

Microtribological characterization of group V and VI metal-carbide wear-resistant coatings effective in the metal casting industry

J. Esteve^{a,*}, E. Martínez^a, A. Lousa^a, F. Montalà^b, L.L. Carreras^b

^aUniversitat de Barcelona, Departament de Física Aplicada i Òptica, Avda. Diagonal, 647, E-08028 Barcelona, Catalunya, Spain

^bTratamientos Térmicos Carreras, Pte. Enginyer Playa 38-42, E-08205 Sabadell, Catalunya, Spain

Abstract

The molds used in metal casting and molten metal injection industrial processes can be protected with a novel thin film coating that reduces the wear of the molds after repeated usage, and greatly eases the unmolding operation. These coatings are based on the group V and VI metal carbides and are obtained by plasma assisted arc deposition from pure metal targets and argon and hydrocarbon gas mixtures. The coatings are deposited on the inner surface of the hot working steel molds, with a metal nitride thin film inter-layer. The carbide layer compositions are over-stoichiometric in carbon. These coatings have a low chemical reactivity against molten metals and they show a low friction coefficient and wear rate, these last properties being enhanced when the carbon content in the carbide layer is increased. We examine the surface mechanical properties of these coatings: hardness, friction coefficient and wear rate as measured by micro-indentation and micro-scratch analysis, and we relate these properties to the process parameters of the coating deposition. Finally, we discuss the mechanisms that may account for the notable performance of these coatings. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hard coatings; Metal carbides; Microtribology; Hardness

1. Introduction

Transition metal carbides and nitrides have found widespread use as protective hard coatings because of their hardness and wear resistance. Among them, TiN, TiC and WC are those with higher hardness as bulk materials, and are also the more used as thin film coatings. Other transition metal carbides and nitrides are not so extremely hard, but may have good success in specific applications. This is the case for Mo and Ta carbides [1–3], two refractory metal carbides, with bulk hardness of 16.6 and 15.5 GPa, respectively, and with good wear resistance at high temperatures [4]. Mo and Ta carbide thin film coatings, obtained by reactive arc

deposition and over-stoichiometric in carbon, show inferior hardness to the stoichiometric bulk materials, but still better wear resistance. They have demonstrated very good performance in some specific industrial applications, as is the case of wear protection of the steel molds used in the aluminum and aluminum alloys injection cast molding. The coatings are applied on the inner surface of the mold parts, with an intermediate thin layer of TiN intended to improve the carbide adhesion to the steel. The coated molds show longer life cycles than uncoated molds and also those molds coated with only the TiN thin film, and furthermore they show better unmolding performance with reduced adhesion of the cast aluminum alloys to the mold parts.

In this work we study the hardness and mechanical properties of these coatings when deposited on polished hardened steel test coupons, and also their wear behav-

* Corresponding author. Tel.: +34-93-402-11-34; fax: +34-93-402-11-38.

E-mail address: jesteve@fao.ub.es (J. Esteve).

ior with the micro-pin-on-disk technique at room and higher temperatures.

2. Experimental

2.1. Preparation of the coatings

The coatings were obtained in a physical vapor deposition (PVD) multi-cathode arc deposition system at Tratamientos Termicos Carreras (TTC), Sabadell, Spain. The deposition chamber is equipped with six DC cathodes for arc evaporation of refractory metals, and the metal parts to be coated are located in a central rotatory holder that can also be DC biased up to 1200 V. A low-pressure reactive vapor deposition process with simultaneous ion bombardment forms the coatings. The coating execution procedure consists in a sequence of time-programmed steps that include: glow discharge surface cleaning; ion bombardment heating of the parts; deposition of the various layers of the coating; and finally, cooling of the parts down to room temperature under an inert gas atmosphere.

The coating applied to the mold parts consists of two layers of approximately equal thickness: the first layer of TiN, and the second of molybdenum or tantalum carbide. This coating is deposited onto the hardened steel mold parts after an accurate cleaning, but without any previous mechanical polishing of their inner surfaces. The TiN layer is obtained by vapor deposition from pure titanium cathodes with the standard argon and nitrogen reactive gas mixture. Molybdenum and tantalum carbide layers are obtained by vapor deposition from molybdenum and tantalum metal cathodes in a reactive gas mixture of hydrocarbons and argon of proprietary composition.

