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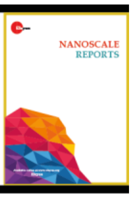

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Study of a-C:H thin films deposited by Plasma Immersion Ion Implantation for mechanical and tribological applications

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ABSTRACT:
The tribological and mechanical properties of DLC films deposited on the surface of 16MnCr5 steel alloy were investigated. The major concerning of using DLC layers on engine parts are: (i) to reduce friction; (ii) to increase fuel efficiency and to reduce CO_2 emission; (iii) to increase hardness of alloy steel. After polished and ultrasonicated, 16MnCr5 substrates were submitted to PIIID procedures in radiofrequency plasmas (13.56 MHz) generated from atmospheres of methane and argon. Excitation power and total gas pressure were kept constant. It was investigated the effect of methane proportion on the microstructure and mechanical properties of the films using the follow techniques: Raman Spectroscopy (for Hydrogen content and microstructure analysis), Ultra Micro-Tribometer (for friction coefficient) and Nanoindentation (hardness evaluation). Raman analysis confirmed DLC character of the films produced, and the proportion of 80% methane and 20% argon resulted to the best performance of mechanical properties of the films owing to the increase of hardness in until ten times, and reducing the friction coefficient to about 0.2. In addition, thickness for these films varied from 165 nm to 206 nm.

Keywords: PIII&D, DLC, 16MnCr5, Raman; Nanoindentation, Friction Coefficient, Hardness

1. Introduction

DLC films have the property of high tribological performance in a wide variety of operating environments, being established in many industrial applications due to its hardness [1], chemical inertness [2], optical transparency at visible radiation [3], and semiconductor properties [4]. In the literatures, is reported that, different vapor deposition techniques are normally employed to prepare this material in a simple, cost-effective and ecologically correct way [5]. It includes Plasma Immersion Ion Implantation and Deposition (PIIID) technique, pioneered used by Aisenberg and Chabot [6], and later by Koidl [7]. PIIID is an especially interesting tool for the preparation of such films since it enables to control the energy deposited in the growing layer through ionic impacts. In this approach, the samples are immersed directly in plasma excited from organic compound pure or mixed to other gases while high voltage negative pulses are applied to the sample holder [8]. The energy transferred to the matter via ionic collisions, is decisive for the properties of the samples, including the type of microstructure formed in the a-C:H films. In this work PIIID was used to grow a-C:H films over the surface of 16MnCr5 substrates, since this kind of recover over alloy steels usually improves the surface hardness and reduce its friction coefficient. It's in agreement with the automotive industry whereas; engine components may have its performance extended, owing to DLC recover on to this 16MnCr5 alloy steel, in order to resist against shear stress. Hence, microstructure of these films was investigated. Carbon forms a great variety of crystalline and disordered structures because it is able to exist in three hybridizations, sp^3, sp^2 and sp^1 [9]. In the sp^3 configuration, as in diamond, carbon atom's four valence electrons are each assigned to a tetrahedral directed sp^3 orbital, which makes a strong σ bond to an adjacent atom. In the three-fold sp^2 coordinated configuration as in graphite, three of the four valence electrons enter trigonally directed sp^2 orbitals, which form σ bonds in a plane. The fourth electron of the sp^2 atom lies in a pπ orbital, which lies normal to the σ bonding plane. This π orbital forms a weaker π bond with a π orbital on one or more neighboring atoms. In the sp^1 configuration, two of the four valence electrons enter σ orbitals, each forming a σ bond directed along ±x-axis, and the other two electrons enter pπ orbitals in the y and z directions. Our results point out that, microstructure generated in the films deposited here is associated to the presence of amorphous carbons hydrogenated microstructure, that is, a-C:H or DLCH. According literature [10], they are hard materials, containing about 40% of sp^3 sites, 30-40% of H, 1.6 to 2.2 of density (g .cm^{-3}), and 10-20 GPa of hardness.

2. Methods

Glass plates (~50 mm^2) and polished 16MnCr5 steel plaques (~50 mm^2) were employed as substrates for film deposition. Substrates were initially cleaned in ultrasonic (Cristofoli USC 3881) baths, then, 16MnCr5 steel substrates, polished in 3μm alumina grain, were cleaned in deionized water and alcohol baths. And were finally, dried in a hot air flow. The cleaned substrates were positioned at the sample holder of a capacitively coupled plasma system fully described in a previous work [11]. The system, was then, pumped down to10^{-1} Pa and the plasma cleaning procedure developed by Oliveira [12] was conducted for 600 s to remove the surface native oxide. Methane and argon were inserted in the reactor in different proportions (50%, 60%, 80% and 90%), then the pressure, p, was checked by a Barocel capacitive pressure gauge: p = 1.9 Pa for the fourth conditions. Plasma was generated by an application of radiofrequency power (13.56 MHz at 100 W) to the topmost electrode while grounding the chamber walls. The lowermost substrate holder was biased with high voltage negative rectangular pulses. Pulse magnitude, width and frequency were -3600 V, 30 μs and 300 Hz, respectively, producing a duty cycle of 0.01. Deposition time was 5400 s for all the experiments. Table 1 provides the conditions.

