*Superficies y Vacío **9**, 276-279, Diciembre 1999* *ãSociedad Mexicana de Ciencia de Superficies y de Vacío*

Mechanical and tribological properties of tungsten carbide sputtered coatings

J. Esteve, E. Martinez,
Departament de Fisica Aplicada i Optica, Universitat de Barcelona, Catalunya, Spain

G. Zambrano, P. Prieto
Departamento de Fisica, Universidad del Valle, Cali, Colombia

C. Rincon
Departamento de Fisica. Universidad Autonoma de Occidente, Cali, Colombia

H. Galindo
Departamento de Fisica. Universidad de los Andes, Merida, Venezuela

Tungsten Carbide (WC) hard coatings have been obtained on steel substrates by r.f. magnetron sputtering process. Two layer coatings have been deposited in order to improve adhesion on steel. The lower layer was tungsten metal and the upper WC layer was obtained by reactive sputtering of the tungsten target in Ar and methane gas mixture. AES and SIMS confirmed that the WC layer composition depends on the reactive sputtering gas composition. Film microhardness were measured by microindentation and coating adhesion by microscratch. Measurement results showed that high hardness coatings can be prepared at a relative low temperature and that good adhesion on steel is achieved with the two layer coating. Nanowear measurements showed a noticeable dependence of this applied functional property on the coating compositions.

1. Introduction

Tungsten Carbide (WC) thin films have been classically used as protective hard coatings due to their good mechanical properties [1]: high hardness and corrosion resistance and low wear properties, that are sustained up to 400 ^{o}C [2,3]. Recently, this material has increased its technological interest because of its use in composite coatings WC-C [4-7].

Different processes, such as plasma spraying, physical vapor deposition (PVD) and mostly chemical vapor deposition (CVD) have been used for depositing WC coatings. Typically, CVD processes are carried out at temperatures above 500 ^{o}C, which do not allow the coatings to be applied on hardened steels without significantly affecting the substrate mechanical properties.

Sputtering deposition is a PVD process that is increasingly used in industrial hard coating deposition because it is a low temperature process and it uses unpolluting products. In the present work, r.f. magnetron sputtering process has been used to obtain WC/W bilayer coatings on steel substrates. The sputtering was carried out from a pure W metal target and using pure Ar or Ar/CH_4 mixture as sputtering gas. The W intermediate layer was deposited in order to improve the adhesion of the WC film to the steel substrates. The reactive sputtering process we have used allows obtaining both WC and W layers in a single deposition process.

The coatings have been analyzed in their composition in order to determine the gas mixture proportion and the reactive sputtering parameters that allow the obtention of the optimum WC film. The bilayer coatings have been characterized in their hardness, adhesion and wear behavior.

2. Experimental details

The deposition system used was a r.f. magnetron sputtering working at a rather high sputtering gas pressure and at a high current density (Table 1).

The sputtering cathode was a 35 mm diameter and 5 mm thick pure tungsten target and was continuously water cooled. The substrates were located at distance of 5 cm. The chamber was evacuated to 10^{-5} mbar before the deposition by a turbomolecular pump. The sputtering gases were Ar or Ar/CH_4 mixture in the case of reactive sputtering. The total chamber pressure and the relative gas fluxes were controlled by separate mass flow controllers.

Coatings were deposited onto carbon steel substrates, which were previously hardened to 9 GPa, polished with 1 μm diamond paste, etched in dilute HNO_3 and ultrasonically cleaned in alcohol and acetone. The substrates were mounted on a resistively heated holder with controlled constant temperature during the deposition process. The target and the substrates were separately pre-sputtered in Ar plasma during 10 min. before deposition. In all the runs, the substrate temperature was fixed at 350 ^{o}C. This temperature was chosen for optimal adhesion and deposition rates. The W intermediate layers were deposited

Table 1. Sputtering conditions for the deposition of WC/W coatings

Target	pure W metal
Substrates	hardened carbon steel
Target-substrate distance	5 cm.
Sputtering gas	Ar
Reactive sputtering gas	Ar/CH_4 mixtures
Substrate temperature	350 ^{o}C
Sputtering gas pressure	$5x10^{-2}$ mbar
Sputtering parameters	500-600V, 150mA, ~80W r.f. power density 12W/cm^2

with pure Ar gas sputtering. The WC layers were deposited with Ar/CH_4 gas mixtures. We essayed different increasing methane concentrations: 7%, 17%, 24% and 31%.

