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Tribochemically Active Ti–C–S Nanocomposite Coatings

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We demonstrate a new concept of self-adaptive materials, where sulphur is incorporated into TiC/a-C coatings and may be released in, for example, a tribological contact. By reactive sputtering with H₂S, sulphur goes into the carbide to form a TiC_xS_y phase in an amorphous carbon matrix. The addition of sulphur lowers the friction against steel. Significantly lower friction is obtained against a tungsten counter-surface, as WS₂ is generated in the contact. Annealing experiments and formation energy calculations confirm that sulphur can be released from TiC_xS_y. Ti–C–S coatings are thus chemically active in tribological contacts, creating possibilities of new low-friction systems.

Keywords: TiC/a-C, Tribology, Sulphur, Reactive Sputtering

Introduction In many technical applications, surfaces that provide low-friction as well as wear resistance and mechanical stability are desirable. So-called self-adaptive, or self-lubricating, materials have attracted significant interest in recent years, and the development of coatings that actively change in a tribological contact is a promising route.[1–3] A well-known example is the concept of nanocomposite coatings combining a hard carbide phase with a softer carbon matrix, such as TiC/a-C coatings, where lubrication is obtained by graphitization of carbon on the surface.[4–6] The friction, hardness, wear-resistance and other properties of the coatings can be tuned by varying the relative amounts of the carbide and the matrix phase. Further design possibilities are offered by doping with another element; a metal, such as aluminium,[7] nickel [8] or silver,[9] or non-metals such as oxygen or nitrogen. The addition of weakly carbide-forming metals, such as aluminium and nickel, increases the driving force for graphite formation

and thereby enhances the possibilities of lubrication. However, lubrication by graphitic carbon requires the presence of intercalation species such as water molecules, in order to decrease the strength of the interplanar bonding.

Another commonly used class of materials in low-friction applications is the transition metal dichalcogenides (TMDs), most commonly WS₂ and MoS₂. These materials are characterized by their highly anisotropic crystal structure, consisting of planar sheets of metal atoms surrounded by chalcogen atoms, forming layers with very low shear strength along the direction of the sheets.[10] In tribological contacts, the material is often observed to align in such a way that sliding occurs within these easily sheared layers, leading to exceptionally low friction.

TMDs can be introduced into the tribological contact in several ways. Solid coatings of pure or doped TMDs have been described in numerous studies.[10–14]

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In these, tribofilms consisting of aligned crystalline TMD form in the sliding interface, even for coatings that are completely amorphous in the as-deposited state. Additional elements are often added to TMD coatings, most commonly C, N and/or some metal, with the main purpose of improving their mechanical properties.[15–23] TMDs are also commonly used as lubricant additives, where they may be added either in pure form, as in MoS₂ grease, or as other compounds, that react to form TMD tribofilms in the tribological contact, with MoDTC lubricant additives as the most common example. In recent years, inorganic fullerene-like WS₂ nanoparticles have attracted a large interest as lubricants, and have shown promising results when embedded in solid coatings or porous materials, added to grease or dispersed in oil.[24–26] An alternative way of providing TMD lubrication is to synthesize it within the tribological contact, by supplying appropriate reactants that can form the TMD through tribochemical reactions. This concept has been successfully applied to tungsten-doped diamond-like carbon coatings, where the presence of sulphur-containing extreme pressure lubricant additives significantly lowered the sliding friction, and formation of WS₂ in the contact could be confirmed.[27] An advantage of this concept, as compared to using TMD coatings, is that it may allow for the use of coatings that are mechanically superior to the often relatively soft TMD coatings, while still providing low friction by TMD lubrication.

In the current work, this concept is used in a novel way, by supplying both reactants in the solid state. Sputtered nanocomposite TiC/a-C coatings are doped with sulphur, by means of reactive sputtering with H₂S, leading to the formation of a solid solution. The sulphur-containing carbide phase has also been modelled by first-principles calculations using supercells. Magnetron sputtering occurs far from equilibrium and it is well known from other studies that metastable solid solutions are easily obtained in TiC.[8] As will be shown in the present study, such solid solutions are indeed possible. The release of sulphur from the sulphur-containing carbide under certain conditions can then be expected, a concept which is explored by having tungsten present in the tribological contact. A potential advantage of this

approach is that the presence of sulphur in the tribological system can be limited to only those parts where it is beneficial. In many applications, particularly in combustion engines, efforts are made to exclude sulphur for environmental reasons. By restricting the release of sulphur to the parts of tribologically loaded components where the conditions are sufficiently severe, the total amount of sulphur in the system can be kept to a minimum. The Ti–C–S materials system demonstrates a new concept of solid solutions from which the doping element can be released in a controlled manner.

