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Tribological Properties of Cr- and Ti-Doped MoS_2 Composite Coatings under Different Humidity Atmosphere

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Abstract

Solid-lubricant MoS_2 coatings have been successfully applied in high vacuum and aerospace environments. However, these coatings are very sensitive to water vapor and not suitable for applications in moist environments. In this work, Cr- and T-doped MoS_2 composite coatings were developed. The results demonstrated that these composite coatings are promising for applications in high humidity environments. MoS_2-Cr and MoS_2-Ti composite coatings with different Cr or Ti content were deposited on high speed steel substrate by unbalanced magnetron sputtering. The composition, microstructure, and mechanical properties of the as-deposited MoS_2-metal composite coatings were analyzed by energy dispersive analysis of X-ray (EDX), X-ray diffraction (XRD), and nanoindentation experiments. The tribological properties of the coatings were evaluated against an alumina ball under different relative humidity atmosphere using a ball-on-disc tribometer. The MoS_2-Cr and MoS_2-Ti coatings showed a maximum hardness of 7.5 GPa and 8.4 GPa at a dopant content of 16.6 at% Cr or 20.2 at% Ti, respectively. The tribological test results showed that, with a small amount of Cr and/or Ti doping, the

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tribological properties of MoS_2 coatings under humid atmosphere could be significantly improved. The optimum doping level was found to be around 10 at% for both MoS_2-Cr coatings and MoS_2-Ti coatings to show the best tribological properties, with both the lowest friction coefficient and wear rate. The excellent tribological properties of the MoS_2-Cr and MoS_2-Ti coatings with an appropriate metal doping level in moist atmosphere are found due to their ability to form stable transfer layer on the surface of the counterbody, which supplies lubrication for the contact surface.

Keywords: Physical Vapor Deposition, MoS_2-metal composite coatings; Tribological properties; Hardness; Humidity atmosphere

1. Introduction

Many industrial and engineering applications require two surfaces to slide over one another, resulting in friction and wear. Examples include various cutting and forming tools, and generic wear components (gears, bearings, engine parts, etc.) as well. Nowadays, surface coating has increasingly become a routine step in tools' manufacturing industry. These tribological coatings can effectively reduce friction, improve wear resistance, increase tool lifetime, improve tool performance, and enhance the productivity as well. Practically, two main properties are fundamental to tool coatings: high hardness and lubricity. The higher hardness of the hard coatings gives the tools much greater protection against abrasive wear, while the lower coefficient of friction means that the tool will work with less force due to the reduced resistance.

Transition metal nitrides, carbides and carbonitrides, include TiN, TiCN, TiAlN, CrN-based, and ZrN-based coatings have proved to be very successful and are widely used in improving the

performance of cutting and forming tools, because of their high hardness, wear resistance, and chemical stability [1]. However, these conventional hard coatings generally exhibit a high coefficient of friction and cause abrasive wear on the opposing surface. Therefore, lubricants are still required in many practical applications.

For centuries, liquid lubricants were used to limit the contact pressure and reduce the temperature produced by friction. But, in many cases, for instance in vacuum environment, at high temperature application conditions, for food and medical apparatus, and so on, the presence of liquid lubricants is not recommended or forbidden for contamination and/or safety reasons. As an alternative, solid lubricants are often used in many industrial applications [2], which cause less or no contamination compared to liquid lubricants. Solid lubricants are appealing in promoting dry machining to avoid environmentally harmful liquid lubricants either fully or partially. MoS_2 is the most widely used lamellar compound solid lubricant.

Since the pioneer work of Spalvins [3], solid-lubricant MoS_2 coatings produced by physical vapor deposition (PVD) processes have been successfully applied in high vacuum and aerospace environments [4,5], e.g. bearings and gears in artificial satellites, for many years. The solid lubricant coating reduces the friction and protects both its own surface and the opposing surface in contrast to the conventional hard coatings. In normal terrestrial atmosphere, however, MoS_2 is prone to water adsorption from air because of its hygroscopic property. Hence, it is very sensitive to water vapor [5-7], resulting in poor tribological properties, including increased friction coefficient, degraded wear resistance, and reduced lifetime. Therefore, MoS_2 coatings are not suitable for practical applications in moist environments.

In the past two decades, co-sputtered MoS_2-metal composite coatings or MoS_2-metal multilayered coatings [8-20] have been widely reported by many research groups to exhibit

improvement in hardness, adhesion strength, and tribological performance in air over the pure MoS_2 coatings. Particularly, among these co-deposited coatings, the MoS_2-Ti composite coatings (trade-marked by Teer Coatings Ltd as MoST^{TM}) have been intensively investigated [8-16]. The MoST^{TM} composite coatings have given excellent industrial results for a wide range of cutting and forming tool applications at normal cutting speeds, showing big improvements in comparison with conventional hard coatings. Similar to the MoST composite coatings, MoS_2-Cr composite coatings have also attracted lots of attentions [15-20]. Chromium may behave similarly to titanium in the MoS_2-metal composite coating system, and in some specific applications, such as in machining brasses and stamping of copper-based coinage, chromium is expected to give better performance [15].

In this work, MoS_2-Cr and MoS_2-Ti composite coatings with different Cr or Ti contents were deposited on high speed steel (HSS) by unbalanced magnetron sputtering. The tribological performance of the as-deposited coatings under different relative humidity atmosphere was evaluated using a ball-on-disc tribometer against alumina ball.

