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Tribological performance of TiN supported molybdenum and tantalum carbide coatings in abrasion and sliding contact

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Abstract

Transition metal carbides are used in industry as protective hard coatings as they combine high hardness and wear resistance with a lower friction coefficient than nitrides. Tantalum and molybdenum carbides are examples of coatings that are widely used industrially in some specific applications. For example, they are often employed as protective materials against wear and adhesion in die-casting moulds. Although these metal carbides do not present an extremely high hardness, they possess excellent low friction and wear resistant properties. These interesting properties make these coatings excellent candidates for use in applications that involve sliding contact situations. In this paper, we present a tribological characterization of tantalum and molybdenum carbide coatings, each in two variants with different chemical composition, in abrasive and sliding wear conditions against alumina and hardened steel. The results were compared to those of a titanium nitride reference coating. It was found that the tantalum and molybdenum carbide coatings were not as resistant to abrasion as the titanium nitride. However, due to their extremely low friction coefficient values they were considered superior in sliding applications against both steel and alumina.

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1. Introduction

Transition metal nitrides have been extensively used in industry as protective hard coatings because of their hardness and wear resistance. Among these coatings, the most popular one is titanium nitride, which possess a high hardness. However, its behavior in applications that require low friction is not completely satisfactory [1,2]. Metal carbides can overcome this problem, and materials such as tungsten carbide have been introduced as low friction coating for industrial components [3]. Moreover, some transition metal carbides have demonstrated their excellent performance in specific applications, even if they do not posses an extremely high hardness [4–6]. This is the case of tantalum and molybdenum carbides, two refractory metal carbides with bulk hardness of 16.6 and 15.5 GPa, respectively [7]. As and example, tantalum and molybdenum carbide coatings are used industrially for wear protection of steel moulds employed in injection cast molding of aluminum and aluminum alloys [8]. In this application, the high wear resistance and low friction coefficient at high temperatures seem to be more important than high hardness [9].

In a previous work, we have reported on the deposition and mechanical properties of tantalum and molybdenum carbide coatings to be used in the metal casting industry [8]. In that work, we claimed that the excellent wear behavior of these coatings at high temperatures was the determinant factor for its good performance in die-casting. The present paper deals with a more complete and systematic tribological characterization of the coatings with the aim of extending their use to other industrial applications. We characterized the wear behavior in abrasive and sliding conditions of tantalum and molybdenum carbides with different carbon contents by means of dimple grinding and ball-on-disc tests.

2. Experimental

2.1. Coatings deposition

Coatings were deposited in an industrial PVD multi-cathode arc deposition system at Tratamientos Térmicos

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Table 1
Properties of the coatings

Sample	Thickness (nm)	Carbon content (%)	Roughness, R_a (nm)	Surface hardness[a] (GPa)
TiN/steel	1500 ± 50	–	99 ± 9	21.0 ± 0.2
TaC low C/TiN/steel	780 ± 50/750 ± 50	53 ± 4	96 ± 10	14.0 ± 0.3
TaC high C/TiN/steel	630 ± 50/740 ± 50	68 ± 5	139 ± 12	7.5 ± 0.1
MoC low C/TiN/steel	720 ± 50/700 ± 50	65 ± 3	158 ± 12	15.5 ± 0.2
MoC high C/TiN/steel	600 ± 50/720 ± 50	81 ± 4	173 ± 14	8.2 ± 0.2

[a] Hardness measured at a depth of 10% of coating thickness.

Carreras (TTC), Sabadell, Spain. The deposition chamber is equipped with six DC cathodes for arc evaporation of refractory metals. Substrates to be coated were located in a central rotatory holder that was DC biased up to −200 V. The deposition procedure involves the following steps: glow discharge surface cleaning, titanium ion bombardment heating of the parts, deposition of the different layers of the coating, and finally, cooling of the parts down to room temperature under inert gas atmosphere.

For the purpose of this work, coatings were deposited onto AISI D-2 steel test coupons. The coupons were previously hardened and tempered to 58–59 HRC and polished to a surface roughness of about $R_a = 60$ nm. The coatings consisted of a base layer of TiN deposited directly onto the steel substrates and an upper metal carbide layer (either tantalum or molybdenum carbide). The TiN layers were produced by vapor deposition from pure titanium cathodes with a standard argon and nitrogen reactive gas mixture. Tantalum and molybdenum carbide layers were obtained by vapor deposition from molybdenum and tantalum metal cathodes in a reactive gas mixture of acetylene and argon. The gas mixture was controlled as to produce both quasi-stoichiometric TaC and Mo_2C coatings (labeled “low carbon content”) and coatings over-stoichiometric in carbon (labeled “high carbon content”). More details about the deposition procedure can be found in a previous work [8]. A detailed description of the investigated coatings and their relevant properties are listed in Table 1.