Table 1: Plasma excitation conditions for all a-C:H deposition.

Substrate	Steel Alloy 16MnCr5
Gas system	CH$_4$/Ar in 4 four different proportions.
Composition	CH$_4$/Ar
Methane proportion	90, 80, 60 and 50
Argon proportion	10, 20, 40 and 50
Bias Voltage	3600 V
Frequency	300 Hz
Pulse time	30 μs
Work pressure	4.5 Pa
Deposition time	5400 s
RF Power	100 W
Frequency source:	13.56 MHz

Profilometry was used to measure the thickness and roughness of the films. The equipment was a Dektak 150 (Veeco Company), scanning 500 μm of distance in a frequency of 200 Hz using silicon tip. Deposition rate was 285 mn /5400 s equals to 0.05277 nm/s, which is much lower than the a-C:H films deposited by Rangel (2010) [11], once these films deposited using methane has much lower deposition rates than the same films deposited using acetylene, whereas the C ions are in > at.%, in the plasma phase. The micro-structure of the films was investigated by Raman Spectroscopy in a Renishaw S 2000 using an argon laser (514.5 nm). Spectra were acquired directly from samples prepared on steel 16MnCr5 in the wave number region 800 to 2000 cm^{-1}. The friction coefficients was determined using ball-on plaque technique with Tribometer Setter - UMT (ultra microtribometer), at (20 ± 1 °C) It was used the reciprocal linear module with a displacement of 10 mm, a steel AISI 4040 ball of 4 mm in diameter, a constant force of 2 N and an average speed of 10 mm/s for 300 s. One scratch test was performed on each specimen. Hardness of the films was evaluated using the nanoindentation data acquired in a Hysitron Triboindenter. A multiple step load function presenting maximum and minimum loads of 100 and 1.000 μN, respectively were applied to a diamond Berkovich tip, providing hardness results for ten different depth. This is a load-partial-unload method. The load application and removal rates were 1 s and 1 s, respectively, while dwell time was of 1 s for all the tests. The procedure was repeated for 15 times in each film deposited. Is not there a different loading rate for each depth. In addition, Nuclear Reactive analysis (NRA) were selected to verify the carbon contents over the reaction to

C (p,p) C at 1,75 MeV; (HRS) Hydrogen Recoil Spectrometry for H contents and; (RBS) Rutherford Back-Scattering for contaminants contents the films with oxygen: reaction to O(α, α)O at 2,4 MeV over to glass substrates [13, 14].

3. Results

3.1 Nuclear Reactive analysis (NRA)

Table 2 shows the results for the elemental composition (%) of the films as a function of the methane (%) in the PIIID. The content of other elements, referred to as contaminants is also presented.

Table 2: Elemental composition of the films as a function of methane proportion in the deposition plasma, determined by nuclear analysis techniques.

Samples % CH_4	**Elements**		
	C (± 3.0 %)	**H (± 3.0 %)**	**Contaminants (± 1.0 %)**
50	57.0	40.0	3.0
60	57.6	40.4	2.0
80	54.3	43.5	2.2
90	52.0	47.0	1.0

In those attempts, the probing ion beam had a density ranging from 1.6 to 2.4 × 10^{15} at/cm^2. It is observed a slight fall of C amount as % CH_4 increases, while H contents follow the opposite trend. Contaminants proportion was also reduced with increasing the proportion of the organic precursor in the plasma phase. Therefore, as one considers the H proportion in the films, they may be classified as a a-C:H. The presence of C and H in the structure is consistent with the precursor (CH_4) composition. However, the proportion of H in the film is substantially reduced as compared to that in methane molecule (80 %), suggesting H abstraction during the film deposition. The result is explained by the fragmentation of the organic molecule under the plasma environment, producing low energy radicals that promptly react with radicals on the solid surfaces. Hydrocarbon gas such as methane is ionized in plasma, resulting in H^+ ions. They trend to create covalent bonds with C^+ ions. Furthermore, charged species formed in the plasma phase (CH^+, CH_2^+ and CH_3^+); bombard the growing layer due to the polarization of the sample holder. Moreover, in organic materials, deposition of energy through ionic collisions induces, amongst other effects, bond rupture with emission of chemical species [15]. As hydrogen constitutes lateral or terminal groups in such materials it is very prone to be emitted upon bombardment, generating dangling bonds [16]. As these species are extremely unstable, they tend to be consumed through structural organization by crosslinking and carbon bond in saturation. The recombination rate tends to increase resulting in lower defect concentrations, that is, in a better organized structure, but even, active sites still remain in the solid structure. Hence, species as O and N are expected in the structure of plasma deposited materials since residual radicals with the structure, during deposition, making so, reactions with O and atmospheric whit H_2O_{vapour} when the samples are exposed to the atmosphere, to reduce dangling bonds [17].