The morphology and thickness of the bilayer coatings were determined from cross-sectional SEM micrographs. Samples were cut for observation using a diamond saw. Compositional Auger analysis was done on the coatings surface and also deep in the coating bulk by means of Ar ion depth etching. The homogeneity of the layers was analyzed by SIMS depth profiling with oxygen ion etching.

The microhardness of the bilayer coatings was measured by the dynamical microindentation method with a Nanotest 550 instrument (MicroMaterials Ltd., UK). The load-penetration curves were obtained using a Berkovich diamond indenter and hardness values were deduced by the Oliver&Pharr analysis method [8]. The adhesion of the coatings to the steel substrate was evaluated by the microscratch method using a spherical diamond indenter of 50 μm radius. Nanowear tests were carried out using a scanning probe microscope (SPM) [9,10] and the AFM image of the resulting wear marks were obtained for increasing number of wear cycles.

3. Results and discussion

The W layer is deposited on the steel substrate by sputtering the W target with pure Ar gas. The process causes a considerable substrate temperature increase that is automatically balanced by a reduction of the substrate holder heating power. After the prefixed deposition time of 1 hour, the Ar gas is substituted by an Ar/CH_4 mixture without any intermediate step. The WC deposition proceeds during one hour.

From the cross-section SEM micrographs (Fig. 1), the bilayer coating structure can be observed with a gradual interface transition. The W lower layer shows a definite columnar dense structure and the upper WC layer appears to be dense without any columnar feature. The coating surface is flat, smooth and scattered with numerous low height spherical bumps. The deposition rates were obtained from the layer thickness measured on the SEM micrographs. The pure W deposition process presents the highest deposition rate (2.2 μm/h). The reactive sputtering processes have lower deposition rates (Fig. 2) that decrease to 0.4 μm/h for a 31% of CH_4 in the gas mixture.

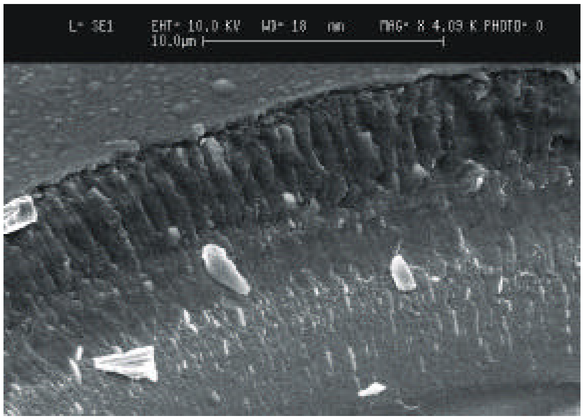

Fig. 1. Cross-section SEM micrograph of a WC/W bilayer coating on steel.

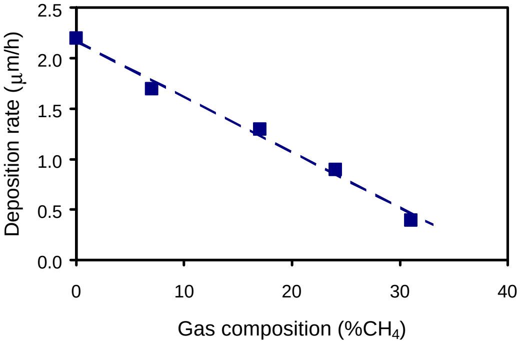

Fig. 2. Deposition rate as a function of the reactive sputtering gas composition.

The composition of the WC layers in atomic percent was deduced from the surface Auger analysis and also from the bulk Auger analysis performed in craters etched to the half of the layer thickness. The bulk compositions have been represented in figure 3. In all the samples, surface analysis show a composition richer in carbon than the respective bulk composition. Samples obtained with reactive sputtering gas concentrations of 17 and 24% CH_4 show a W/C atomic composition approximately 40% in W, that may correspond to the quasi-stochiometric β-WC_{1-X} cubic phase. However, the composition of the layer obtained with the 7% CH_4 gas mixture approaches the pure tungsten and the very thin layer obtained with 31% CH_4 is a carbon rich layer.

SIMS depth profiles show that layer compositions are homogeneous in depth. In the profile of figure 4, that corresponds to the coating obtained with 17% CH_4, it can be seen a smooth transition between the WC and W layers. The sample obtained with the 31% CH_4 gas mixture shows a pronounced increase of carbon content near the film surface.

