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Influence of composition and structural properties in the tribological behaviour of magnetron sputtered Ti–Si–C nanostructured thin films, prepared at low temperature

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ARTICLE INFO

Article history:

Received 5 February 2009

Received in revised form

29 September 2009

Accepted 5 October 2009

Available online xxx

Keywords:

PVD coatings

Friction

Wear

Hardness

Residual stresses

ABSTRACT

Within the frame of this work, low temperature Ti–Si–C films were deposited on high-speed steel and stainless steel substrates by combined dc/rf magnetron co-sputtering. Composition analysis revealed the existence of two distinct regions: (i) a silicon doped sub-stoichiometric titanium carbide zone and (ii) a titanium rich zone. Structural analysis confirmed the different nature of the prepared films within each of the two zones. The residual stress states (σ_r) were relatively low, and the hardness values ranged between 11 and 27 GPa, with a dependence on the composition as well as on the structural features. The tribological results showed quite similar trends, with both friction coefficients and wear revealing a straight correlation with the composition, and consequently, the different structural arrangements. In general terms, the obtained results showed that the friction coefficient of the samples tended to decrease with increasing C_C/C_{Si} atomic ratio, indicating an improvement in tribological behaviour for the samples with the highest carbon contents. In terms of wear resistance, the films with a stoichiometry very close to TiC, Si doped sub-stoichiometric titanium carbide films, presented the best behaviours, revealing that a compromise between the best friction and wear, must be made in order to select the optimum coating.

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1. Introduction

Ternary systems of the family TM–Si–N (TM = a transition metal) have been extensively studied due to the outstanding properties as diffusion barriers [1–3], as well as in several cases of mechanical protection. The particular case of the Ti–Si–N system can be pointed out as one of the most well studied coating system, revealing in some particular conditions extremely high hardness values, which can commonly reach values twice as high (or even higher) as those of TiN [4–6]. These films were claimed to result in a two-phase structure, where TiN grains are embedded in an amorphous matrix of silicon nitride [1,4,7]. The superhardness appears due to the hindering of the mechanisms of deformation and mechanical failure, because the dislocations will be repelled into grain boundaries [4–6]. The two involved phases should be strong materials with a high cohesive energy in the interface. The nature of the components, crystal size, and the amount of each phase determines the final properties of the material [8]. Anyway, it is well-known

that beyond hardness, another property plays a fundamental role in several mechanical/tribological-based applications: wear.

Having in mind that C-based or Me–C coatings are known to exhibit low friction coefficients and better wear rate than those of the Me–N system [9], other multifunctional coating material system is gaining importance for wear-based applications: the Me–Si–C (Me = transition metal), especially that of Ti–Si–C, studied for instance by Zehnder et al. [10] for wear protection applications. The basic idea is to take profit of the good wear properties of C-based coatings systems and, at the same time, trying to put Si acting similarly to what is observed in the Me–Si–N system, trying to bring together the positive inputs of both hardness and wear resistance. Anyway, research on the Ti–Si–C system has turned towards a new family of materials, the MAX phases, in which the Ti_3SiC_2 phase is the most investigated one [11].

Generally, the MAX phases, $M_{n+1}AX_n$ (with $n = 1–3$), are known to exhibit a unique catalog of properties, which can be observed in a large number (to date almost 60) of structurally related compounds consisting of an early transition metal (M), a group-A element and C and/or N (X). In general, these phases comprise ceramic as well as metallic characteristics [12], which can be understood as a similar approach to that of joining wear and hardness in one material only. The most studied materials system is Ti_3SiC_2 , which exhibits an

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interesting deformation mechanism via kink formation bestowing these materials metallic and ductile mechanical properties [13–15]. The successful synthesis of MAX phases in thin films has drawn much attention to these unique materials and introduced a new field of potential applications [16–19]. The major disadvantage, however, is that most of the thin films within this MAX phase family can only be synthesized at preparation temperatures above 700 °C and on textured or single crystalline templates substrates [20–22]. Thus, the choice of technologically relevant substrates is constrained, growing the need of developing extensive research programs. Lower growth temperatures, on the other hand, may result in a nanocomposite material, which has been demonstrated as a promising candidate for protective coating in electrical friction contacts owing to its metallic conductivity and resistance to wear and corrosion [21]. Thus, the purpose of this work is to present experimental results on the deposition and tribological characterization of Ti–Si–C films and to advance a qualitative explanation for the correlation between the deposition conditions and tribological properties (friction coefficient and wear strength). At the same time, the paper tries to compare the mechanical and tribological properties of the obtained Ti–Si–C films with those of similar films of MAX phase-type.