Experimental and Theoretical Coatings were deposited on silicon and high-speed steel substrates by reactive DC magnetron sputtering using elemental C and Ti targets and H₂S gas. The coatings were analysed by X-ray photoelectron spectroscopy (XPS), grazing incidence X-ray diffraction (GI-XRD), scanning electron microscopy (SEM) and nanoindentation. The tribological properties were studied using a ball-on-disc setup, with steel balls or W-coated steel balls as the counter-surface. A cross-section sample was prepared from the tribofilm from the test against a W-coated ball, and studied by transmission electron microscopy (TEM). First-principles calculations with supercells consisting of 64 atoms were performed using the projector augmented wave method, which is based on density functional theory. Calculations were also performed using the exact muffin-tin orbitals (EMTO) method with the coherent potential approximation (CPA). Details regarding the deposition, analysis and theoretical calculations can be found in supplementary information online.

Results and Discussion

Chemical and Structural Characterization. When increasing the flow of H₂S, the sulphur content of the coatings was seen to increase as well, as presented in Table 1, up to about 21 at.% for the maximum H₂S flow used in this study. The crystal structure was studied by GI-XRD, and for the pure Ti–C coatings the pattern was characteristic of cubic TiC, which has the NaCl (B1-type)

Table 1. Composition of the coatings, and composition of the TiC_xS_y phase.

H ₂ S flow (sccm)	Elemental composition				Composition of TiC _x S _y phase			Lattice parameter (Å)
	Ti (at.%)	C (carbide) (at.%)	S (at.%)	C (free) (at.%)	Ti	C _x	S _y	
0	54	37	0	9	1	0.68	0.01	4.33
0.5	52	35	2	11	1	0.67	0.03	4.34
1	54	31	5	11	1	0.57	0.10	4.40
1.5	51	27	9	14	1	0.51	0.18	4.51
2.0	51	20	17	10	1	0.42	0.33	4.72
2.5	51	18	21	9	1	0.36	0.42	4.81

structure with a lattice parameter of 4.33 Å. However, as the sulphur content of the coatings increased, the diffraction patterns systematically changed as the peaks moved towards lower angles, indicating a significantly increased size of the unit cell (Figure 1). At the same time, the peaks broadened, which is a sign of decrease in grain size of the crystals. Calculations using Scherrer's equation [28] give a crystal grain size of approximately 15 nm for the Ti–C coating, which decreases with increasing sulphur content. Furthermore, measurements using a θ - 2θ setup (not shown) indicates a (111) texture for pure Ti–C, which becomes less pronounced with the addition of sulphur. In cross-section micrographs taken by SEM, the grains of the pure TiC film are seen to be elongated in the direction normal to the substrate, i.e. in the [111] direction. The addition of S changes the microstructure so that the grains become smaller and likely less elongated in the [111] direction, as well as more randomly oriented. A certain lattice expansion for the carbide phase in sputtered TiC/a-C has been reported in several studies. Larger lattice parameters are often seen as the crystal grain size is decreased, and Lewin et al. [29] have suggested this to be an effect of charge transfer across the interface. However, the lattice expansion due to this effect is small, compared to the observations in this study. For the maximum sulphur content of 21 at.%, the lattice parameter was about 4.81 Å, an increase of more than 10% compared to pure TiC. Thus, the lattice expansion cannot be accounted for by grain size and charge transfer. Furthermore, the trend with increasing unit cell size with increasing sulphur content is a strong indication that sulphur is dissolved into the carbide, thereby expanding the lattice. A hexagonal Ti_2SC (or $\text{Ti}_4\text{S}_2\text{C}_2$) phase has been

