Monday Morning, October 2, 2000

Surface Engineering
Room 201 - Session SE+TF-MoM
Hard and Superhard Coatings

Moderator: A. Inspektor, Kennametal Inc.

8:20am **SE+TF-MoM1 Plasma Deposition of Hard and Thermal Resistant Coatings in the System Si-B-C-N***, **D. Hegemann**, C. Oehr,* Fraunhofer Institute for Interfacial Engineering and Biotechnology, Germany*; R. Riedel,* Technical University Darmstadt, Germany*; H. Brunner,* Fraunhofer Institute for Interfacial Engineering and Biotechnology, Germany

As a result of covalent bonding, the four elements boron, carbon, nitrogen and silicon can form superhard materials. Considering the well-known diamond-like and cubic boron nitride films, which are limited by their temperature resistance and adhesion, respectively, further research in the as before mentioned system is required. Thus, BCN and SiBCN thin films are very promising candidates which are therefore investigated. A capacitive rf discharge in an asymmetrical but confined geometry is chosen for the deposition experiments to sustain well defined plasma conditions. The bias voltage depending on delivered power and pressure is taken as control parameter. Due to the use of single-source precursors - pyridine borane (PB) and triazaborabicyclodecane (TBBD) for BCN, tris(dimethylamino)silylamino-bis(dimethylamino)borane (TDADB) for SiBCN - relative low substrate temperatures (300°C) can be applied yielding amorphous films. Ar or N@sub 2@ in an excess of 50:1 serves as carrier gas. Both with BCN and SiBCN film deposition, several regimes of different chemical composition become apparent increasing the bias voltage. An influence of the used precursor is merely observed at low biases. At moderate bias voltages films comparable to thermal CVD processes are obtained. Further increasing the bias yields hard coatings up to 13.5 GPa and 30.8 GPa measured by microindentation for BCN and SiBCN, respectively. It is found that the hardness scales mainly with the carbon content of both films, analogously. Annealing the films for 5 h in argon or air exhibits a thermal and oxidation resistance of the SiBCN films exceeding 1200°C. On the other hand, BCN films start to decompose at about 1000°C in argon and 800°C in air. Moreover, the SiBCN films show lower internal stresses (1-2 GPa) compared to BCN, which is attributed to a stabilization effect of sp@super 3@ hybridized carbon by silicon incorporation.

8:40am **SE+TF-MoM2 Structure and Mechanical Properties of Ti-Si-C Coatings Fabricated by Sputtering and Pulsed Laser Deposition***, S.H. Koutzaki, **J.E. Krzanowski**,* University of New Hampshire*; J. Nainaparampril,* Systran, Inc.*; A.R. Phani,* University of New Hampshire

Nano-structured coatings consisting of mixtures of carbide compounds can provide a useful route to developing super-hard materials. Heterogeneous nano-structured coatings can be obtained by either deposition of multilayer structures or by depositing film compositions that undergo a natural phase separation due to thermodynamic immiscibility. In the present work, we have taken the latter approach, and deposited films by RF co-sputtering from dual carbide targets, as well as by pulsed-laser deposition (PLD) using ternary carbide targets. We have examined a number of ternary carbide systems, and to date the most promising coatings have been obtained in the Ti-Si-C system. In this system, the TiC and SiC phases are highly immiscible and phase separation on deposition is likely to occur. We first examined sputter-deposited TiC coatings with varying SiC content. It was found that the nano-indentation hardness increased with SiC content, with a maximum hardness nearly twice that of the sputtered-deposited TiC films at a SiC content of 15 at. %. We further analyzed these films using high-resolution TEM, XPS and X-ray diffraction. Since cubic SiC has an X-ray pattern almost identical to that of TiC, the extent of phase separation could not be determined by that method. However, XRD did demonstrate a general disordering of the films with increasing SiC content. High-resolution TEM also revealed that films of higher SiC content exhibited a mottled structure and nano-scale phase separation within the grains. Further studies were conducted comparing PLD TiC and TiC-12 at.% SiC films (the latter made using a ternary target). The Ti-Si-C coatings exhibited about 25% higher hardness levels in comparison to TiC alone.