2.2. *Abrasive and sliding wear characterization*

The abrasive wear resistance of the coatings was evaluated in a dimple grinder, equipment normally used for thinning of specimens for transmission electron microscopy. The grinder is equipped with a steel wheel 20 mm in diameter. The tests were performed with a normal load of 20 g and using 1 μm diamond slurry as abrasive. The small size of the abrasive diamond particles was chosen to obtain smooth abrasion in very shallow superficial craters, taking into account the low thickness of the coatings. The volume of the abrasion craters was measured with an optical interferometric surface profilometer (Wyko NT-2000). Several craters were made onto each sample and the calculation process developed by Kassman et al. [10,11] was used to compute the coating abrasion rate and separate the coating and substrate contributions. Basically, the calculation procedure consists on measuring the worn volumes of the coating (V_c) and the substrate (V_s) and insert these values in the following expression:

$$SL = \frac{V_c}{\kappa_c} + \frac{V_s}{\kappa_s} \tag{1}$$

where S is the sliding distance, L the total applied load and κ_c and κ_s the wear constants for the coating and the substrate, respectively.

The sliding wear resistance was determined by a conventional ball-on-disc test apparatus. The friction force was continuously registered during the experiment with a calibrated load transducer. Tests were conducted in laboratory atmosphere: a temperature of 22 ± 1 °C and a relative humidity of 40 ± 5%. Sintered alumina and steel balls 6 mm in diameter were used as counterparts and three tests were performed for each coating–ball combination to check the consistence of the results. Prior to each test the samples and the balls were cleaned with ethanol. The test parameters were wear track of 5 mm diameter, sliding speed of 50 mm/s, normal load of 5 N and a total sliding distance of 80 m. Coatings specific wear rate, κ', was determined by using the equation:

$$\kappa' = \frac{V}{Fs} \tag{2}$$

where F is the applied load, s the sliding distance and V the worn volume. This worn volume was calculated from the profile of the wear tracks as measured with the Wyko profilometer. The wear mechanisms were investigated by analyzing the wear tracks in a scanning electron microscope, Leo 1550 equipped with facilities for EDS analysis.

3. Results

3.1. *Coatings morphology*

All the coatings deposited on the polished steel coupons are uniform and had a specular appearance with a shiny light gray tint for both carbide coatings with low carbon content and a dark gray tint for those with high carbon content. Fig. 1 shows an SEM micrograph of a cross-section through the high carbon tantalum carbide coating. The carbide layer was continuously adhered to the TiN layer, which also shows a

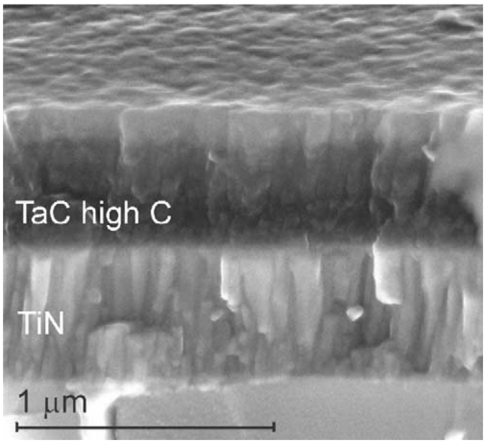

Fig. 1. Cross-sectional SEM micrograph showing the high carbon tantalum carbide coating and its supporting TiN layer.

good adherence to the steel substrate. Both the layers contain a columnar structure, although most evident in the TiN layer. All coatings showed a flat surface scattered with low rounded protrusions originated from droplets coming from the metallic cathode arc spots. Table 1 lists layer thicknesses as measured from SEM micrographs and coating roughness obtained with the Wyko profilometer.

3.2. Abrasive wear

The abrasive wear behavior of the coatings is shown in Fig. 2, which plots the abrasive wear rate of the investigated coatings as a function of their hardness. There is evidently a clear correlation between hardness and abrasive wear, which agrees with the results found in literature [12,13]. Tantalum carbide and molybdenum carbide coatings low in carbon content, i.e. nearly stoichiometric, presented the highest hardness and the best abrasive behavior.

