Project No. 5304.1	Novel Materials	TOP NANO 21
Final Report	(Poster Segment: Materials and Surfaces)	

Nanocomposite TiN/Si_3N_4 coatings produced by arc PVD

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Abstract:
This project has shown that the deposition of nanocomposite hard coatings is possible using a combination of arc-PVD and Unbalanced Magnetron Sputtering. The codeposition of titanium nitride and silicon nitride leads to coatings with hardness values up to 45 GPa and a five times better oxidation resistance as compared to pure TiN. Nanoindentation measurements indicate that the hardness increase is probably due to changes in the nanostructure of the coatings. The oxidation resistance origins in the encapsulation of the TiN grains, which are between 10 and 25 nm in diameter, by Si_3N_4 acting as a diffusion barrier.

Project results:

TiN and Si_3N_4 by arc PVD

Nanocomposite hard coatings, which consist of a nanocrystalline hard phase which is percolated by a strong amorphous phase, exhibit outstanding mechanical and chemical properties [1]. A deposition system, which was used for Unbalanced Magnetron Sputtering (UBM-PVD), has been adapted to produce coatings by a combined reactive process involving vacuum arc PVD and UBM-PVD. The modifications aimed at providing maximum compatibility with the installations of the industrial partner IonBond and hence direct transfer of the results to production. Metallic titanium was used as the arc cathode since it combines high deposition rates with high plasma densities and high coatings quality. Elemental silicon was supplied by DC UBM sputtering, since arc evaporation destroys the silicon target due to the insufficient electrical and thermal conductivity of silicon. For this reason a hybrid process combining arc-PVD for TiN and UBM-PVD has been used to deposit nc-TiN/a-Si_3N_4 nanocomposites.

Hard, scratch-resistant and well-adherent TiN coatings could be deposited successfully on steel and silicon wafers. Following the expectations for unfiltered arc PVD, undesired droplets of molten target material are incorporated into the deposited layers, however to an extent which is well tolerable for tool coating applications. These droplets form as a consequence of the rapid local overheating when the arc passes over the cathode. The density of droplets with diameters above 10 µm was about $5/cm^2$. Increased operating pressure lowered the droplet concentration, while changes in the discharge currents were invariant to this problem.

Incorporation of silicon into TiN

Initial experiments showed that for stationary substrates (no sample rotation) silicon contents up to 14 atomic percent (corresponding to about 25 at% Si_3N_4) could be obtained. Due to the different deposition rates of the two processes arc-PVD and UBM-PVD of a factor 10 to 100, the incorporation of silicon with sample rotation (which is common in an industrial coater) was limited to several atomic percent. This is however, sufficient to increase the oxidation resistance to a large extent , as is shown below. By XPS measurements it could be shown that silicon is present in the coatings as silicon nitride.

Hardness and oxidation resistance

The hardness of the coatings was determined by nanoindentation on polished sample surfaces. Values of 30 GPa for TiN at a Young's modulus of 430 GPa were measured. An increase of the hardness was observed as the silicon content in the coatings was raised to 5 at% (see figure 1). The modulus, however, was not affected by the silicon content, which indicates constant residual stresses for all silicon contents. This is a strong indication that the hardness increase is due to changes in the nanostructure of the coatings and not a consequence of residual stresses ("stress hardening"). Time restrictions did not allow an in-depth examination of the nanostructure of these coatings.

The resistance of a wear-protective coating against oxidation is a decisive property for its usability. We could demonstrate in this project that already small amounts of silicon (3 at%) lead to a reduction of the oxidation rate in air by a factor of more than five (see figure 2). The oxidation rates compare well with published results of UBM-PVD deposited nanocomposite TiN/Si_3N_4 [2]. Since silicon nitride is an efficient barrier against oxygen diffusion, TiN nanograins which are encapsulated by Si_3N_4 oxidize slower and show less recrystallization.

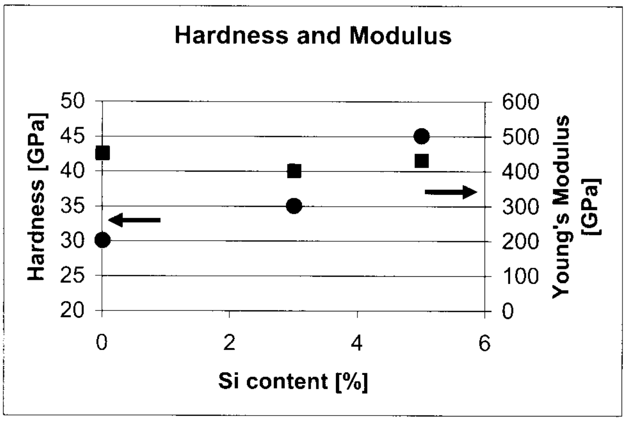

Figure 1: The hardness of arc-PVD deposited TiN can be increased by the addition of silicon nitride. The Young's modulus stays constant, indicating constant residual stresses in dependent of the silicon content.

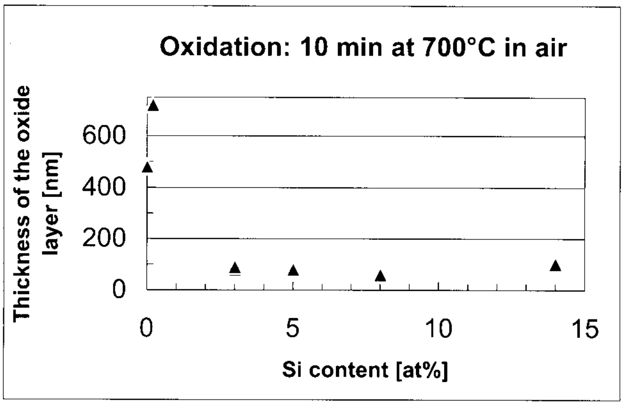

Figure 2: Already minor additions of silicon cause a markedly enhanced oxidation resistance of TiN/Si_3N_4 nanocomposite coatings.

[1] J. Patscheider, *MRS Bull.* 28/3 (2003) 180

[2] M. Diserens, J. Patscheider, F. Lévy, *Surf.Coat. Technol.* **120-121** (1999) 158

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