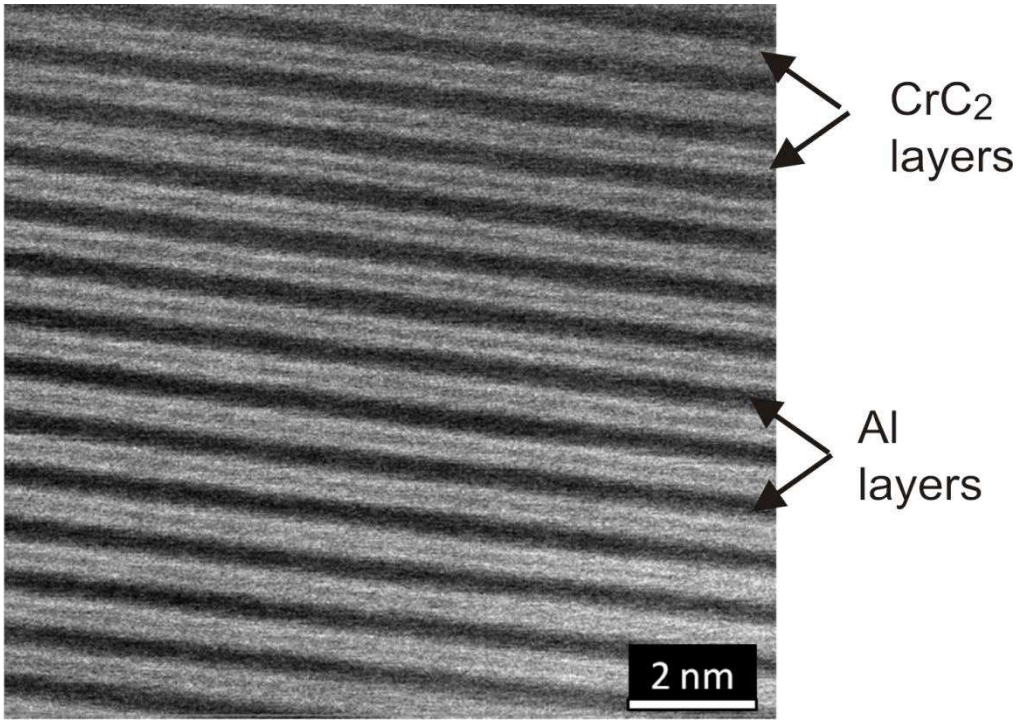
The vertical Argon ion beam bombards a target comprising two plates (composite target) of Ti and Si. This bombardment causes ejection of Ti and Si atoms which travel to form a coating on the right-hand substrate (usually Si (100) for analysis purposes). The relative areas of Ti and Si can be adjusted to change the Ti:Si composition of the coating. The sputtering is done in Nitrogen partial pressure. Nitrogen reacts with the deposited film and forms a TiSiN coating. The horizontal Argon or Nitrogen ion beam provides the EAD and can be used not

only to provide additional bombardment, but also, to increase Nitrogen content in the film. This relatively simple arrangement allowed samples to be produced with microhardness approaching 40 GPa even though the component elements have much lower hardness values. The microstructure of such samples is shown in Fig. 4 with grain sizes of order 5 nm for a hard coating with optimised properties.



For the second EPSRC-funded programme (EPSRC Grant EP G033471/1), the same dual ion beam system was used to form Cr_2AlC coatings in a special natural nano-layered structure known as a MAX- phase. In this system the target now had three plates of Cr, Al and C. These nanolaminated structures are relatively stable and have the general formula Mn+1AXn where n is 1,2,or,3; M is a transition metal such as Cr, Ti, A is an element from the A-group of the periodic table and X is either C or N. X-Ray diffraction and High Angle Annular Dark Field Transmission Electron Microscopy data shown in Figs 5 and 6 indicate the crystalline nature of the coatings formed and their lamella structure.





Another MAX phase coating (Ti_3SiC_2) could not be formed in this way. Other research laboratories have also found that this second material requires a crystalline substrate and a substrate temperature exceeding 900 ^oC before it can be synthesised. Such a special crystalline requirement and high temperature severely limited possible applications of this material in thin film form and the challenge was to form the MAX- phase of Ti_3SiC_2 at much lower temperature; ideally below 700 ^oC so that the coating could be deposited onto steel. A new coating rig was designed which allowed sequential coating of each element (Ti-Si-C-Ti-Si-C…) to minimise the required atom diffusion distances from deposited locations to MAX-phase sites. This new system has succeeded in forming MAX Ti_3SiC_2 at temperatures of order 600 ^oC. Once formed this MAX-phase material is stable up to 1500 ^oC, has high conductivity ( ) and good radiation-resistance ( )

What are the next challenges? There are over 70 possible MAX phases; each one with its own special characteristics and application. Many have the properties akin to those of ceramics but they are much easier to machine and, instead of being brittle, they tend to be self-healing; i.e. the planes in the typical MAX structure slide under load and, up to a certain load, will recover when the load is removed. We need to scale up the size and throughput of our MAX phase coating process which requires collaboration with and support by the coating industry. There are other EAD processes which can be used to provide specific surface topography on materials, act as a film-substrate mixing agent to form alloys bonded to a surface of a material. We welcome enquiries on your coating problem.