9:00am **SE+TF-MoM3 Hard and Superhard Coatings - A Review***, **W.D. Sproul**[1],* Reactive Sputtering, Inc. **INVITED**

Hard coatings such as titanium carbide deposited by the high temperature chemical vapor deposition (CVD) process first made their commercial appearance in the late 1960s. The single layer coatings were soon supplanted with multilayer CVD coatings, but it was difficult to apply these coatings to high speed steel (HSS) tooling or steel alloys without damaging the metallurgical properties of the steel. In the early 1980s, several physical vapor deposition (PVD) techniques became available for depositing hard coatings such as titanium nitride or titanium aluminum nitride onto HSS. One of the driving forces in the PVD coatings business has been a desire to increase the hardness of the coatings with the ultimate goal of matching or exceeding the hardness of diamond. Today superhard (hardness greater than 40 GPa) coatings exist. The hardening mechanisms for achieving superhardness fall into two categories, intrinsic and extrinsic. Intrinsic materials such as diamond, cubic boron nitride, and some ternary compounds rely on high bond energies and short bond lengths to achieve superhardness whereas the extrinsic nanostructured multi-layer and nanocrystalline materials rely on the microstructure to restrict dislocation movement to achieve superhardness. A hardness exceeding that of diamond has been reported for a nanocomposite of titanium nitride and silicon nitride. Coating hardness is only one property that should be considered when engineering a surface. Coating toughness should also be factored in especially in situations where impact loading will occur. Today advances are being made in high-density plasma (HDP) PVD techniques that will have a direct impact on future PVD hard coatings. The high degree of ionization in HDP systems will allow new compounds synthesis at temperatures well below the thermodynamic equilibrium point. Perhaps in the near future crystalline alpha alumina will be deposited below 500 degrees C by HDP PVD techniques.

9:40am **SE+TF-MoM5 Unbalanced Magnetron Sputter Deposition of Al-Ti Ceramic Coating for High Speed Milling Application***, **X. Zeng**,* Gintic Institute of Manufacturing Technology, Singapore

Hard coatings for high speed machining consist of multiple layers because of the requirements for high adhesion strength to the substrate, high thermal stability, high hardness and low friction coefficient and good compatibility. Traditionally used coatings like TiN, CrN and their alloyed nitride coatings have high hardness and good adhesion on common tooling materials used in industry. However, these coatings usually have poor performance in high speed machining applications, especially in the cutting of hardened tool steels, because of phase transition (oxidation) at high temperatures. Ti-Al alloyed nitrides seem to be one of the most promising coatings for this application due to its high thermal stability, low friction coefficient and high hardness. This paper reports the development of a multilayered Ti-Al ceramic hard coating on tunsten carbide ballnose endmills for high speed milling using an unbalanced magnetron sputtering system @footnote 1@. The process parameter dependence of the coating properties was studied. X-ray diffractometry, x-ray photoelectron spectroscopy, nanoindentation and scratch test were used to characterize the structural, compositional and mechanical properties of the coatings. High hardness, up to 40 GPa, good adhesion strength, up to 100 N in scratch critical load, and high oxidation resistance were achieved, leading to excellent performance in high speed milling on hardened tool steel at a machining speed of 260 m.min@super -1@. The results show that the tool life with this coating is improved by a factor of 4 or better, under the testing conditions used, compared to the uncoated WC tools. The surface finish of the machined steel achieved with this coating is also significantly better. @FootnoteText@ @footnote 1@ X.T. Zeng, J. Vac. Sci. Technol., A 17, (1999) 1991

10:00am **SE+TF-MoM6 Thermal Stability and Mechanical Properties of Nano-scale W/ZrN Multilayers***, **A. Madan**,* Northwestern University*; J. Ji, S.A. Barnett,* Applied Thin Films, Inc.