2. Experimental details

MoS_2-Cr and MoS_2-Ti composite coatings, with a thickness of around 3.5 μm, were deposited by a Teer UDP-550 unbalanced magnetron sputtering system which has been described in detail in our previous works [21,22]. In the bottom part of the deposition chamber, a cryogenic-type cold trap (PolyCold System Inc., California, USA) was installed. The temperature of the cold trap is controlled between -105 and -115 ^{o}C during the whole process of coating deposition. On one hand, the Polycold system is helpful for accelerating the pumping rate of the vacuum system

so as to achieve a high level of base vacuum. Particularly, on the other hand, the Polycold system is effective for removal of residual water vapor in the deposition chamber, and consequently reduces oxygen contamination in the as-deposited coatings, which is critically important for the MoS_2 coatings.

In this work, one elemental chromium or titanium target and two molybdenum disulfide compound targets were used. Coating deposition was conducted in a flowing pure Ar atmosphere with a working pressure around 0.15 Pa. All the targets were direct current (DC) power sputtered. The sputtering current applied onto the MoS_2 targets was fixed at 0.8 A. In order to control the metal dopping level in the as-deposited composite coatings, the DC current applied on the Cr or Ti target was changed batch by batch. For depositing the MoS_2-Cr coatings, the sputtering current applied on the Cr target was adjusted from 0 to 1.0 A, and correspondingly, the Cr content in the resultant coatings changed from 0 to 33.8 at%. While for depositing the MoS_2-Ti coatings, the sputtering current applied on the Ti target was adjusted from 0 to 2.5 A, and the Ti content in the resultant coatings changed from 0 to 29.7 at%. Mirror-finished high speed steel (HSS) discs with a diameter of 50 mm were used as substrates. Before loading into the vacuum chamber, the HSS substrates were ultrasonically cleaned in a series of alkaline solutions, washed in deionized water, dried by nitrogen gas blowing and further dried in an oven at 100°C. Then the precleaned substrates were mounted on a vertical substrate holder which rotated continuously around the central axis at a speed of 10 rpm. Prior to coating deposition, the vacuum chamber was pumped down to 2×10^{-4} Pa or lower, and the substrates were *in situ* cleaned with an argon plasma at a bias of –500 V for half an hour. During deposition, a negative pulsed direct current (PDC) bias of -70 V, with a frequency and duration of 50 kHz and 2.0 μs respectively, was applied to the substrates. Similar to our previous work

[21,22], in order to enhance coating adhesion onto the substrate, a multilayer structure was constructed. It started with a Cr or Ti bonding layer (~100 nm), followed by a gradient Cr-MoS_2 or Ti-MoS_2 ramping layer (~400 nm) in which Cr or Ti content was decreased while MoS_2 content was increased gradually, and finished with the MoS_2-Cr or MoS_2-Ti composite top layer. Even for the "pure" MoS_2 coatings referred in this paper, they also started with the Cr or Ti bonding layer and followed by the gradient ramping layer. Only in the top layer of these "pure" MoS_2 coatings, the metal doping content is zero.

After deposition, the composition of the as-deposited coatings was measured by energy dispersive analysis of X-rays (EDX), which is attached to a scanning electron microscope, operating at 8 keV and using the INCA quantitative analysis software. The microstructure of the coatings was analyzed by X-ray diffraction (XRD) which was performed on a Philips x-ray diffractometer in a θ-2θ scan mode using Cu K_α radiation (40kV, 30mA). Micro hardness of the coatings was measured using a Nanotest 550 nanoindenter equipped with a Berbovich diamond indenter (a three-sided pyramid), with the maximum indentation depth around 300 nm. For each sample, eight points were measured and the average hardness and standard deviation were obtained.

To evaluate the tribological properties of the as-deposited composite coatings, sliding wear tests were carried out at room temperature (~24 ^{o}C) against an alumina ball with 9.5 mm in diameter using a pin-on-disc tribometer (CETR UMT-2) under a normal load of 20 N. The sliding linear speed and total sliding distance were set at 10 cm/s and 700 m, respectively. The normalized wear rate was calculated from the preset normal load, total sliding distance, wear track diameter, and cross-sectional area of the wear track which can be measured by a surface profilometer. After the pin-on-disc tests, the morphology and composition of the wear track on the coating

sample and the contact area of the alumina ball were analyzed by SEM attached with EDX. In order to investigate the influence of humidity on the tribological properties of the as-deposited composite coatings, wear tests were conducted in an enclosed chamber connected with a water bubbler and dry air supplier. The relative humidity in the testing chamber was precisely controlled at ≤8% (will be referred as 0% or dry atmosphere in this work), 25%, 50%, 75%, and ≥98% (will be referred as 100% or extreme humidity atmosphere in this work), respectively.

3. Results and discussions

The Cr and Ti content in the as-deposited MoS_2-Cr or MoS_2-Ti coatings are shown in Fig.1a and Fig.1b, respectively, as a function of the DC sputtering current (I_{Cr} or I_{Ti}) applied on the Cr or Ti target. It is as expected that Cr and Ti content increased almost linearly with the increase of I_{Cr} or I_{Ti}. With the increase of I_{Cr} from 0 to 1.0 A, the Cr content in the MoS_2-Cr coatings monotonously increased from 0 to around 33.8 at.%. The Ti content in the MoS_2-Ti coatings increased from 0 to 29.7 at.% with the increase of I_{Ti} from 0 to 2.5 A. The typical EDX spectra of these coatings are shown in the inserts of the figure. No oxygen content was detected in the as-deposited coatings, either pure MoS_2, or MoS_2-Cr or MoS_2-Ti composite coatings.