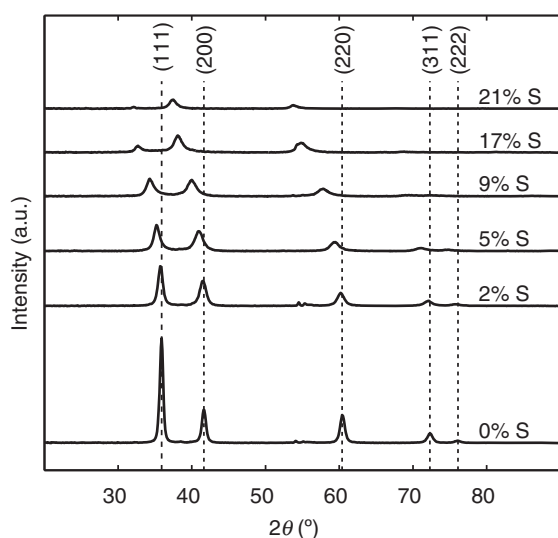


Figure 1. X-ray diffraction patterns for Ti–C–S coatings of varying sulphur contents. The addition of sulphur leads to lattice expansion as well as a decrease in grain size and a more random orientation of the grains.

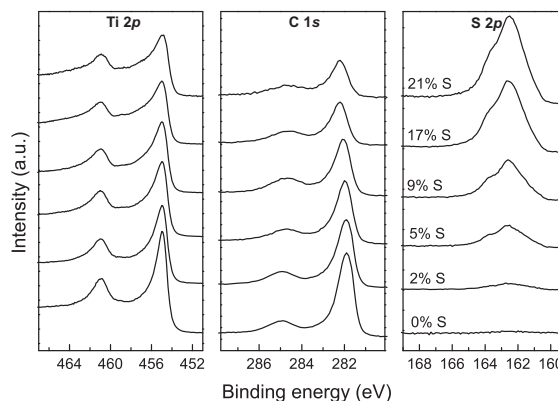


Figure 2. X-ray photoelectron spectra for samples containing 0–21 at.% S. The Ti 2 p peaks and the C 1 s carbide peak (at 282 eV) broaden with the addition of S, indicating a change in the chemical bonding in the TiC_xS_y phase.

reported, but no indications of this was observed for any of the coatings.[30,31] The coatings presented in this work were selected from a larger number of deposited coatings, some of which were deposited using a negative bias potential and/or substrate heating. The sulphur doping and lattice expansion of the TiC_xS_y phase was observed under all studied conditions.

The XPS spectra in Figure 2 reveal the presence of two distinct chemical states for carbon. The C 1 s peak has one contribution at a binding energy of about 282 eV, which can be ascribed to carbon in the carbide phase, and one at 284–285 eV, which corresponds to free carbon in the matrix phase. By deconvoluting the spectra, the amounts of carbon in the carbide can be separated from the free carbon (C–C) in the matrix, and the results summarized in Table 1 show that about 9–15% of the carbon is found as free carbon. The composition of the sulphur-containing carbide phase can thus be calculated and its formula written as TiC_xS_y . The carbon content (x) of the carbide phase decreases as the sulphur content (y) increases. The total amount of sulphur and carbon, i.e. $x + y$, is rather constant at about 0.7–0.8, although there is a slight tendency towards higher values for the highest sulphur contents. This suggests that the sulphur atoms substitute for carbon atoms in the lattice. It can be noted that there is a significant number of vacancies on the carbon sites in the un-doped as well as the sulphur-doped coatings, but this substoichiometry is a well-known phenomenon in sputtered TiC_x . [32] A further indication that the sulphur goes into the carbide lattice is the shape of the Ti 2 p peak in Figure 2. The peak shape changes as the peak becomes broader with the addition of sulphur, indicating a change in the chemical bonding of the titanium atoms. The binding energy for Ti in TiS is reported as 454.2 ± 0.2 , [33] which is similar to Ti in TiC . [34] Other possible compounds would be Ti_2S_3 and TiS_2 , but the reported binding energies for these are significantly higher at 458.8 and 458.5 eV, respectively. [35]

The S $2p$ peak, seen in Figure 2, can be deconvoluted using only one contribution with the S $2p_{3/2}$ peak situated at a binding energy of 162.0–162.3 eV. For comparison, the S $2p_{3/2}$ peak in TiS is reported to have a binding energy of 162.3 ± 0.2 . [33] TiS has the NiAs structure with the S atoms coordinated by a trigonal prism rather than an octahedron of Ti atoms, but the similarity in binding energy still indicates that the S atoms in Ti–C–S are surrounded by Ti atoms. The other possible alternatives are S bonded to S, or S bonded to C, both of which would give a binding energy more than 1 eV higher than the one observed. [34] The S in Ti–C–S should, therefore, be found in the TiC_xS_y phase, and as there is no indication of more than one chemical state, it is likely present only in the carbide phase. However, there could be additional chemical states of S if the binding energy is very close to that of S in TiC_xS_y . The binding energy for S in Ti_2S_3 and TiS_2 is 160.8 and 161.5 eV, respectively, and S should thus not be present in these forms. [35]

The clear correlation between increased sulphur content and lattice expansion indicated that the S goes into the carbide lattice, and the observed changes in chemical bonding further suggest the formation of a TiC_xS_y phase. We therefore suggest that the sulphur atoms are dissolved in the carbide and situated on the carbon sites.