For the purpose of the analysis of this work, equivalent coatings were deposited onto AISI D-2 steel test coupons. The coupons were previously hardened and high-temperature tempered to HRC 58–59, corresponding to a Vickers hardness $H \cong 6.5$ GPa and then polished to a surface roughness of approximately $R_a = 60$ nm. This surface finish of the substrate produces a coating with a surface roughness much lower than that measured on the coated surface of the mold parts, but it is needed in order to obtain low dispersion in the nanoindentation hardness results, and also to obtain reproducibility on the scratch and pin-on-disk measurements.

The thickness of coatings deposited on the steel coupons is similar to the mean value of the thickness of the coatings produced in the manufacture of the molds. The coatings on steel coupons have been deposited with two reactive gas mixtures: first, the gas composition that leads to thin films of stoichiometric Mo_2C and TaC; and second, the gas composition used in the

production of coated mold parts, which has a higher hydrocarbon proportion and has been optimized to obtain coatings with the best efficiency during the live mold operation. This second gas composition produces carbides that are over-stoichiometric in carbon. In what follows, both types of carbides will be labeled as ‘low carbon content’ and ‘high carbon content’ respectively.

2.2. Mechanical and tribological characterization methods

The thickness of the coatings has been measured in the craters produced on their surface by the CALOTEST rotating ball erosion method, and also from scanning electron microscope (SEM) micrographs of the cross-sections of the steel coupons prepared by impact fracture.

The microhardness of the coatings has been studied with the nanoindentation method by using a NanoTest 550 (Micro Materials Ltd., Wrexham, UK) characterization system fitted with a sharp Berkovich diamond indenter, with a tip radius of 200 nm. The same system has been used to study the adhesion of the coatings to the steel coupons by the scratch test method, by using a 50- μm radius diamond spherical tip, a 2-mm long scratch path, and an increasing normal load along the scratch, from 0.1 up to 5 N.

The friction and wear behaviors were studied using a ball-on-disk micro-tribometer. This is a home-built tribometer capable of testing the wear and measuring the friction at room, but also at high temperature. It is of reduced size compared to standard pin-on-disk systems. The track radius described on the sample can be varied from 1 to 10 mm and the test balls have diameters from 0.2 to 2 mm. These reduced dimensions facilitate the test on small areas of a flat sample surface, and the system is especially suitable for wear studies on thin film hard coatings. The sample can be heated to 450°C during the test by means of an electrically heated rotating sample support. The test ball is pressed against the rotating sample surface by a fixed normal load, which can range from 50 mN up to 5 N, and the frictional force is continuously registered with a resolution of 10 mN. The test atmosphere can be chosen to be vacuum, or dry or humid gases. In this work, all the wear tests were carried out in dry air and at atmospheric pressure. The tests were conducted under a sliding velocity of 0.060 m s^{-1} and along a total sliding distance of 30 m, unless sample failure with severe wear appeared before this point. The wear rates on the surface of the sample were estimated from the wear volume of the coating in the wear tracks as measured from the track profiles, obtained with a diamond stylus profilometer. Wear rates on the test balls were deduced from the diameter of the wear scars on the balls, measured on the SEM micrographs of the balls taken after completion of the wear test.

Table 1

Mean thickness values for each layer as obtained from the Calotest trial on each coating

	Mo carbide thickness (nm)	Ta carbide thickness (nm)	Ti nitride thickness (nm)
High C content	800	920	650
Low C content	720	830	650

3. Results and discussion

The coatings deposited on the polished steel coupons are uniform and have a specular appearance, with a light clear gray shiny tint for the low carbon content carbides and a dark gray shiny tint for those with high carbon content. The thickness of all the carbide layers and of the TiN intermediate layers is very similar, between 600 and 800 nm each. Table 1 shows the mean thickness values as measured by the CALOTEST for each coating. It can be observed that the high carbon layers grow slightly thicker than the low carbon ones for the same deposition times. Similar thickness values can be deduced from the SEM micrograph in Fig. 1. In this micrograph the cross-section of the high carbon-content molybdenum carbide coating is observed. The coating shows a flat surface scattered with some spherical protrusions, which probably originated from droplets coming from the metallic cathode arc spots. The carbide layer is continuously adherent to the TiN layer, which also shows a good adherence to the broken steel substrate. The absence of delaminations in spite of the stress generated during the violent impact fracture of the hardened steel substrate means a good adhesion of the coating to the substrate.