Fig.2 shows the XRD patterns of the as-deposited MoS_2-Cr and MoS_2-Ti coatings. Besides the diffraction peaks arisen from the HSS substrate (marked as HSS in the figure), there was a evident peak at around $2\theta=34°$ for "pure" MoS_2 coatings (Cr or Ti content in the top layer is zero) which could be assigned to the MoS_2 (100) plane. According to Arslane et al. [13], this type of coatings with the basal planes parallel to sliding direction not only supplies good lubrication property but also is more resistant to oxidation because of the edge sites are protected. With the incorporation of metal component, either Cr or Ti, the MoS_2 (100) diffraction

peak disappeared, and no other peaks related to the coating material can be observed, indicating that the composite coatings become of amorphous structure. This fact could be attributed to the lattice distortion caused by metal incorporation.

Fig.3 displays the hardness of MoS_2-Cr and MoS_2-Ti composite coatings as a function of Cr or Ti content. The change in hardness for both coatings showed a similar trend. In lower metal content region, the coating hardness increased with the increase of doping content. A maximum hardness of about 7.5 GPa or 8.4 GPa was obtained at around 16.6 at%Cr or 20.2 at%Ti for the MoS_2-Cr and MoS_2-Ti coatings, respectively. The hardness enhancement of the MoS_2-metal composite coatings can be ascribed to solid solution hardening effect, i.e. the distortion of the MoS_2 lattice caused by the incorporation of doping metal atoms [15]. When studying both multilayered and monolayer co-deposited MoS_2-metal composite coatings, Lince et al. [23] found that the incorporation of metal components into the MoS_2 coatings led to a denser coating structure, and thus believed that the densification fact is responsible for the coating hardness enhancement. When the metal doping content increased further, the coating hardness decreased rapidly. This fact might be due to the possible formation of discrete metallic particles [15].

3.1 Tribological properties

During wear testing, the friction coefficient of the wear pairs was automatically recorded. Fig.4 shows the traces of friction coefficient of the MoS_2-Cr and MoS_2-Ti composite coatings in the wear tests against alumina under different relative humidity atmosphere. For pure MoS_2 coatings, the friction coefficient under dry atmosphere (RH=0%) is very low, around 0.05. However, the pure MoS_2 coatings are very sensitive to moisture, and their friction coefficient increased monotonously with the increase of RH value. With a small amount of metal incorporation (Cr

content ≤ 16.6 at% or Ti content ≤ 15.2 at%), the MoS_2-metal composite coatings have a similar friction coefficient with pure MoS_2 under dry conditions. But these composite coatings are very stable against moisture. Their friction coefficient remains at a very low level (≤ 0.1) under various humidity conditions, except that of the MoS_2-16.6at%Cr and MoS_2-15.2at%Ti coatings under the extreme 100% RH atmosphere. For the coatings with higher metal content (Cr content ≥ 23.5 at% or Ti content ≥ 20.2 at%), however, the friction coefficient becomes very high and unstable, which results in very high wear rate. The average friction coefficient in the relative steady stage of the MoS_2-Cr and MoS_2-Ti coatings under different RH atmosphere is shown in Fig.5.

It is interesting to note that for the MoS_2-Cr coatings with higher Cr content, the friction coefficient under dry atmosphere is very high (~ 0.8). With increasing the RH value in the testing atmosphere, the friction coefficient was evidently reduced and a minimum friction coefficient is obtained under a certain RH value. It was further noticed that the higher the Cr content is in the coating, the higher RH value will be under which the minimum friction coefficient is obtained. For the highest Cr-doped composite coating in this work (MoS_2-33.8at% Cr), the friction coefficient is inversely proportional to the RH value, and its minimum friction coefficient was obtained at the extreme RH=100% humidity condition, clearly indicating that the moisture plays a role of lubrication for the higher Cr-doped MoS_2 composite coatings. Based on the above-mentioned experimental phenomena, it can be concluded that for the coatings with lower Cr content (≤ 16.6 at%), the MoS_2 solid lubrication plays the major role on the tribological performance of the MoS_2-Cr composite coatings. But for the higher Cr-doped coatings (Cr content ≥ 23.5 at%), water vapor becomes more and more important in determining the tribological behavior of the coatings. Similar to the higher doped MoS_2-Cr coatings, a minimum

friction coefficient was also obtained at a certain RH for the higher doped MoS_2-Ti coatings. But the relationship between the Ti content and the RH value showing the minimum friction coefficient was not so clear or consistent for the MoS_2-Ti composite coatings.

Mohrbacher, et al. [24] once reported that the fretting behaviour of PVD TiN coatings vibrating against corundum counterbody was very sensitive to the relative humidity in the ambient atmosphere. Fretting at a low relative humidity is characterized by high friction coefficient above unity. At high relative humidity, the coefficient of friction dropped significantly down to around 0.2. It was found that during the fretting tests, TiN coatings degraded by oxidational wear. Initially, the degraded coating material was transferred to the corundum counterbody where it forms a compact oxide layer having a mixed stoichiometry between TiO and TiO_2. During further fretting, loose wear particles having a highly defective rutile (TiO_2) structure are emerging in the contact zone. The incorporation of environmental moisture in the defective debris results in a low shear strength layer effectively reducing the coefficient of friction. Similarly, the high friction coefficient of the highly doped MoS_2-Cr and MoS_2-Ti composite coatings in dry atmosphere might also be ascribed to the tribo-oxidation of the Cr or Ti components. With increasing RH, the incorporation of moisture with the oxide wear debris could form soft hydroxides with low shear strength, which resulted in a great decrease of friction coefficient. The resultant wear surfaces would become very smooth and available for hydro-dynamic lubrication with water [25].