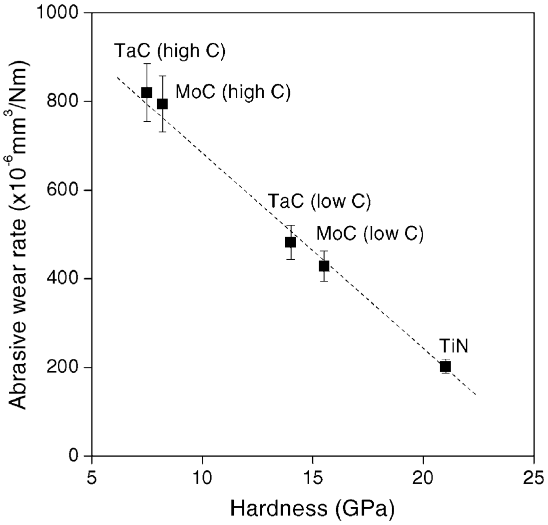

Fig. 2. Abrasive wear rate as a function of hardness for the five coatings when tested in the dimple grinder.

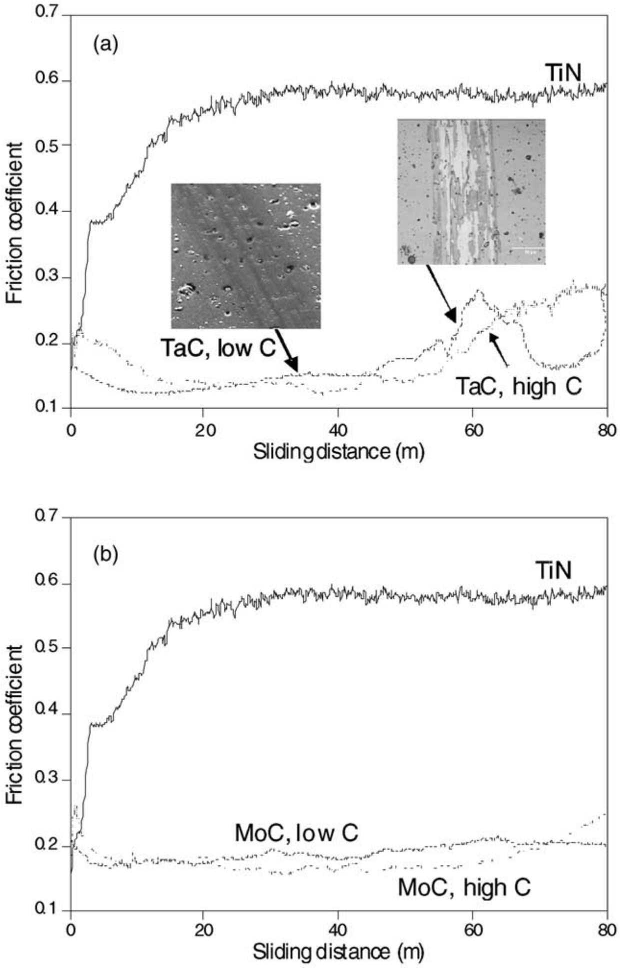

Fig. 3. Friction coefficient against alumina as a function of sliding distance for the tantalum carbide coatings (a) and the molybdenum carbide coatings (b) compared to the titanium nitride reference coating. The insets, showing low carbon tantalum carbide, are representative micrographs of the wear track in the steady-state and at the end of the test.

3.3. Friction and wear in sliding

Fig. 3 plots the friction coefficient as a function of the sliding distance for the tantalum carbide (a) and molybdenum carbide (b) coatings when sliding against alumina balls in ball-on-disc tests. It is striking that, in the steady-state friction stage, all the metal carbide layers presented much lower friction coefficients than the titanium nitride. Moreover, the friction coefficient values were generally lower for the tantalum carbide coatings (Fig. 4). These friction coefficient values are similar to those reported for titanium carbide coatings measured in comparable conditions [14]. The tantalum carbide coatings, however, showed an irregular behavior with an increase in the friction coefficient plot after 50 m of sliding (Fig. 3a). This was probably caused by the exposure of TiN inside the wear track, as can be seen in the right micrograph in Fig. 3a. The molybdenum carbide coatings, on the other hand, showed a low stable friction coefficient value up to the end of the sliding test.