2. Experimental procedure

The Ti–Si–C films were synthesized by magnetron sputtering, using two targets: a titanium target, connected to a dc power unit, with current densities varying from 1.6 to 3.2 mA/cm²; and a carbon target, connected to a rf power unit, with applied power densities varying from 0.32 to 1.59 W/cm². In order to vary the Si content in the samples, different amounts of silicon pellets were placed on the Ti or C targets, within the erosion zone. For all depositions, the substrate holder was sweeping over the two targets with a constant frequency of 5 sweeps/min. Substrate temperature (300 °C), substrate bias (–50 V dc), target to substrate distance (65 mm) and argon flow rate (100 sccm) were kept constant during all the experiments.

The chemical composition of the coatings was investigated with a Cameca SX-50 Electron Probe Micro Analysis (EPMA), operating at 15 keV as acceleration voltage. The elemental quantification was performed by comparing the peak intensity in the sample and in standards for each element, and applying a ZAF correction (which uses fundamental factors to correct for the effects of atomic number, absorption and fluorescence) to the results.

Regarding the tribological characterization, the dynamic friction coefficient and the wear behaviour of the coatings (abrasion wear) have been estimated using a ball-on-disk tribosystem, CSM Instruments type. In this arrangement, a sphere shaped static partner was loaded on to the test sample with a calibrated force of 5 N. The static partner (the ball of AISI 100Cr6 steel with 6 mm in diameter, hardened and low tempered, with a final hardness of 62 HRC) was mounted on a stiff lever, designed as a frictionless force transducer. The sample is in rotation on the sample holder. As the sample is rotating, resulting frictional forces acting between the ball and sample, are measured by very small deflections of the lever using a Linear Variable Differential Transformer – LVDT sensor (in this case, the acquisition rate was 5 Hz). Thus, the LVDT sensor measures the tangential force F_t and provides then the friction coefficient values (the dynamic friction coefficient).

Wear rates for both the ball and sample are calculated from the volume of material loss during a specific friction run. This simple method allows the determination and study of friction and wear behaviour of the samples. The calculation of the worn track section for each sample was also done using a profilometer, Taylor Hobson type. Fig. 1 shows the example of the calculation of the worn track section result obtained for a worn track, using the profilometer. In

fact, by help of the TriboX Software, it has been calculated for each sample the volume of material lost after the wear test taking into account the transversal area of the worn track, the length of it (the length of circular channel obtained in depth, on the sample surface) and the applied load.

For all wear tests, the annular type wear surfaces were characterized by a wear track of 10 mm in diameter. The linear speed of the rotating plateau was 4.8 cm/s. The maximum number of laps (the stop condition) was 450. Before all the wear tests, the samples and the balls were cleaned with isopropanol. The environmental conditions for all tribological tests were: $T = 24$ °C and 30% of relative humidity.

The residual stresses, σ_r , were obtained by the deflection method and applying the Stoney's equation, using substrate curvature radii, before and after coating deposition. Film's hardness and Young's modulus were determined from the loading and unloading curves, carried out with an ultra low load-depth sensing Berkovich nanoindenter from CSM Instruments (Switzerland). The maximum load used was 30 mN, with a loading time of 30 s, holding 30 s and unloading in 30 s, producing an average number of 15 indentations per sample.

3. Results and discussion

The variable deposition conditions and the thickness of the films, measured by ball cratering, are presented in Table 1. Fig. 2a shows the composition of the as-deposited samples as a function of P_C/I_{Ti} ratio (P_C stands for the rf power applied to C target and I_{Ti} corresponds to the DC current applied to Ti target). As expected, an increase of the C content was obtained with the increase of the P_C/I_{Ti} ratio (from 3.9 to 44.2 at.%), while a systematic decrease of the Ti content was also observed (from 81.5 down to 48.8 at.%), as a reflex of the same power ratio variation. The Si content shows a two fold behaviour, where the samples with the highest Ti contents – from 81.5 to 67.4 at.% (and lowest C contents) presented higher Si contents (between 8 and 9.5 at.%), while the others revealed significantly lower amounts of this element.