Generally, the wear rate of the highly doped MoS_2-metal composite coatings (with Cr or Ti content $\geq$ 20 at%) is very high, about two orders in magnitude higher than that of the lower doped composite coatings, as observed in our work. In many cases, these coatings were wore out during the sliding wear tests. These coatings will be further investigated in our future work. Later

on in the present paper, the investigation on the tribological properties of the MoS_2-metal composite coatings will be focused on the lower doped coatings (i.e. with Cr content $\leq$ 16.6 at% or Ti content $\leq$ 15.2 at%).

Fig.6 compares the wear rate of the pure MoS_2 coatings and MoS_2-Cr (a) and MoS_2-Ti (b) coatings with lower metal content. Under dry conditions, the wear rate of pure MoS_2 coating is similar to that of the MoS_2-9.6at%Cr, and evidently lower than that of the MoS_2-16.6at%Cr coating. With the increase of RH value in the testing atmosphere, the wear rate of the pure MoS_2 coating increased rapidly, while that of both the MoS_2-9.6at%Cr and MoS_2-16.6at%Cr composite coatings decreased gradually when the RH was increased up to 50% and thereafter increased when RH was increased further. At RH=75%, the wear rate of the pure MoS_2 coating (2.2×10^{-5} mm^3/Nm) is about 30 and 7 times higher than that of the MoS_2-9.6at%Cr (8.0×10^{-7} mm^3/Nm) and MoS_2-16.6at%Cr (3.0×10^{-6} mm^3/Nm) coatings, respectively. Under all testing conditions, the MoS_2-9.6at%Cr coating exhibited the lowest wear rate, indicating the optimum Cr doping level for the best wear resistant MoS_2-Cr coatings is around 10 at%.

For both the MoS_2-9.5at%Ti and MoS_2-15.2at%Ti coatings, a very low wear rate ($\leq2.0\times10^{-7}$ mm^3/Nm) was measured and this excellent wear resistance could be remained even the relative humidity of the testing atmosphere was increased up to 75%. The MoS_2-9.5at%Ti composite coating always shows the lowest friction coefficient and wear rate in various RH atmosphere, indicating that the optimum Ti doping level for the best wear resistant MoS_2-Ti coatings is also around 10 at%.

Fig.7 shows the morphology of the wear scar on the Al_2O_3 ball and the corresponding EDX spectrum taken from the contact area after the sliding wear test against the pure MoS_2 coating in a RH=75% atmosphere. Only a very little amount of Mo was detected in the contact area on the

alumina ball, indicating that there was little MoS_2 transfer layer formed on the alumina ball, which is responsible for the higher wear rate of the pure MoS_2 coatings in high humid atmosphere. The bad tribological properties of the pure MoS_2 coatings under humidity conditions could be interpreted that the water vapor and/or oxygen atoms go into the space between the sulphur planes, disrupt the bonding between the plane [13]. Thus, pure MoS_2 coating is not able to form stable transfer layer on the counterbody.

Fig.8 shows the morphology of the wear scar on the Al_2O_3 ball and the corresponding EDX spectrum taken from the contact area after sliding against the MoS_2-9.6at%Cr composite coating in a 75% RH atmosphere. In contrast to the case against the pure MoS_2 coating, evident Mo, S and Cr signals were detected in the contact area on the alumina ball after sliding wear against the MoS_2-9.6at%Cr coating, indicating that a transfer layer composed of Mo, S and Cr was formed on the alumina ball. The formation of this lubricious transfer layer prevents the direct contact between the Al_2O_3 ball and the MoS_2-Cr coating and results in the lower wear rate of the coating. For the MoS_2-Ti composite coatings with lower Ti content, the formation of a similar lubricious transfer layer on the alumina counterbody's contact surface was also confirmed, as shown in Fig.9, which leads to the excellent wear resistance of the composite coatings.

The addition of small amount of Cr or Ti atoms might enter the space between the sulphur planes and prevent the water vapour entering the coating. The lower doped MoS_2-Cr or MoS_2-Ti coatings still remains the lamellar base structure of MoS_2 material, so they are able to form stable transfer layer and provide good tribological properties in high humidity atmosphere. However, when the limit of the solubility reaches, the Cr or Ti would no longer stay in the interstitial sites but precipitate out forming discrete metal or multilayer, bad tribological properties would be observed.

4. Conclusions

Pure MoS_2 coatings exhibit excellent tribological properties in dry atmosphere, but they are very sensitive to moisture. Their friction coefficient and wear rate increased significantly with the increase of relative humidity. With a small amount of Cr or Ti (≤16 at%) doping, the tribological properties of the resultant composite coatings remain excellent even the relative humidity is increased up to 75%. When the doping content is further increased (>20at%), the tribological behavior of these composite coatings changed distictively, and their wear resistance is greatly degraded. The optimum doping level was found to be around 10 at% for both MoS_2-Cr coatings and MoS_2-Ti coatings to show the best tribological properties, with both the lowest friction coefficient and wear rate. The excellent tribological properties of the MoS_2-Cr and MoS_2-Ti coatings with an appropriate metal doping level in moist atmosphere are found due to their ability to form stable transfer layer on the surface of the counterbody, which supplies lubrication for the contact surface. These excellent tribological properties demonstrated a very promising applicability of the MoS_2-Cr and MoS_2-Ti composite coatings in wide range working conditions, from dry to high humidity atmospheres.