Nanolayered thin films show an enhanced hardness and improved mechanical properties as compared to the individual layer components. The high-temperature stability of these films is important for various technological applications e.g. dry-cutting. We report on the thermal stability and mechanical properties of polycrystalline, immiscible W/ZrN nanolayered films. W/ZrN multilayers of bilayer periods 2 to 40 nm were sputter deposited in a dual-opposed-cathode unbalanced-magnetron sputtering system. The W fraction was varied from 0.3 to 0.8 by adjusting the relative power on the two targets. The 1 micron films were annealed at

[1] **Featured Speaker - Science and Technology in the 21st Century**

temperatures from 750°C to 1000°C in inert atmospheres. The as-deposited and the annealed films were characterized using x-ray diffraction, cross-sectional transmission electron microscopy (XTEM), and nanoindentation. The as-deposited films showed an enhanced hardness in comparison to the rule-of-mixtures values irrespective of the bilayer period or the layer composition ratio. High- and low-angle x-ray diffraction (XRD) showed that the layered structure was stable after annealing at 1000°C for 1 h. XTEM results for as-deposited and annealed films will be presented. The annealed films show hardnesses as high as 44 GPa. The excellent high-temperature stability of the W/ZrN nanolayered structures arises because W and ZrN are mutually immiscible.

10:20am **SE+TF-MoM7 Growth and Characterization of ZrN/ZrB@sub 2@ Nanolayered Coatings for High Temperature Applications***, **K Martin**, J. Ji, I. Kim, S.A. Barnett,* Applied Thin Films, Inc.*; A. Madan,* Northwestern University*; P. Hedge, A. Inspektor,* Kennametal, Inc.

There is a great need for cutting tool coatings that perform well at elevated temperatures, both because of the desire to cut at higher rates and to eliminate coolant fluids. However, current cutting-tool coating materials fail rapidly under these conditions because of poor high-temperature properties. The ZrN/ZrB@sub 2@ nanolayered system is expected to provide a unique combination of properties including high hardness, excellent stability at elevated temperatures, low chemical solubility in Fe and good thermal expansion match with cemented carbide tools. In this investigation, ZrN/ZrB@sub 2@ nano-layered coatings were deposited using a dual-cathode magnetron sputtering system. The key properties including hardness, adhesion, and residual stress were evaluated as a function of composition, bilayer period, and substrate bias. The hardness values for as-deposited coatings ranged from 30-38 GPa and increased to 49 GPa after annealing at 1000°C. Low and high angle XRD revealed that the superlattice structure was stable at elevated temperatures. The increase in hardness after annealing is attributed to the transition of the soft amorphous ZrB@sub 2@ to the crystalline form. Adhesion testing verified that the coatings adhered well on cemented carbide inserts even after annealing at 1000°C.

10:40am **SE+TF-MoM8 Fabrication of Al-Pt Coating on Ni Base Superalloys and Studies of Their Structure***, M. Ghoranneviss, **H. Parchamy Aragy**,* Islamic Azad University, Iran*; A. Sedghi,* International Iran Khomani University, Iran*; A. Shokohi,* Islamic Azad University, Iran

Thin film coating are formed on the enginneering materials to improve their physical and mechanical properties these coating are used mainly in different fields of industrial application and in these respect many research projects conducted to improved their properties.In this research,therefore,the formation of Al-Pt(Aluminum/Platinum)alloys coatings on nickel based super alloys has been studied.Sputtering-ion beam technique under Argon plasma and subsequent heat treatment is been used to fabricate these coating.Ion implantation is applied the Aluminum-Platinum alloys coatings.The main goal of this work is increasing erosion and consequently erosion-corrosion resistance of these coating.Scan Electron Microscope,Glow discharge Spectrometers and X-Ray Diffraction techniques is used to investigate the structure of fabricated coatings.These results correlates with other investigations and these method can be presented as a industrial method for fabrication of these coating.Ion implantation improved these properties but the results not very appreciable.Details will discus in full paper.

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