Theoretical Calculations. To confirm the conclusions drawn from the experimental results, theoretical calculations were performed. The lattice parameter of B1-structured TiC_xS_y was calculated both by supercells, and by means of the CPA, and the results are shown in Figure 3. For TiC_xS_y with no vacancies, $y = 0.0625$, 0.1250, 0.1875, 0.25, and 0.5 structures were calculated with supercells, and $y = 0.0, 0.1, 0.2, \dots, 1.0$ structures were considered using CPA. Both methods give monotonously increasing trends in the lattice parameter with increasing sulphur content, and they result in similar lattice parameters, the difference being 0.1–0.9% for $0.0625 \leq y \leq 0.5$. We find that sulphur significantly increases the lattice parameter of TiC_xS_y and that excellent agreement is observed between the calculated lattice parameters and the experimental ones, the deviation being no more than 1.5%. The calculated lattice parameters are slightly larger than those measured for lower sulphur contents, up to $y \leq 0.3$, and they are somewhat smaller than experimental values for the sulphur-rich coatings. To compare the effect of vacancies on the lattice parameter in TiC_xS_y with that of sulphur, calculations were also performed for $\text{TiC}_{0.875}\text{S}_{0.0625}$ and $\text{TiC}_{0.75}\text{S}_{0.125}$. These structures contain 6.25% and 12.5% vacancies on the carbon sites, respectively.

The calculations show that the presence of 6.25% vacancies decreases the lattice parameter by 0.1%, while 12.5% vacancies decrease it by 0.2%. As previously mentioned, the introduction of sulphur in TiC has roughly a

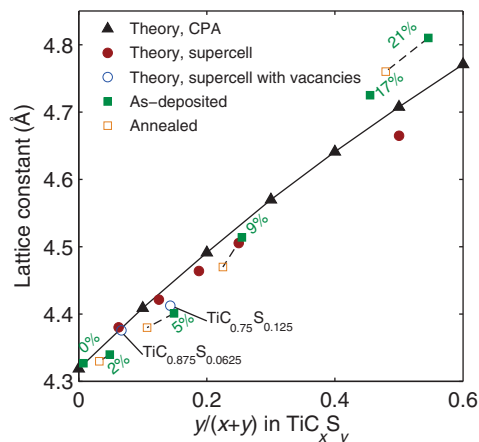


Figure 3. The lattice parameter as a function of $y/(x+y)$ in TiC_xS_y , i.e. the fraction of filled carbon sites that are occupied by a sulphur atom. Experimental data are shown for as-deposited as well as annealed coatings, with labels showing the S content (in at.%) for as-deposited coatings. Data points corresponding to the same coating before and after annealing are connected by dashed lines. Theoretical values are calculated by the EMT–CPA method, as well as using supercells with and without vacancies.

10 times larger effect on the lattice parameter: 6.25% S on the carbon sites results in 1% increase, and 12.5% S increases it by 2%. Therefore, we can conclude that the relatively large changes in the lattice parameter presented in Figure 3 are primarily due to the varying sulphur content, rather than to presence of vacancies.

Figure 4 shows the calculated electronic density of states (DOS) of TiC and $\text{TiC}_{0.5}\text{S}_{0.5}$. In TiC, there is a pseudo-gap at the Fermi level, E_F (Figure 4(a)). States below this pseudo-gap are bonding, while states above it are of antibonding character. [8] In TiC, the bonding states are filled, and the antibonding states are empty.