The reason is mainly due to the lower number of Si pellets that were inserted in the C target. Plotting the atomic concentration ratios, C_C/C_{Ti} and C_{Si}/C_{Ti} , as a function of the target power ratio, P_C/I_{Ti} (see Fig. 2b), it is possible to see the existence of two distinct regions.

The first one corresponding to target power ratios, P_C/I_{Ti} , up to 500 W/A, where the samples revealed C_{Si}/C_{Ti} atomic ratios between 0.10 and 0.12, and relatively low C_C/C_{Ti} atomic ratios (below 0.31). Due to the higher Ti concentration in comparison to both C and Si, this zone will be noted in the text as a titanium rich zone.

The study of structural evolution of these coatings, by X-ray diffraction, was analyzed previously [23]. Summarizing the analysis, we may say that the coating with highest Ti concentration (TiSi_{0.11}C_{0.04}) presents a peak located close to the angular position of the reflection on planes (002) of α -Ti (ICDD card nr. 44-1294), slightly shifted to higher angles probably due to substitution, or

Table 1
Composition and thickness of the prepared films.

Sample	Deposition parameters				Thickness (μm)
	P_C (W)	I_{Ti} (A)	Si pellets	P/I ratio	
TiSi _{0.11} C _{0.04}	100	1.0	10	100	2.0
TiSi _{0.10} C _{0.10}	200	1.0	10	200	2.0
TiSi _{0.10} C _{0.19}	300	1.0	10	300	2.4
TiSi _{0.12} C _{0.30}	400	1.0	10	400	1.9
TiSi _{0.01} C _{0.36}	500	1.0	5	500	2.0
TiSi _{0.05} C _{0.84}	500	0.5	5	1000	1.9
TiSi _{0.10} C _{0.90}	500	0.5	10	1000	1.6

Fig. 1. Example of the calculation of the worn track section.

Fig. 2. (a) Variation of atomic concentration as a function of power applied on C target to current on Ti target ratio. (b) Variation of concentration ratio (C_C/C_{Ti} and C_{Si}/C_{Ti}) as a function of power applied on C target to current on Ti target ratio.

even inclusion, of smaller C or Si atoms in the α -Ti structure. Also observed was the constant shift of the peak to lower angular positions, approaching the position of the reflection in (1 1 1) planes of the fcc structure characteristic of TiC (ICDD card nr. 32-1383), with the increase of C content ($TiSi_{0.01}C_{0.36}$), but still too far apart to be indexed to the NaCl-type TiC structure. The peaks cannot be indexed to any known $TiSi_x$ structure which suggests the development of metastable-type phases.

The second region corresponds to the films prepared with higher target power ratios, P_C/I_{Ti} . In this zone, the films presented C_C/C_{Ti} atomic ratios around 0.9. Furthermore, the C_{Si}/C_{Ti} atomic ratios keep relatively low values (in fact, almost unchanged when compared to those in the previous zone) and thus this zone will be noted throughout the text as a Si doped TiC_x zone. In fact, the results of XRD revealed also a different nature of these films in terms of the type of structural arrangements. In straight correlation with the composition results, the films from this second zone.

The structural analysis of the films of this zone [23] revealed mainly sub-stoichiometric fcc NaCl-type TiC structure, with a (1 1 1) preferential orientation. The sample with highest non-metal content ($TiSi_{0.10}C_{0.90}$) presents two relatively broad peaks that may be indexed to reflection on (1 1 1) and (2 0 0) planes of fcc NaCl-type TiC structure. The broader peaks indicate a tendency for amorphization, probably due to higher Si content (twice higher when compared to the sample $TiSi_{0.05}C_{0.84}$).

Fig. 3 presents the variation of the dynamic friction coefficient (average values) as a function of the C_C/C_{Ti} atomic ratio. From the results plotted in this figure, the first observation that can be drawn

is that the dynamic friction coefficient of the samples decreased with the increasing of the C_C/C_{Ti} ratio, showing a straight dependence with the films particular composition (and consequently their structural features), namely that of C.

The sample with the lowest C content ($TiSi_{0.11}C_{0.04}$) – sample from the Ti rich zone – exhibits the highest dynamic friction coefficient, while the samples with the lowest C contents – samples from the Si doped TiC_x zone – are those showing the lowest dynamic fric-

Fig. 3. Plot of friction coefficient values as a function of the atomic ratio C_C/C_{Ti} and films hardness.