The analysis of the scratch test results also gives a measure of the adhesive cohesion of the coatings. Fig. 2 shows the friction coefficient vs. the applied normal force along a 2-mm long scratch test performed on the high carbon-content molybdenum carbide coating. Two

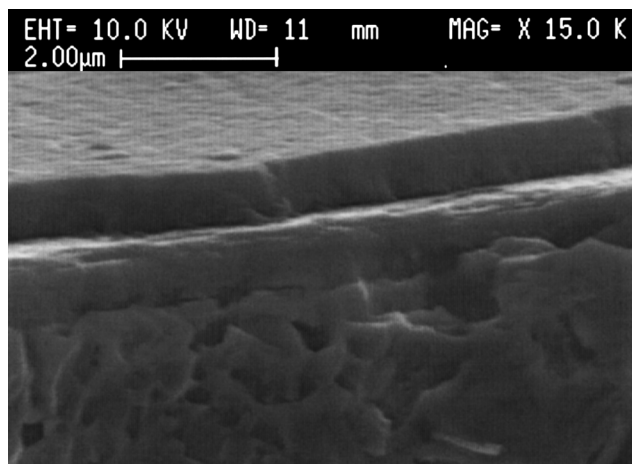


Fig. 1. SEM image of the cross-section of the molybdenum carbide–titanium nitride coating on steel.

sudden changes are observed in the friction coefficient evolution: first at a critical load $Lc_1 = 1$ N; and second at a critical load $Lc_2 = 4.3$ N. These changes are related to the adhesive failure of the carbide layer and the TiN layer, respectively, as confirmed by the optical microscopy observation of the scratch path. It should be noted that these Lc values are not directly comparable with the higher Lc values that would be obtained with the scratch test carried out with the more standard 200- μ m radius spherical indenter. The instantaneous spikes of the friction coefficient observed in the initial portion of the scratch, before the first critical load, are probably due to the diamond tip coming across a droplet protrusion.

In Fig. 3a,b the results of hardness measurements on molybdenum and tantalum carbide are presented. The hardness values are calculated from the analysis of the loading–unloading curves obtained with the dynamic nanoindentation technique on the coated steel test coupons, following the Oliver and Pharr analysis method [5]. Several indentations were made on each sample, with maximum load values in the range 5–100 mN. These load values produced maximum penetration depths in the range 100–800 nm. For each maximum penetration depth, a set of indentations in different depth sample locations was made, and the corresponding hardness values averaged. The dispersion of every set of measurements is taken as the error bars associated which each data point in Fig. 3. The hardness values measured at the lower penetration depths are associated to the carbide layers, which are first encountered

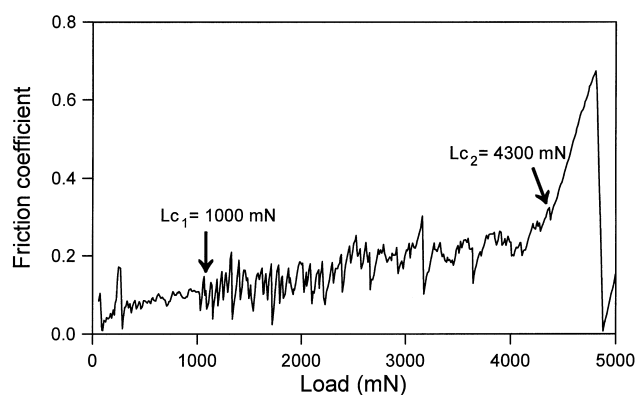


Fig. 2. Friction coefficient vs. normal load data obtained from the microscratch measurements on the molybdenum carbide–titanium nitride coating on steel.