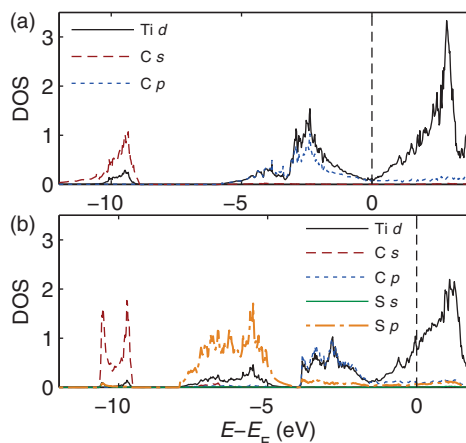


Figure 4. Electronic DOS calculated for TiC (a), and for $\text{TiC}_{0.5}\text{S}_{0.5}$ (b). The d partial DOS is displayed for Ti atoms, and s and p states are shown for C and S atoms. E_F is denoted by vertical dashed lines.

Figure 4(a) shows that the DOS below E_F is dominated by Ti d and C p orbitals, their DOS features being substantially overlapped, and these states correspond to the strong covalent Ti–C bonds. The empty antibonding states above E_F are built up by Ti d orbitals that hybridize with C $2p$ states (Figure 4(a)). In $\text{TiC}_{0.5}\text{S}_{0.5}$, however, the Fermi level lies above the pseudo-gap (Figure 4(b)), i.e. some of the antibonding states are filled. Ti d and C p orbitals corresponding to Ti–C bonds give about equal contributions to the states right below the pseudo-gap, similar to TiC. Mainly, S p orbitals build up the large DOS feature between -8 and -4 eV with a smaller contribution from Ti d orbitals. These states correspond to the Ti–S bonds. The overlap between the S p and Ti d features is significantly smaller than that of the Ti d and C p orbitals, showing that the Ti–S bonds are weaker than the Ti–C bonds.

Calculated charge density maps (not shown) for TiC and $\text{TiC}_{0.5}\text{S}_{0.5}$ show that sulphur atoms in $\text{TiC}_{0.5}\text{S}_{0.5}$ have a smaller charge density around them than carbon atoms, and the charge density maxima can be found further away from the centre of the atoms, which is consistent with their larger size. These effects, together with the fact that in TiC_xS_y some of the antibonding states are filled, cause the observed increase in the lattice parameter. The theoretical bulk moduli for the structures calculated by the EMTO–CPA method were also evaluated, and found to decrease with increasing sulphur content (i.e. with y). The calculated bulk modulus for pure TiC was 248 GPa, while the value for $\text{TiC}_{0.5}\text{S}_{0.5}$ was 164 GPa. It can also be noted that substituting C with S in TiC increases the energy of the carbide, the difference being about 2.2 eV per formula unit for $\text{TiC}_{0.59375}\text{S}_{0.40625}$, where the S content is close to the highest S concentration in the deposited coatings.

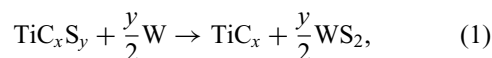
Mechanical Properties. The mechanical properties of the coatings were studied by nanoindentation. The hardness of the un-doped Ti–C coating was 10 GPa, which is rather low for a TiC/a-C material, but others have reported similar values.[32] Furthermore, other Ti–C coatings deposited but not presented in this work reached hardness values up to 15 GPa. With the addition of sulphur, the hardness decreased somewhat to values between 5 and 7 GPa. The doping with sulphur changes the chemical composition of the carbide phase as well as the morphology and microstructure of the coatings, and it is not clear to which degree each effect is responsible for the decrease in hardness. In binary Ti–C coatings, it is known that the hardness can vary with the amount of a-C matrix.[36] As can be seen in Table 1, however, the amount of free carbon in the coatings presented here is in the range of 9–14 at.% for all coatings, without any clear trend regarding the sulphur content.

The Young's modulus decreased from 230 GPa for the Ti–C coating to 80–140 GPa for the sulphur-containing

ones. The trend of reduced Young's modulus and hardness in the sulphur-containing coatings can be correlated to the reduced bulk modulus obtained in the theoretical calculations above. We, therefore, suggest that the addition of weakly bonded sulphur atoms to the carbide phase leads to a decrease in Young's modulus.

Removal of Sulphur. The results of the current study show that it is possible to insert sulphur into the carbide lattice. Since the TiC_xS_y phase is not previously known, and the conditions during magnetron sputtering are far from equilibrium, it is reasonable to assume that sulphur might be removed. A simple test to investigate this possibility was performed by heating the samples for 60 min in vacuum at 500°C. After this annealing, the samples were again analysed by XPS, and a decrease in sulphur content was observed, as seen in Figure 2. Furthermore, XRD showed a decrease in lattice parameter compared to the as-deposited coatings. The relationship between sulphur content and lattice parameter for the annealed coatings follows the trend for as-deposited coatings closely. With the release of sulphur, the fraction of vacant carbon sites should have increased, but the composition remains well within the homogeneity range for TiC_x . No change in the appearance or adhesion of the coatings was noted after the annealing process, further suggesting that the removal of sulphur is not detrimental to the cohesion of the coatings.