Fig. 4. Dynamic friction coefficient evolution (and micrographs of correspondent worn tested surfaces) as a function of number of revolutions for two representative samples, $\text{TiSi}_{0.11}\text{C}_{0.04}$ and $\text{TiSi}_{0.10}\text{C}_{0.90}$.

tion coefficients, in agreement with previous results from TiC-type system [8,24–28]. According to these, increasing the C content and keeping the crystalline structure of cubic TiC lattice, the friction coefficient also decreases. Moreover, for higher amounts of C, the friction coefficient will decrease even more, if the TiC crystallites are embedded in an amorphous C tissue due to the solid lubricant effect of C [8].

Fig. 4 shows the variation of the dynamic friction coefficients during the wear tests and the surface aspects at the end of friction – wear tests, for two samples representative of each of the two different zones: $\text{TiSi}_{0.10}\text{C}_{0.90}$ from the Si doped TiC_x zone and $\text{TiSi}_{0.11}\text{C}_{0.04}$ indexed to the Ti rich zone.

At the same time, a closer look to both variations and having in mind the chemical composition of the films, it seems clear that beyond the variation of the friction coefficients of samples within each of the compositional zones (see Fig. 3), there are some differences that are worth to be mentioned. First of all, at the beginning of the each test, the dynamic friction coefficients increased very fast and then kept a relatively high level, but with a significantly different grade of dispersion along the medium. The samples within the Ti rich zone, shown here by the $\text{TiSi}_{0.11}\text{C}_{0.04}$, showed a relatively high grade of dispersion in comparison with the ones from TiC rich zone, as demonstrated by the sample with a composition of $\text{TiSi}_{0.10}\text{C}_{0.90}$, which in fact seems also to have a slight decrease of friction coefficient as the number of revolutions evolves. On the contrary, and though the high degree of dispersion may not allow a better analysis, all samples within the Ti rich zone have always a relatively constant average value along the test duration.

Gulbinski and co-authors reported that also Ti–Si–C sputtered films show the same important decrease in the values of friction coefficient when an excess of carbon is present. Again, this excess of C is supposed to be present in an amorphous, a-C:H (acting again as a solid lubricant), matrix, which they claim that may coexist with small TiC grains (nanocrystalline), and probably amorphous SiC [29]. In the present study, the samples from the Si doped TiC_x zone have C_C/C_{Ti} atomic ratios below 1, and thus the reduction of the friction coefficients is probably much more related with the formation of that TiC-type phase. Furthermore, and taking the previous studies into account, it maybe be concluded that a continuous decrease in the friction coefficients may occur if the C content occurs in the samples prepared within the framework of this study. Anyway, the possibility of having some kind of amorphous SiC_x surrounding the nanocrystalline TiC_x grains would be also consistent with the reduction of the friction coefficients in the films from this carbide zone, acting then this silicon carbide phase as a solid lubricant.

Beyond the composition related aspects, Gulbinski et al. revealed also that, for TiC crystalline coatings, the increasing of C

Fig. 5. The sample and ball wear rates as a function of the C_C/C_{Ti} atomic ratio.

amount leads to a higher hardness and lower friction coefficients [28]. This decreasing of friction coefficient based on the hardness modification is explained by the reduction of the real contact area and the decrease of surface roughness. In the present study, this is also a factor to take into account as it can be observed from Fig. 3. In agreement with the findings of Gulbinski et al., a decrease of the friction coefficients was also observed with the increase of hardness, and thus one may conclude that indeed the reduction of contact area may be playing an important role for this decrease. Besides the solid lubricant role that this silicon carbide phase could be playing, one must consider that this controlled amount of amorphous SiC_x phase could give the film the necessary toughness.

Another important aspect related with the tribological performance of these low temperature Ti–Si–C coatings is that of direct comparison to the behaviour of the so-called MAX phases systems. Among the already wide variety of available MAX phase systems, an interesting example maybe that of Ti_3SiC_2 , which Emmerlich et al. reported that alumina substrates coated with this film system, revealed quite similar values for the dynamic friction coefficient values, varying between 0.6 and 0.8. These results were obtained using almost the same experimental arrangement (with a normal load of 0.24 N and ball-counterparts from Al_2O_3) [12]. These values are relatively higher than those obtained in this work, which maybe even more relevant if one takes into account that a normal load of 5 N was used in the characterization presented here.