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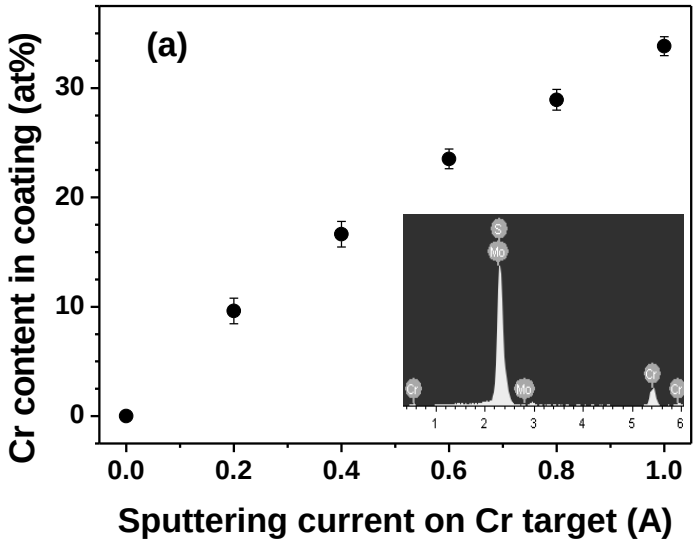
List of Figures:


(a)
Cr content in coating (at%)
Sputtering current on Cr target (A)
0
10
20
30
0.0
0.2
0.4
0.6
0.8
1.0
S
Mo
Cr
Mo
Cr
Cr
1
2
3
4
5
6

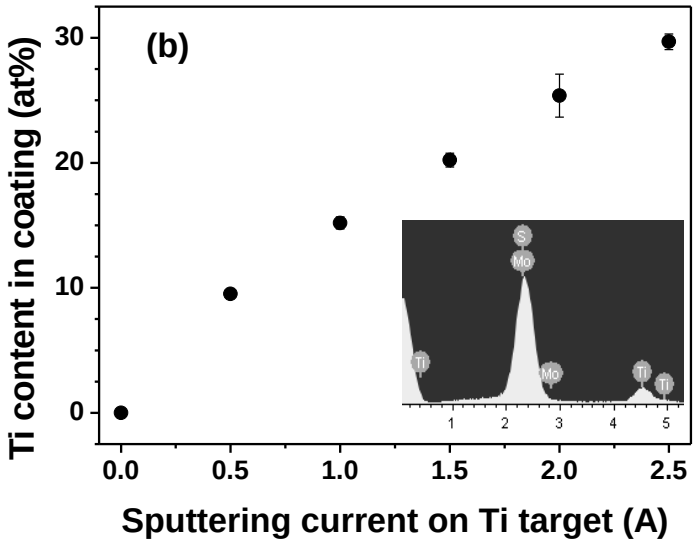

(b)
Ti content in coating (at%)
Sputtering current on Ti target (A)
0
10
20
30
0.0
0.5
1.0
1.5
2.0
2.5
S
Mo
Ti
Mo
Ti
Ti
1
2
3
4
5

Figure 1

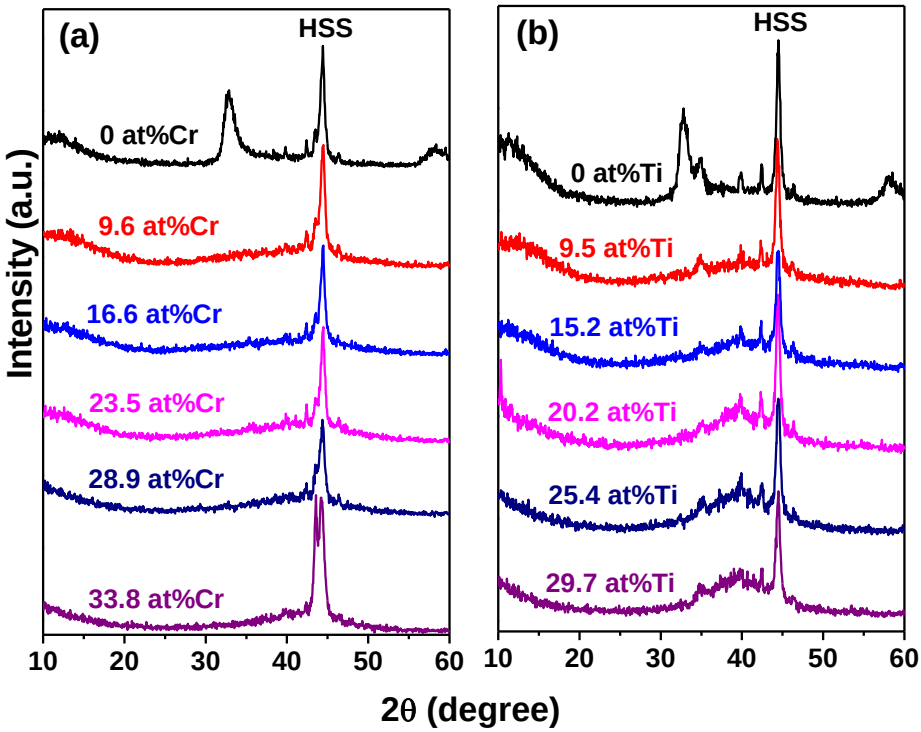

(a)
HSS
0 at%Cr
9.6 at%Cr
16.6 at%Cr
23.5 at%Cr
28.9 at%Cr
33.8 at%Cr
(b)
HSS
0 at%Ti
9.5 at%Ti
15.2 at%Ti
20.2 at%Ti
25.4 at%Ti
29.7 at%Ti
Intensity (a.u.)
10
20
30
40
50
60
2θ (degree)