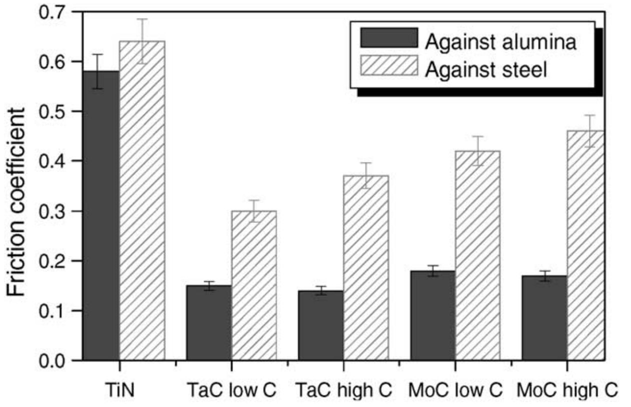

Fig. 4. Friction coefficient in the steady-state regime as measured from the ball-on-disc tests performed with alumina and steel balls.

Against alumina the wear rate was computed during the first 30 m of sliding, i.e. in the steady-state friction stage before the appearance of the TiN in the track. The most wear resistant coating was shown to be the tantalum carbide with low carbon content (Fig. 5a). In the wear track of the TaC coating with high carbon content the surface was smooth and without any indications of abrasion (Fig. 5b). In case of the wear track produced in the TiN coating, an abrasion scar was clearly seen (Fig. 5c).

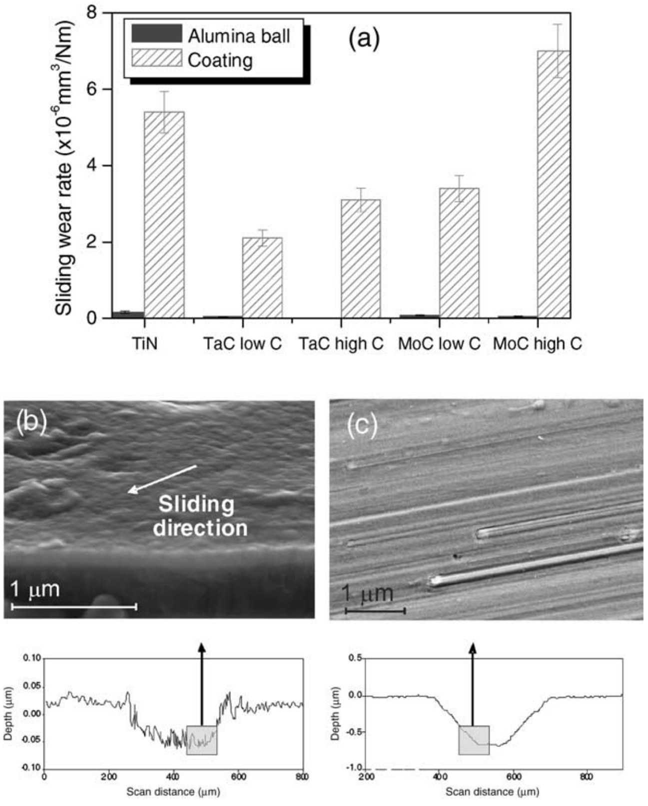

Fig. 5. (a) Sliding wear rate of the ball and the coating measured from ball-on-disc tests performed with alumina balls. (b) SEM micrograph corresponding to the cross-section of a wear track in the tantalum carbide coating with high carbon content. (c) Micrograph of the wear track in the TiN coating.

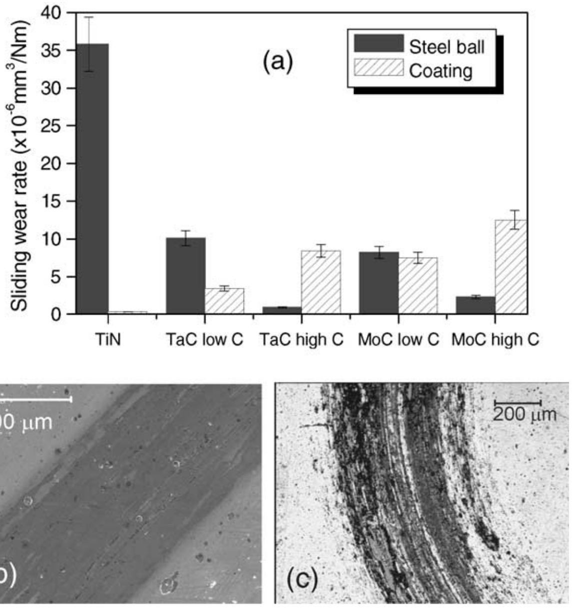

Fig. 6. (a) Sliding wear rate of the ball and the coating measured in ball-on-disc tests performed with steel balls. (b) Wear track for the tantalum carbide coating with low carbon content. (c) Wear track in the titanium nitride coating.