Regarding the wear behaviour of the analyzed coatings, the sample wear rate as a function of the C_C/C_{Ti} atomic ratio is shown in Fig. 5. From this figure, it can be seen that similarly to what has been shown for friction coefficients, the best wear behaviour is also provided by the samples with the highest carbon contents – Si doped TiC_x zone – revealing once again the importance of the samples composition (mainly that of C) and the particular structural arrangements that maybe developed. At the same time, a higher grade of dispersion (see Fig. 4) is correlated with a higher wear rate of the films.

Related with this evolution and taking also into account the approximate testing conditions, Martinez-Martinez et al. [8] reported similar friction and wear tendency behaviours for TiC/a-C films, prepared by magnetron sputtering. These authors concluded that it is mainly the friction properties (not hardness) that are controlling the wear resistance of the films. However, they reported values of dynamic friction coefficient smaller than the ones presented in this work by the samples in the Si doped TiC_x zone. This could lead to the conclusion that in the present case, the fact that in this carbide zone the atomic ratio C_C/C_{Ti} is still below 1, means that the possibility to have that C amorphous phase is very reduced and thus, even if the SiC_x amorphous may have grown, the behaviour may be significantly improved if the C content is increased.

Fig. 6. The samples wear rate as a function of films hardness.

Fig. 6 shows the dependence of wear rate on hardness and similarly to what has been observed for friction, again higher values of hardness seem to have a positive effect in the wear behaviour. Again, the reduction of the real contact area and the decrease of surface roughness are most probably the main factors that may explain the positive effect. Furthermore, and beyond this positive effect, it is worth notice that the obtained hardness values are even higher than those of the Ti_3SiC_2 MAX phase system that were grown at 900°C on Al_2O_3 and MgO substrates by Emmerlich and co-workers [21].

For these unexpected high values of hardness, the lattice distortions that may occur due to the existence of some possible vacancies (especially in the C sites) if a SiC_x amorphous matrix develops and/or the existence of some Si atoms within the C sites are factors that would result in the development of intrinsic residual stresses, which would then result in hardening of the films.

Fig. 7 shows some evidences that in fact this may be occurring, showing that the hardness increase is associated with an increase in the stress levels, and thus acting as a hardening factor.

Fig. 7 correlates also the Young's modulus and the residual stress of the Ti–Si–C films with hardness, showing an almost linear behaviour. This means that the changes induced in the films structure cause increase of the residual stress, inducing an increase in hardness and Young's modulus [23]. The highest values of this parameter are registered, of course, in the TiC reach zone, showing a very high strength to plastic deformation. At the same time, this means a very low capacity for bending; in consequence, at least for tribological applications, in order to obtain a good adherence of it on the substrate and missing spalling, it is necessary a base – substrate with high hardness too. The obtained values for this parameter are a little lower in comparison of standard Ti_3SiC_2 MAX phase [12] but comparable with these in the Si doped TiC_x zone.

Fig. 7. Residual stresses and Young's modulus as a function of films hardness.

4. Conclusions

The present work proposed some possible correlations between the composition of the films, the mechanical properties, the dynamic friction coefficient and the wear behaviour of the samples.

The samples with the highest carbon content, closed to the stoichiometric TiC, and with a small amount of Si showed the higher hardness and higher compressive residual stress values. These samples characterize the so-called Si doped TiC_x zone. They also presented the best wear behaviour, which is connected with the lowest dispersion grade of the dynamic friction coefficient, due to the fact that the bearing ball did not destroy the film to reach the substrate.

It is clear that a good tribological behaviour of the films is provided if the two parameters the friction coefficient and the wear capacity are optimized. If for the improving friction conditions the target is to decrease more the friction coefficient, for the wear capacity it is important to control at the same time hardness vs. toughness of the films.

Taking into account our experimental conditions and obtained results, we concluded that the careful control of the structural and compositional aspects is able to provide to the films the optimal tribological properties, even better than Ti_3SiC_2 MAX phase properties reported by other authors. The control of the amount of SiC_x amorphous phase related to the TiC crystalline phase is one of the maximum importances for whole structure, not only for the friction conditions but also for the general durability of the films during wear tests.

Acknowledgement

This work was sustained by the Romanian Council of Scientific Research (CNCSIS).

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