Figure 2

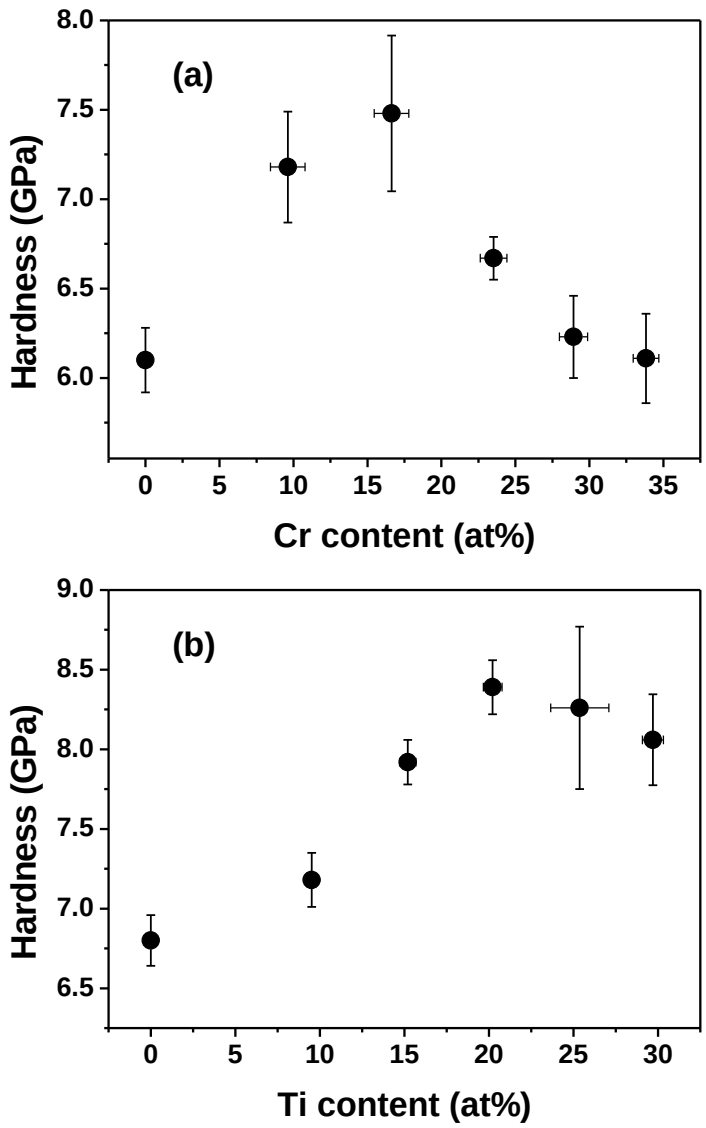

(a)
Hardness (GPa)
8.0
7.5
7.0
6.5
6.0
0
5
10
15
20
25
30
35
Cr content (at%)
(b)
Hardness (GPa)
9.0
8.5
8.0
7.5
7.0
6.5
0
5
10
15
20
25
30
Ti content (at%)