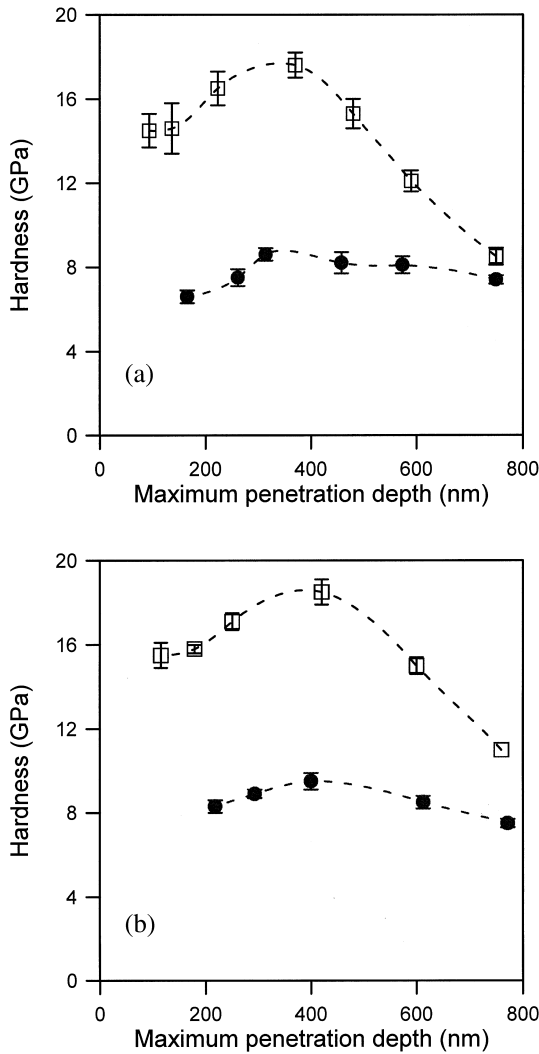


Fig. 3. Hardness values for different maximum penetration depths measured on tantalum carbide (a) and molybdenum carbide (b) coatings. The square data points correspond to low carbon content carbides and the circle data points to high carbon content carbides.

by the Berkovich indenter. It is observed that both molybdenum and tantalum carbides behave very similarly. The low carbon-content tantalum carbide layers show a hardness of approximately 14 GPa, slightly lower than that of the bulk TaC phase, and the low carbon-content molybdenum carbide layers show hardness values of approximately 15.5 GPa, slightly lower than the bulk Mo₂C phase. On the contrary, the high carbon-content layers show a much lower hardness, approximately 7.5 GPa. An increase in the measured hardness values is observed when the indentations go to higher maximum penetration depths. The maximum hardness values are measured for maximum indentation depths of 400 nm, which correspond to the superior hardness of the TiN intermediate layer. The measured hardness values, 17–19 GPa, are lower than the TiN bulk phase hardness, 21 GPa, because of the cushion effect of the upper carbide layers. With even

deeper maximum penetrations, the measured hardness tends to the values of the hard steel substrate, 6.5 GPa.

The friction and wear tests on the coated steel coupons were carried out against tungsten carbide balls of 0.8 mm diameter and surface roughness of $R_a = 30$ nm, and against 1-mm diameter hardened-steel ball bearings with surface roughness $R_a = 25$ nm. The tests were carried out at three temperatures: 20, 180 and 320°C. The normal load applied was 500 mN and the running time 10 min. The friction force registered as a function of time showed a decrease of approximately a factor of two after an initial short spinning time of approximately 10 s (equivalent to 60 spin revolutions or 0.6 m sliding distance). After this initial reduction, the friction force either remained almost constant with slight fluctuations until the end of the test, or increased rapidly and caused a deep wear track on the sample and a trembling and noisy sample spin.

Fig. 4a shows the friction coefficient values observed for the steel balls sliding against each coating at different temperatures. The molybdenum carbide coating with high carbon content shows the lower friction coefficient at room temperature and also at higher temperatures; the tantalum carbide coating with high carbon content shows a similar behavior, but with higher friction values. The low carbon content coatings show