Hardness values were measured by microindentation with a maximum load of 20 mN in order to avoid interlayer and substrate effects. Hardness

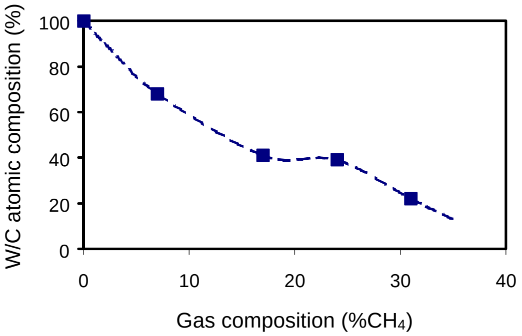

Fig. 3. W/C atomic composition in the layer as a function of the reactive sputtering gas composition.

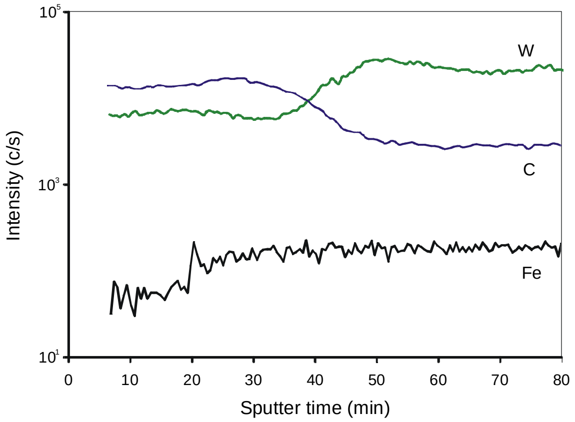

Fig 4. SIMS depth profile of the WC layer for the 17% CH_4 coating.

values obtained for the upper layer depend on the layer composition. Films deposited from 17% and 24% CH_4 gas mixtures showed the highest hardness: 24 and 26 GPa, largely superseding the W layer hardness. The hardened steel substrate did not change its hardness value (9 GPa) before and after coating deposition.

The scratch tests were produced on the coatings starting at 0 load and increasing it at a constant rate of 32.5 mN/s up to a maximum of 2000 mN. Friction forces were measured during the scratch tests with a tangential force sensor added to the diamond probe. Figure 5 shows the friction coefficient vs normal load along the scratch for both, the WC/W sample deposited with 24% CH_4 and an analogous WC sample deposited without the W interlayer. In the lower load range, both samples showed a very low friction coefficient. Beyond a threshold load, the friction coefficient increases due to the onset of the cohesive failure of the coatings. An abrupt change of friction coefficient appears at the critical load, L_C, due to the adhesive failure of the coatings. The WC/W samples with the W interlayer showed higher critical loads, L_C, than the WC single coatings.

The wear test was carried out by multiple dry sliding of a 200 nm radius diamond tip on the sample surface. The scan area was 3 μm x 3 μm and the constant applied load was 10 μN. Figure 6a plots the depth of the wear marks as a function of the number of wear cycles. All the coatings showed an initial regime with relatively high wear followed by a long regime of lower wear. The AFM image of the wear mark produced by one wear cycle (Fig. 7a) shows a roughness similar to that of the bare sample surface. However, the roughness observed after 15 wear cycles (Fig. 7b) is highly reduced, and so, the wear rate also decreases.

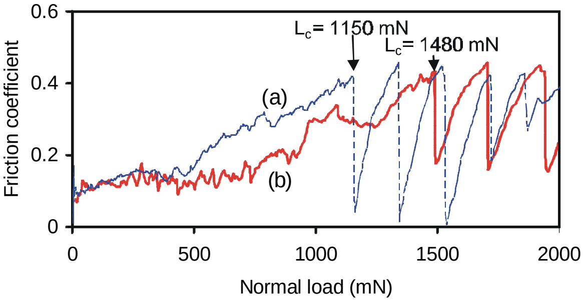

Fig. 5. Friction coefficient vs normal load data obtained from the microscratch measurements on the coatings: (a) 24% CH_4 WC on steel, (b) 24% CH_4 WC/W on steel. The arrows indicate the adhesive failure of the coatings at the critical load values (L_C).

