



**INTERNATIONAL CONFERENCE ON
METALLURGICAL COATINGS
AND THIN FILMS**

PROGRAM AND ABSTRACTS

**Town and Country Hotel
San Diego, California
April 10-14, 2000**

**Sponsored by:
Advanced Surface Engineering Division
of the
American Vacuum Society**



The zirconium diboride growth mechanism can be activated when no zirconium tetrachloride is introduced in the reactor. However, the use of a $ZrCl_4$ flowrate affects the composition and the adhesion of the films :

- Oxygen concentration in ZrB_2 films is constant in the substrate when no $ZrCl_4$ is used. This oxygen concentration decreases along the substrate when $ZrCl_4$ is added to the reactive gas mixture.

- The concentrations of the Zircaloy-4 alloying elements at the film-substrate interface are strongly dependent on the $ZrCl_4$ flowrate. A particular attention is paid to describe the behaviour of tin (its concentration in Zircaloy-4 is about 1.4 wt %). Zirconium tetrachloride addition tends to slow down tin accumulation at the film-substrate interface. Finally, the consequences of the use of an additional flowrate of $ZrCl_4$ on the adhesion of the zirconium diboride film are presented.

¹J.F. Pierson, T. Belinonte, H. Michel, Surface and Coatings Technology, 116-119 (1999) 995

²**BP-5 Use of Intense Pulsed Ion Beams for Materials Processing Applications, T.J. Renk, P. Provencio, Sandia National Laboratories, M.O. Thompson, Cornell University, P.G. Sanders, Harvard University, K. Kasuya, Tokyo Institute of Technology, Japan**

Intense pulsed high-power ion beams have been shown to produce enhanced surface properties by changes in microstructure caused by rapid heating and cooling of the surface. Additional improvements can be effected by the mixing of a previously deposited thin-film layer (surface alloying or ion beam mixing) into any number of substrate materials. We have conducted surface treatment and alloying experiments with Al, Fe, and Ti-based metals on the RHEPP-1 accelerator (maximum voltage 800 kV, dose 2-10 J/cm²) at Sandia National Laboratories. Ions are generated by the MAP gas-breakdown active anode, which can yield a number of different beam species including H, C, N, Ar, and Xe, depending upon the injected gas. Enhanced hardness and wear resistance have been produced by treatment of 440C stainless steel, and by the mixing of Pt into Ti-6Al-4V (beta-phase) alloy. Mixing of a thin-film Hf layer into Al 6061-T6 alloy (Al-1.0Mg-0.6Si) has improved its corrosion resistance by as much as four orders of magnitude in electrochemical testing, compared with untreated and uncoated Al6061. The improved wear resistance of 440C steel is evidently caused by the dispersal and reduction in size of carbide second-phase particles, as well as the formation of a lath martensite surface microstructure. In the case of the Ti alloy, the melted zone (2 microns thick) is observed to contain relatively large areas of nanocrystalline alpha-phase Ti, in which the Pt forms a metastable solid-solution. The resultant lattice strain may be contributing to the enhanced wear properties of this layer. In addition, there are enhanced numbers of dislocations extending up to 200 microns below the surface, well beyond the heat-affected zone. The mixing process has been used to measure the liquid-phase diffusion coefficient of As into Si, and various alloying metals (Mo, Sn, Zr, and Hf) into Ti. On a per-pulse basis, the diffusion in these materials appears to be quiescent during the irradiation process. We have also treated polymers and Si wafers using reduced beam power (0.5-2 J/cm²). Surface roughness of polyethylene fibers increased after treatment, resulting in increased bonding within an epoxy matrix. Melting and recrystallization of single-crystal Si was observed to be epitaxial, even after a multi-microsecond melt period. At higher beam doses (8-20 J/cm²), significant ablation and redeposition takes place. We are investigating the use of this high-kinetic energy process to form congruent thin-films of materials such as amorphous carbon and YBCO.

BP-6 Vacuum Electric Arc Plasma Source with Flux Separation, A. Rothem, VIP (Vacuum Ion Plasma Technologies) Ltd., Israel, V.M. Bashkov, A.I. Dodonov, V.I.T Ltd., Russia, V.M. Diamant, VIP (Vacuum Ion Plasma Technologies) Ltd., Israel

Vacuum electric arc technique of coating deposition has gained wide acceptance in implementation of solid wear resistant coatings on instruments and machine parts. However, the presence of micro-particles in plasma flux (drops of molten cathode material) limits the technique application by forming coating irregularities, disrupting the composition and the desired coating structure. The present work relates to the development of highly efficient vacuum electric arc source with plasma flux separation. The flux separation is based on special separation of ionized and neutral (including micro-particles) plasma components by methods based on plasma-optics principles. The source allows fluxes of both gas and gas-metal plasma and provides for coating deposition at a rate of up to 40 microns/hour and the surface etching at a rate of up to 8 microns/hour with minimal plasma flux cross section of 300cm². The coatings grain structure is much finer than that of traditional coatings, which results in higher plasticity in conjunction with high micro-hardness and high compressive stress. They are virtually non-porous and have low surface roughness. The

coatings are highly adhesive to the substrate surface. Composition coatings have been obtained, including ceramics, based on metals like titanium, zirconium, tungsten and aluminum with high micro-hardness over 3000 HV and high plasticity. The functional tests proved their high efficiency, including high wear and corrosion resistance.