3.2 Raman analysis

Figure 1 shows the Raman spectra in the 800-1800 cm^{-1} region for films prepared with different CH_4 proportion. As sp3 hybridization and increases the amount of unordered connections, there is a shift of the G band to the left, corresponding to movies closer to the diamond structures. Moreover, as the position of the G band shifts to the right, it means there is an increased formation of carbon clusters. Other information that may be obtained from Raman spectra is the percentage of hydrogen in the film according to the method proposed in the literature [18,19], based on the determination of the spectrum baseline Raman tilt that appears due to photoluminescence of hydrogen using 514 nm laser . As a general trend, the intensities of the G and D bands increase as the % CH_4 in the plasma is enhanced but with no changes in the spectrum shape. Following the method proposed by Ferrari, Robertson et al. [20, 21], the spectra were deconvoluted into two Gaussians, allowing to evaluate the band peak position (G position), the I(D)/I(G) intensity ratio and the full width at half maximum (FWHM).

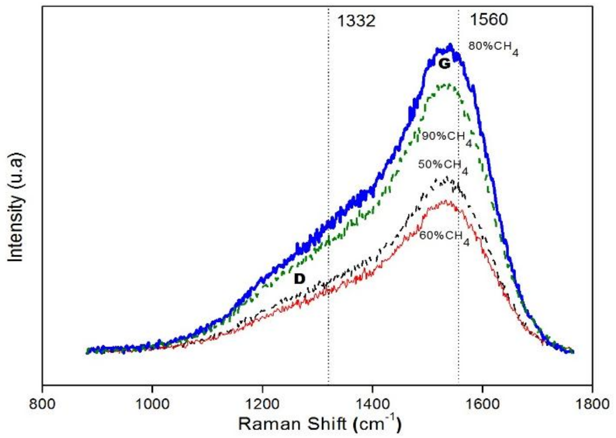

Figure 1: Raman Spectra of DLC as functions of the methane proportion on the plasma composition of 50%, 60%, 80% and 90% of films obtained by PIIID.

I(D)/I(G) assumes values between 0.55 and 0.60 varying, at most 10 % as % CH_4 is increased from 50 to 90 %. Associating such considerations with the prevision of moderate contents of H (< 45 %), films investigated here can be classified as a-C:H instead of polymer-like carbon. It is known that, if I(D)/I(G) results in low values, that is, if is negligible, the sp^2 phase is mainly organized in chains. On the other hand, high I(D)/I(G) values suggest that sp^2 phase mainly in rings. In this case, the π bonds are not fully delocalized on the rings. The low variation in I(D)/I(G) while increasing methane proportion indicates that microstructure, including graphite grain size, as well as H proportion [22] are just slightly affected by such a parameter. Analyzing the G band position data (figure 1), it is observed no dispersion in the G band, but only a slightly shift to lower wavenumbers next to (2 cm^{-1}) as the methane proportion is increased to 80 and 90 %. This change, related to the enhancement in the proportion of sp^3 sites in the film, is very possibly caused by increment in the H proportion. Then, the sample with the highest sp^2 fraction is that prepared with 60 % of methane in the plasma. Since the G band width characterizes the disorder of the D band in the sp^2 hybridization [23], the small growth (~6 %) in the band width as the methane proportion is increased beyond 60 %, observed in Figure 2, also agrees with an elevation in the proportion of sp^3 sites. Consistently with the results of G band position, the sample with 60% of methane. The slender variations in the G band position, band width and ID/IG ratio, despite the significant variation in the methane proportion, may be a consequence of the predominant effect of the ion bombardment on the deposition kinetics. Possibly, stronger changes could have been detected if no ion bombardment was provided. About Pos (G) intensity, there is no significant factor to increase topological disorder if the ranged from 1542 to 1546 cm^{-1} is normal in the visible Raman excitation. Pos G values ranged from 1542 and 1546 cm^{-1} indicates for high H content a character of the films between PLCH and DLCH, because it is a threshold on the curves that define the type of a-C:H films. If we link this analysis plus G peak disorder, it can not consider our films as a ta-C:H, because of the kind of microstructure, previously defined as amorphous carbon containing high sp^2 sites. It reinforces the idea we have from our films, once, for this type of films, presents topologically disordered, but the structural disorder is lowered. It is possible that, high H content provides to the σ bonds formation in order to minimize the free H energy. It can be a good evidence to previous for this films, a good combination between high hardness, favored by structure of C in sp3 sites and aromatic C rings, and low friction coefficients a due to the amount of C on sp^2 sites with high H content.