In order to examine if there is any driving force for the tribochemical formation of WS_2 in the contact between a Ti–C–S coating and a W ball, the stability of TiC_xS_y in contact with tungsten was investigated by calculations of the formation energy. The formation energies (ΔE) were calculated for the following reaction:



where tungsten is of the body-centred cubic structure, WS_2 is of the $\text{P6}_3/\text{mmc}$ structure, and $x + y \leq 1$. The cases where $x + y = 1$ were considered. A diagram showing the formation energy for reaction (1) can be found as supplementary information to this article. Negative formation energies are obtained in the $y = 0.0625 - 0.4$ range, indicating that the removal of sulphur for formation of WS_2 is energetically favourable within this range. Above $y \approx 0.4$, ΔE becomes positive, since the formation of the TiC_x carbide becomes increasingly energetically unfavourable with increasing vacancy content (i.e. smaller x). Thus, it is unlikely that all sulphur in TiC_xS_y forms WS_2 for higher values of y . However, additional calculations (not shown) show that the partial removal of sulphur for WS_2 formation is energetically favourable also at these sulphur contents.

In technical applications, the counter-surface would more likely contain W as a compound, such as a carbide, rather than pure metal. In the case of WC, its formation

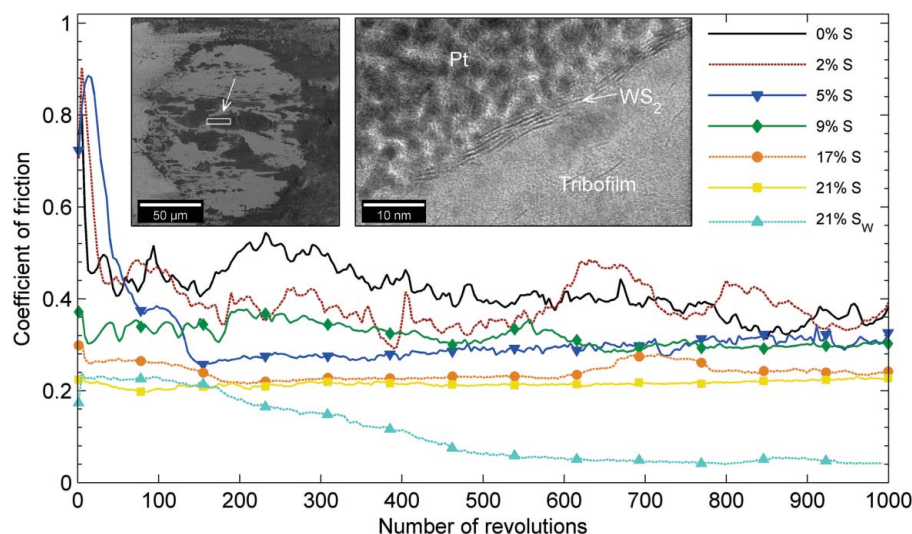


Figure 5. Coefficient of friction of all deposited coatings running against ball bearing steel balls during 1000 revolutions in the rotating ball-on-disc test. For the coating with the highest sulphur content, the result of a test with a tungsten-coated ball is also shown (indicated by a subscript W). The inset is an SEM micrograph of the wear scar on the W-coated ball, where the dark patches are the tribofilm and the bright areas is the W coating, and a TEM cross-section prepared from the marked area in the tribofilm. The bright area to the lower right corresponds to the mostly amorphous tribofilm, while the dark and bright stripes are a few atomic layers of tribochemically formed WS₂, aligned with the easily sheared planes along the sliding direction.

energy is -0.34 eV per formula unit,[37] leading to a slight increase of the total formation energy (ΔE) of the reaction, which however remains negative for a range of TiC_xS_y compositions. The formation of WS₂ should therefore be possible also from WC, although somewhat less favourable than from elemental W.