BP-7 Equipment and Technology for Plasma Coatings Deposition at Low Temperatures, V.M. Diamant, VIP Ltd., Israel, V.M. Bashkov, A.I. Dodonov, V.I.T Ltd., Russia, I.S. Semenov, NII Gozznaka, Russia

In deposition of solid wear resistant PVD-coatings the substrate temperature is one of the important factors that determine the coating quality. Usually, the substrate heating ensures high-quality coatings. However, the necessity in the substrate heating limits the use of the plasma methods. There is a wide range of articles whose heating necessarily results in their features degradation. Moreover, the temperature is often related to the energy parameters of ion or plasma fluxes restricting the control over these parameters which determine the properties of the deposited coatings. This work is related to the method, equipment and technology for deposition of plasma coatings at low substrate temperatures. The possibility to form coatings with required structure and properties regardless of the substrate temperature was proved. The TiN based coating parameters generated at low temperatures are similar to those generated by the traditional method. The results of the method and equipment use for reinforcement of coin dies surfaces (made of steels with low annealing temperature) are provided. The reinforcement coatings increase by up to 4 times the service life of the dies and improve the brightness of coins made from copper-nickel and other alloys.

BP-8 Computed Mean Charge State of a Biased Vacuum Arc Plasma Duct, D.T. Kwok, P.K. Chu, City University of Hong Kong, M.M.M. Bilek, University of Cambridge, United Kingdom, I.G. Brown, University of California, Berkeley, A. Vizir, Russian Academy of Science, Russia

Vacuum arc or cathodic arc metal sources is an attractive and convenient method for depositing high quality thin metal films and metallurgical coatings. Macroparticles micrometers in size can be removed by a curved magnetic filter duct. Biasing the duct wall with a positive voltage can raise the output of the metal plasma. The metal plasma ions consist of several charge states. Time-of-flight (TOF) experiments have shown that the mean charge state will decrease with increasing biased voltage and magnetic field strength applied to the filter duct. We have computed the percentage of ions with different charge states at different biased voltage and magnetic field strength by the particle-in-cell method. It is shown that the simulated mean charge state exhibits the same dropping tendency as we increase the biased voltage and magnetic field strength. We can thus conclude that the reduction in the mean charge state is indeed a natural phenomenon of a metal plasma with multiple ion charge states.

BP-9 Phase Characterization of $Ti_{1-x}Si_xN_x$ Nanocomposite Films, F. Vaz, L. Reboua, University of Minho, Portugal

Recently some authors have focused their attention on the improvement of TiN properties by the addition of Si either by CVD and PVD deposition techniques. These films were characterised as being nanocomposites, consisting of cubic nanocrystallites of titanium nitride embedded in a few angstrom size amorphous matrix of silicon nitride. These coatings were claimed to have extremely high hardness, reaching values as high as 50 GPa.

In the present paper we report, at first, on the preparation of samples within the (Ti,Si)N system by r.f. reactive magnetron sputtering. The second part presents results on coating microstructure as a function of Si content, obtained by XRD using both the common $q-2\theta$ scans and the detector scans modes. These measurements were also used in the characterisation of texture factors and microstress states by the $\sin^2\psi$ method. Furthermore, results of EXAFS experiments together with XRD and TEM results will be used to show the development of a polycrystalline two-phase structure, and a small phase of an amorphous material surrounding the nanocrystals. The deflection method was used to evaluate the macroresidual stress states.

Mechanical properties such as hardness, adhesion and wear resistance will be characterised and discussed as a function of the Si content in the $Ti_{1-x}Si_xN_x$ matrix and several relations will be made concerning the most important deposition parameters. Bias voltage, deposition temperature and working gas flow will be analysed in particular detail. Regarding the preliminary results, the samples with a composition of Si between 5.9 and 10.6 at. % show the better mechanical properties, revealing hardness values more than two times higher than those of TiN. This region is also the one where the most oriented films grow (220 cubic fcc orientation) together with the smallest grains observed. Relations between mechanical properties and phase development, together with relations of structure with deposition parameters will be taken into consideration.