Figure 3

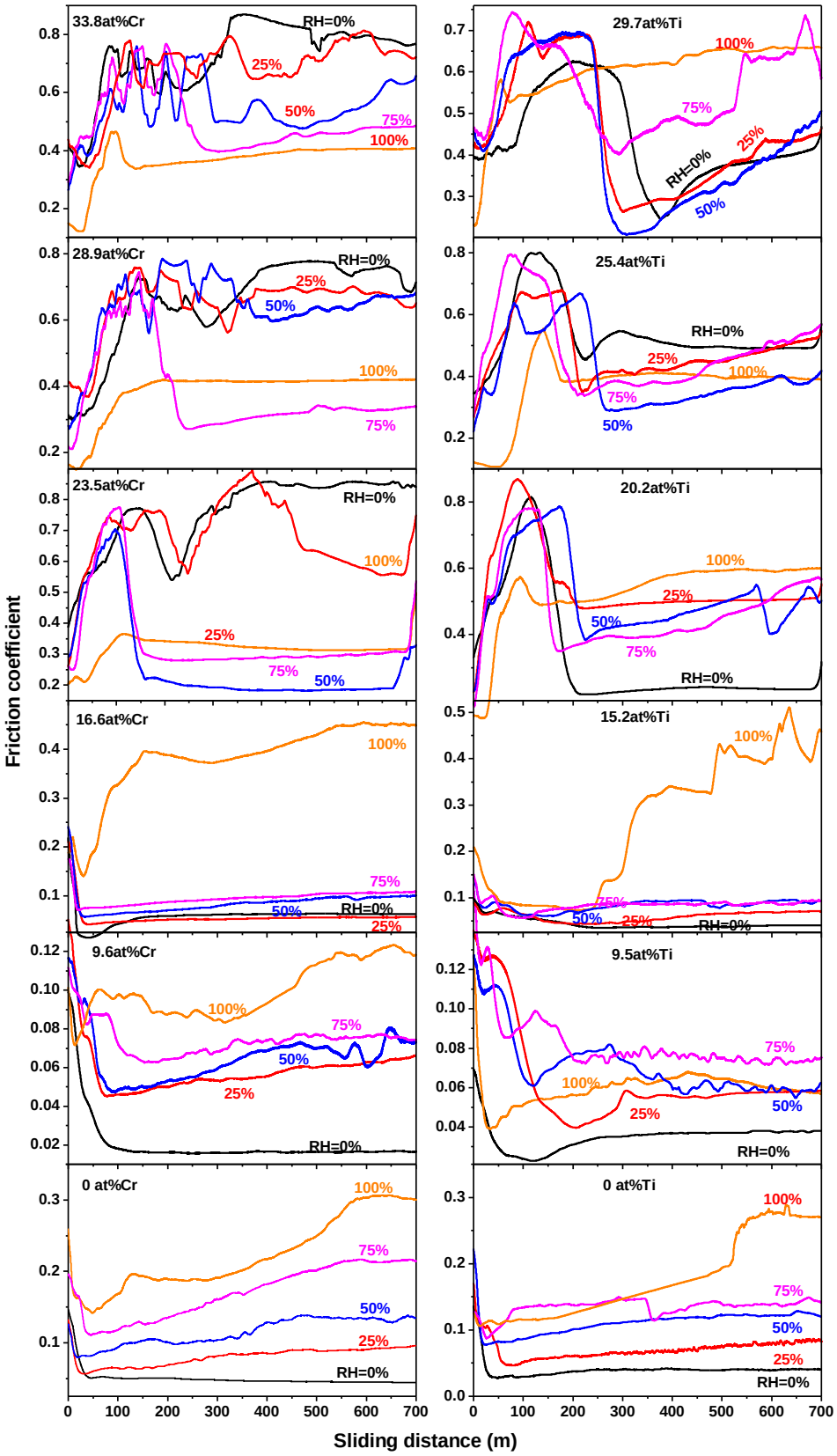

33.8at%Cr
RH=0%
25%
50%
75%
100%
29.7at%Ti
100%
75%
25%
RH=0%
50%
28.9at%Cr
RH=0%
25%
50%
100%
75%
25.4at%Ti
RH=0%
25%
100%
75%
50%
23.5at%Cr
RH=0%
100%
25%
75%
50%
20.2at%Ti
100%
25%
50%
75%
RH=0%
16.6at%Cr
100%
75%
50%
RH=0%
25%
15.2at%Ti
100%
75%
50%
25%
RH=0%
9.6at%Cr
100%
75%
50%
25%
RH=0%
9.5at%Ti
75%
100%
25%
50%
RH=0%
0 at%Cr
100%
75%
50%
25%
RH=0%
0 at%Ti
100%
75%
50%
25%
RH=0%
Friction coefficient
Sliding distance (m)

Figure 4

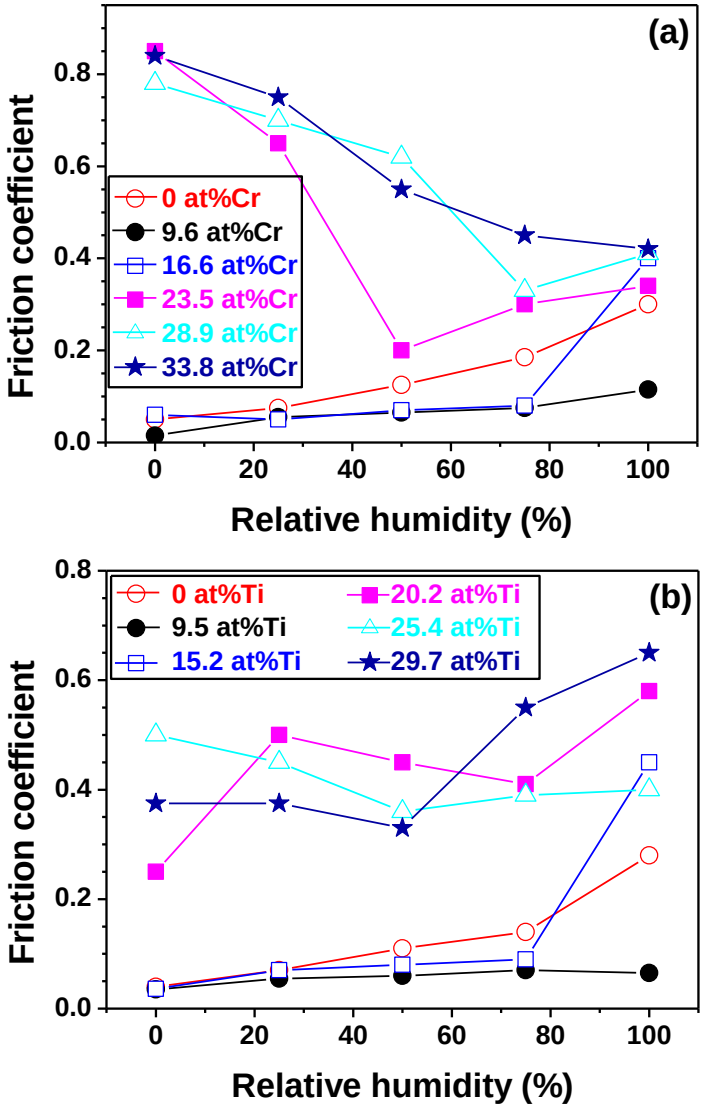

(a)
Friction coefficient
Relative humidity (%)
0 at%Cr
9.6 at%Cr
16.6 at%Cr
23.5 at%Cr
28.9 at%Cr
33.8 at%Cr
(b)
0 at%Ti
9.5 at%Ti
15.2 at%Ti
20.2 at%Ti
25.4 at%Ti
29.7 at%Ti