Tribological Properties. The measured frictional behaviour of all coatings, running against ball bearing steel balls in dry air, is shown in Figure 5. The figure also includes the coating with the highest sulphur content, running against a ball coated with tungsten. The tests using steel balls were performed for 10,000 revolutions, after which all coatings except those with the two highest sulphur contents had shown obvious signs of failure manifested by sudden dramatic increases in friction. Friction results are presented only for the first 1000 revolutions, before the failure of any of the coatings occurred. For the steel balls, a clear trend is seen towards lower and more stable friction for coatings with higher sulphur contents. This is equally true for the initial friction level as for the steady level reached after some tens of revolutions, the latter level typically being significantly lower than the initial. The improved behaviour associated with the addition of sulphur may have several explanations. As seen in the XRD results (Figure 1), the addition of sulphur leads to a decrease in grain size of the TiC crystals, as well as to a less pronounced texture of the coatings. This is expected to increase the cohesion and toughness of the coatings, and may serve as at least a partial explanation for the better performance of the coatings richer in sulphur. A

chemical interaction between sulphur from the coatings and iron from the balls is also plausible, and may lead to the formation of FeS, a well-known solid lubricant, albeit not a low-friction one. The current results are not sufficient to determine whether the improved frictional properties are due to the changed mechanical properties of the coatings, the proposed tribochemical interaction, or to some other mechanism.

The specific wear rates of the two coatings that survived the entire 10,000 revolution test, i.e. the 17% and 21% S coatings, were 1700 and 6400 $\mu\text{m}^3/\text{Nm}$, respectively. The wear for the other coatings could not be estimated due to failure, but should be expected to be higher.

The tungsten-coated ball running against the 21% S coating initially showed a friction behaviour almost identical to that of a steel ball running against the same coating. However, after a few hundred revolutions, the tungsten-coated ball deviated strongly from the stable friction level of 0.2 seen for the steel ball, reaching a lower level of approximately 0.05 during the second half of the test. The low friction observed when using a tungsten-coated ball as counter surface supports the theory that sulphur may be removed from the carbide phase to form WS₂. To further investigate this, the wear scar on the ball was analysed and found to be partly covered by a tribofilm, seen as dark areas in the SEM. A cross-section sample of the tribofilm was prepared by focused ion beam and studied by TEM, see Figure 5. As a part of the cross-section preparation, a protective layer of Pt/C was deposited on the sample surface. The tribofilm was seen to be mostly amorphous, with thin platelets dispersed

throughout the amorphous material. On the outermost surface, planes characteristic of WS_2 , aligned in the sliding direction, were observed. The plane distance is about 0.62 nm, matching that of the (002) planes in WS_2 . For reference, the Ti–C coating without S was also tested against a W-coated steel ball. The friction level was similar to that observed with a steel ball, indicating that no beneficial reaction occurred between this coating and the W counter-surface.

We have, thus, shown that it is possible to release S from a TiCS film to form a solid lubricant in a tribological contact. In an application, a TiCS-coated surface could be matched with a counter surface-containing W, or Mo, to form a low-friction tribosystem. If enough WS_2 , or MoS_2 , is formed to maintain a low and steady friction, the wear is expected to be low. The annealing experiments in the current study show that it is possible to remove S from throughout the coating, indicating that S can be replenished by diffusion from below the very top surface.

Conclusions In summary, we have shown that the sulphur doping of nanocomposite TiC/a-C coatings leads to a solid solution of sulphur into the carbide phase, which then can be described as TiC_xS_y . Increased sulphur content in the doped carbide leads to an observed, significant lattice expansion with lattice parameters more than 10% larger than for TiC. Theoretical calculations using a supercell approach and by means of the EMTO–CPA method, give quantitative values of the increased space occupied of the sulphur atoms, compared to the carbon atoms, and the calculated lattice parameters closely match the experimental values. Annealing experiments show the possibility of removing sulphur from the TiC_xS_y phase, and that sulphur removal leads to lattice contraction.

The tribological properties of the coatings were tested by sliding against steel balls in dry atmosphere, and it was found that increased sulphur content lowers the friction levels and increases lifetime. The improvement, however, may be due to changes in coating topography and mechanical properties as well as the chemical properties. Furthermore, a sulphur-rich coating was also tested against a tungsten-coated steel ball, leading to significantly lower friction levels. Post-test analysis showed the presence of WS_2 in the tribofilm, and formation energy calculations confirm that it is energetically favourable to form WS_2 in the presence of tungsten. It has thus been shown that it is possible to dope TiC/a-C coatings with sulphur, thus offering possibilities of new frictional mechanisms in tribological applications.

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