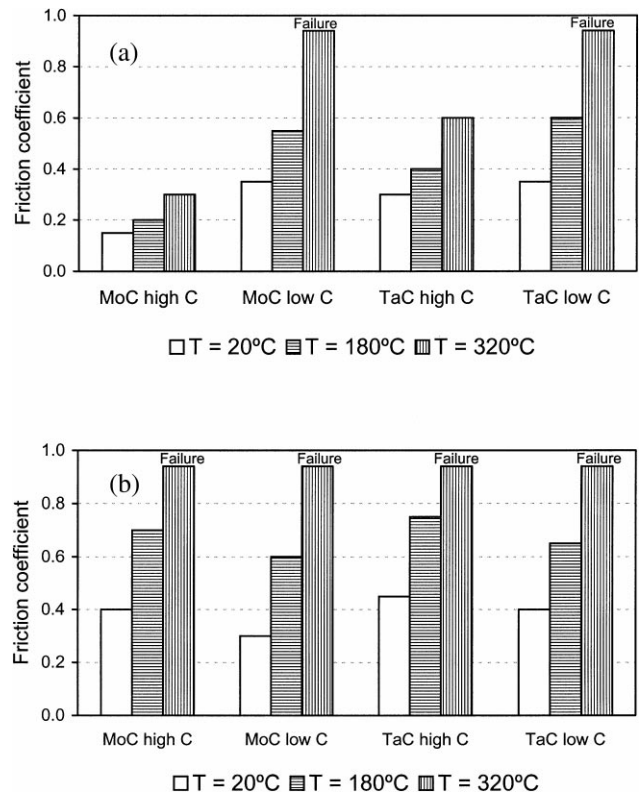


Fig. 4. Friction coefficient values obtained in ball-on-disk experiments for the steel balls (a) and tungsten carbide balls (b) sliding against each coating. Experiments were carried out at three different temperatures.

higher friction coefficients at room temperature, and are not able to survive the wear test at 320°C. The high carbon content carbide coatings show almost no wear track after the test, but the circle described by the steel ball is visible under the microscope in the form of smooth path were the droplets protrusions disappeared. The hard steel balls experience an important abrasive wear over all these coatings.

Fig. 4b shows the friction coefficient values observed for the tungsten carbide ball sliding against the different coatings. In this case all the friction coefficients are high, but here the friction coefficient is slightly lower against the low carbon content carbides. All the coatings suffer an important wear, with wear tracks at room temperature reaching the TiN interlayer. None of the coatings can survive the wear test at 320°C against the tungsten carbide ball. The tungsten carbide ball surface shows no appreciable abrasion after repeated wear tests against these coatings, even at the highest test temperatures.

These results seem to demonstrate that high hardness of the coating is not the important factor in surviving the wear test against steel balls, but low friction at low and high temperatures is. This rule is not true when the wear test is carried out against an extremely hard material, such as the tungsten carbide ball. The satisfactory behavior of the high carbon-content carbide coatings in the high temperature wear test against steel balls can explain the excellent wear resistance of these coatings in the performance of real parts, as is the case of steel molds used in aluminum and aluminum alloys injection cast molding. In fact, the coated molds showed longer life cycles than uncoated molds and molds coated with only the TiN thin film, and furthermore, they show better unmolding performance with reduced adhesion of the cast aluminum alloys to the mold walls.

4. Conclusions

The molybdenum and the tantalum carbide coatings obtained by cathodic arc plasma reactive deposition show excellent behavior as protective coatings on the molds used in aluminum and aluminum alloys injection cast molding. The superior performance is obtained with carbide compositions that are over-stoichiometric in carbon. The high carbon content carbide layers have lower hardness than the stoichiometric ones, but show low friction and a low wear rate in the ball-on-disk tests against steel balls at ambient and high temperatures. This low friction, rather than a very high hardness, seems to be the origin of the excellent protection given to the molds against the injection of molten metal.

Acknowledgements

This work has benefited from the financial support of the Commission for Cultural, Educational and Scientific Exchange between the United States of America and Spain. E. Martínez acknowledges the financial support of the DGR of the Generalitat de Catalunya.

References

- [1] V.A. Kolyagin, A.N. Timofeev, R.K. Chuzhko, I.A. Tomilin, *Inorg. Mater.* 27 (1) (1991) 9.
- [2] A.K. Dua, V.C. George, *Thin Solid Films* 247 (1) (1994) 34.
- [3] Q.Y. Zhang, X.X. Mei, D.Z. Yang et al., *Nucl. Instrum. Methods Phys. Res. B* 127 (1997) 664.
- [4] H.R. Herbolzheimer, K.E. Howard, R.A. Newman, *J. Mater. Sci.* 28 (2) (1993) 482.
- [5] W.C. Oliver, G.M. Pharr, *J. Mater. Res.* 7 (1992) 1564.