Figure 5

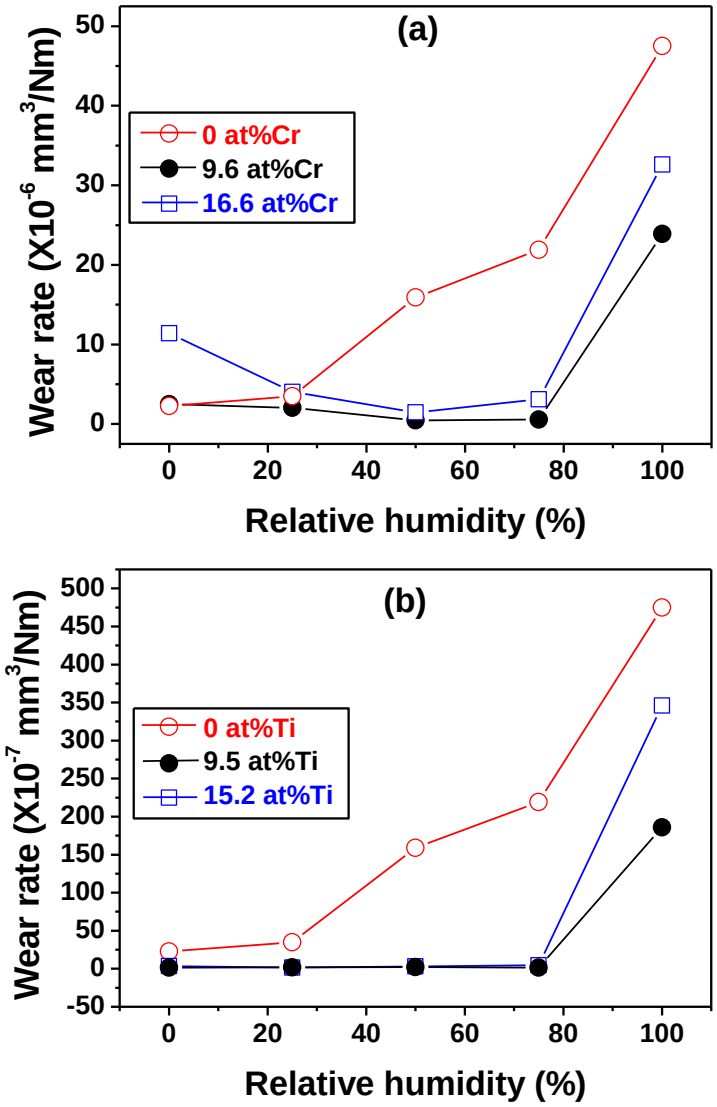

(a)
0 at%Cr
9.6 at%Cr
16.6 at%Cr
Wear rate (X10-6 mm3/Nm)
Relative humidity (%)
(b)
0 at%Ti
9.5 at%Ti
15.2 at%Ti
Wear rate (X10-7 mm3/Nm)
Relative humidity (%)

Figure 6

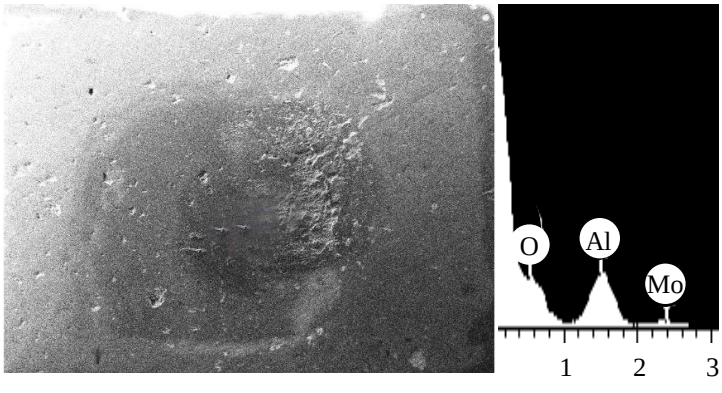


Figure 7

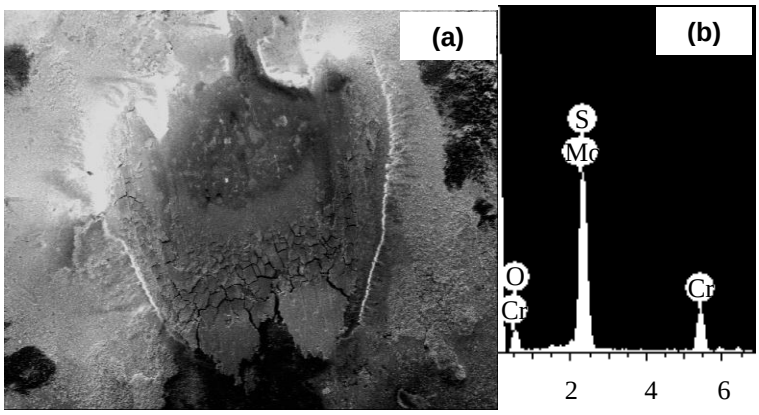


Figure 8

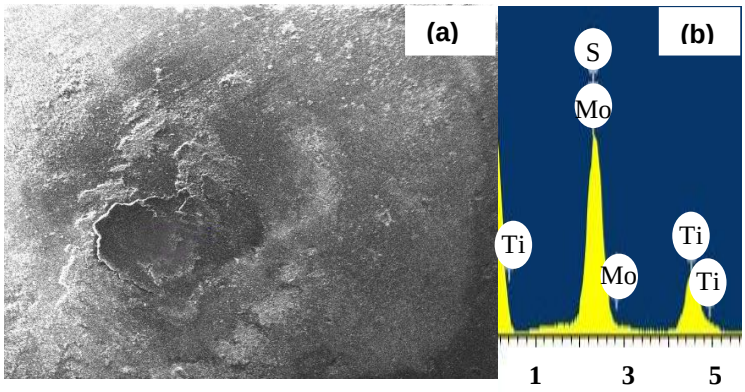


Figure 9