When sliding against steel balls, the behavior of the material was highly influenced by the differences in hardness between the ball and the coating. As can be seen in Fig. 6a, the steel ball was severely worn by coatings with high hardness, i.e. the TiN and the metal carbides with low carbon content. The friction coefficient values in the steady-state stage were lower for the low carbon coating than for the corresponding high carbon coating. There was no apparent failure of all the coatings at the end of the tests. Against steel, the best behavior corresponds to the tantalum carbide coating with low carbon content, as it presented the lowest values for the friction coefficient and the sliding wear rate.

4. Discussion

The results from the sliding against alumina are interesting as they present a conceivable contradiction. Both tantalum carbide and molybdenum carbide coatings could be easily abraded by the alumina ball, as the ball is harder than the coatings. TiN is harder than the metal carbide coatings, yet it is this hard coating that presented the lowest wear resistance. Thus, as the mechanism of wear in TiN is abrasion, the mechanism of wear in the case of the metal carbides is not. On the contrary, wear seems to be more related to tribochemical mechanisms such as formation and removal of transfer layers.

In the early stages of the sliding against alumina, tantalum carbide coatings, which presented the lowest hardness and abrasion wear resistance, indeed showed the best tribological performance concerning friction and sliding wear. One explanation for this could be that, during the first part of the test, the main wear mechanisms was a tribochemical processes that caused a slow removal of material from the coating. Material that in turn formed a lubricating layer in the contact. Slippery transfer layers have been reported in the literature when steel or ceramic balls slide against diamond-like coatings [15,16]. In our case, transfer layers contained a high proportion of carbon (in fact, the debris was a black powder mainly composed by carbon), but they also contained metal oxides. These layers can act as lubricant and be responsible of the very low wear and friction coefficients.

However, the same coatings had a short lifetime. Fatigue at the interface between the carbide and the nitride was probably an important factor, which can be partially due to residual stresses across the interface, together with the disordered structure of this region. After some sliding, abrasive wear was initiated by loose coating fragments. Soon abrasion and fatigue readily wore the tantalum carbide coatings, with low abrasion resistance, down to the TiN layer.

At the same conditions, the molybdenum carbide coatings presented a slightly lower sliding wear resistance and a higher friction coefficient, but they are less susceptible to fatigue. This can be due to the higher hardness and abrasion resistance as compared to tantalum carbide coatings, but also factors such as residual stress and toughness could have a major contribution, even if they could not be quantified for our coatings. Therefore, from this point of view, the best coating for sliding applications against hard ceramic counterparts was the one with low carbon molybdenum carbide as top layer. This coating combined low friction and fatigue resistance with adequate resistance to sliding and abrasive wear, all leading to a long lifetime.

Concerning the wear in sliding against steel, our hypothesis is that the wear mechanisms involved chemical reactions between the worn steel and the material surface. These chemical reactions can lead to the formation of transfer layers, which is often a complicated process that involves reactions between the ball surface, the transferred material, the coating surface (including its oxides) and the environmental conditions [17]. When observing the wear tracks for the TiN, we could see that there was a lot of ball material inside the wear track, mainly iron oxide (Fig. 6b). Probably, metal from the ball stuck to the titanium nitride surface, oxidized, and delaminated, taking small portions of the coating with it. On the metal carbides, we could not observe the same amount of the ball material inside the wear tracks (Fig. 6c). One reason could be thin tribolayers formed in the track, which constituted an easily sheared contact zone and as such did not provoke any picking up of coating material.

If the sliding application is against steel, the main advantage of these tantalum and molybdenum carbide top coatings is, however, their low friction coefficient. In this sense, the use of these coatings instead of TiN is well justified. However, the harder low carbon coatings cause wear of the steel but the worn material does not stick onto the coating surface, as happens in the case of TiN. As the friction is often more important than the wear, we believe the low carbon tantalum carbide coating exhibits the best tribological performance when sliding against steel.

5. Conclusion

Tantalum and molybdenum carbide coatings seem to be good candidates to use as protective hard coatings against wear in sliding applications, especially if very low friction is required. It was found that nearly stoichiometric tantalum and molybdenum carbide coatings performed better tribologically than coatings over-stoichiometric in carbon did. In sliding where the counterpart is alumina the best overall performance was attributed to the molybdenum carbide coating. When sliding against steel the determinant factor was the low friction coefficient presented by the tantalum carbide coating.

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