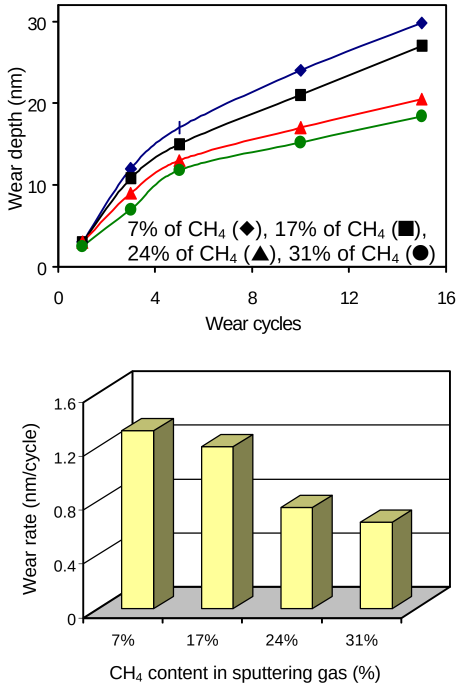

Fig.6. (a) Wear depth as a function of the number of wear cycles and (b) wear rate for the WC coatings with different C contents.

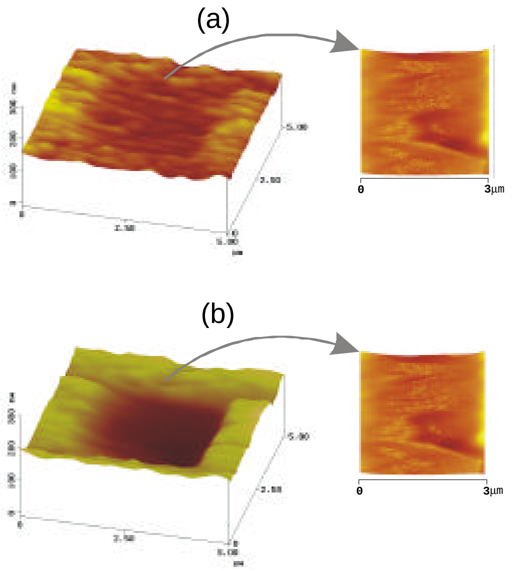

Fig. 7. AFM images of the wear mark produced (a) by one wear cycle and (b) after 15 wear cycles.

The WC layers with higher carbon content show the lowest wear rates (Fig. 6b). These results suggest that the very low wear rates achieved with these WC/W coatings can be imputed to their low surface roughness and their low dry friction coefficient.

4. Conclusions

Magnetron sputtering of a tungsten metal target in an Ar/CH_4 gas mixture proves to be a convenient method for the deposition of wear-resistant hard coatings on hardened steel. A WC/W bilayer coating can be obtained in a single deposition process at a temperature lower than the hardened steel annealing point. The W intermediate layer provides a good adhesion of this coating onto the steel and the WC overlayer provides a great reduction of the wear rate under dry sliding. A range of coating compositions and mechanical behaviors can be obtained by varying the methane concentration in the sputtering gas.

Acknowledgements

J. Esteve and E. Martinez acknowledge the financial support of the CICYT of Spain Government under contract MAT96-0552 and the DGR of the Generalitat de Catalunya. G. Zambrano and P. Prieto acknowledge the financial support of the CYTED (project VIII.7A).

References

[1] J.E. Sundgren, H.T.G. Hentzell, J. Vac. Sci. Tech. A **4** (1989) 2259.
[2 B.M. Kramer, P.K. Judd, J. Vac. Sci. Tech. A **3**(6) (1985) 2439.
[3] J.E. Sundgren, H.T.G. Hentzell, Course on Vapor Deposited Wear Protective Coatings, Chapter I, Continuing Education Institute, Mittenberg, Sweden, 1986.
[4] D.T. Quinto, R. Willd, Balzers Limited, 25th International Conference on Metallurgical Coatings and Thin Films, Invited talk, San Diego, USA, 1998
[5] A. Hoffman, P.J. Evans, D.D. Choen, P.J.K. Paterson, J. Appl. Phys. **15** (1992) 72.
[6] E. Harry, A. Rouzaud, P. Juliet, Y. Pauleau, Thin Solid Films **342** (1999) 207
[7] G. Zambrano, P. Prieto, F. Perez, C. Rincon, H. Galindo, L. Cota-Araiza, J. Esteve and E. Martinez, Surf. Coat. Tech. **108-109** (1) (1998) 323
[8] W.C. Oliver, G.M. Pharr, J. Mater. Res. 7 (1992) 1564
[9] X. Yun, R.C. Hsiao, D. Bogy, C.S. Bathia, IEEE Trans. on Mag. **33** (1) (1997) 939
[10] R.C. Hsiao, D. Bogy, C.S. Bathia, IEEE Trans. on Mag. **34** (4) (1998) 1721