3.3 Friction coefficient

Figure 2 depicts the friction coefficient of the films as a function of the sliding time.

Under a constant force of 2 N, the contact pressure generated with the prescribed load is near to 1.256×10^{-5} N/m^2, which is enough to cause yielding. The major curve slope is concerned to the friction coefficient starting with 0.22 in average and ending with 0.45 (60% methane).

The opposite occurs in the friction coefficient test using the sample, prepared with 80% of methane, which started the test with 0.20, decreasing progressively to 0.18. Friction is the dissipation of energy as there is relative motion between two surfaces [24, 25] at a few high points or asperities. In general, friction between surfaces in contact is affected by a variety of factors, however, it is controlled mainly by the formation and breaking of chemical bonds at the interface between the moving parts.

Saturation of the dangling bonds by atomic hydrogen or other adsorbates leads the friction coefficient of diamond to about μ = 0.22 and, atomic hydrogen [26] acts as lubricants also for graphite and improve its wear and lubricating behavior. Since Enke et al [27] first reported in 1980 that, DLC from using a C source has low friction coefficients reinforcing its use as a lubricant, being in the air 0.10 < μ < 0.40. This is consistent with the results presented here. The friction properties of DLC's have reviewed recently by Grill [28, 29], Donnet [30] and Gangopadhyay [31]. Erdemir et al [32, 33] have found that the friction coefficient on a-C:H from methane having the lowest μ, being the opposite of a-C:H films from acetylene which presents the largest μ.The large spread of values can be understood in terms of deposition system. In general, low values of these coefficients can be attributed to low shear strength of the transfer layer [34].

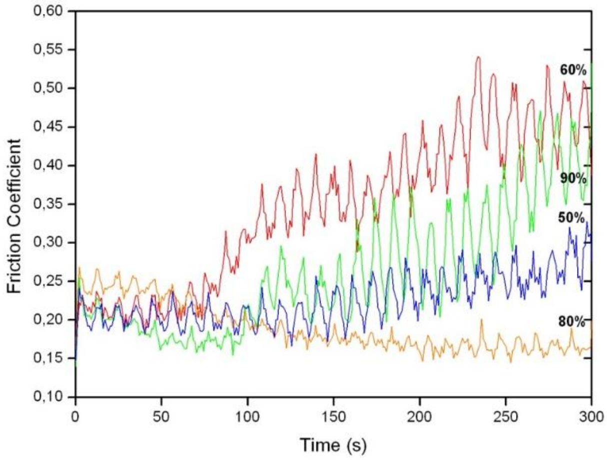

Figure 2 Friction coefficient of the films obtained as function of sliding time.

It is a consistent explanation with Raman analysis, which the layer has a disordered graphite structure, revealing evidence of graphitization of DLC films in the wear track. If the hydrogen is removed from hydrogenated DLC, the dangling bonds formed cause strong interactions between the surfaces in contact, resulting in a slope of friction coefficient as function of loss of hydrogen dry hydrogen [35], similar to that reported for both graphite and diamond [36, 37]. For the best condition, (80 % methane), the final value of about 0.15 was confirmed in ambient air by Donnet and Grill [38], which is the film that contain higher relative % of sp3 sites, than the other 3 films. Analogously, the film prepared with 60% of methane proportion probably, contains higher relative % of sp2 sites, that is, μ isn't reducing with hydrogen content monotonically. Then is considered that microstructural changes reflects spatial variabilities of the samples, even if they classified as a-C:H, mixing either sp2 or sp3 sites.

3.4 Hardness

In Figure 3, hardness of the samples is plotted as a function of the tip penetration depth. For the bare 16MnCr5, hardness keeps roughly constant around 2.0 GPa while for the samples containing the films, it progressively decreases with increasing depth. Considering shallower depths, where the influence of the substrate mechanical properties is reduced, it is possible to verify the influence of methane proportion on the hardness of the a-C:H films. Even though, all films performed higher hardness than the pure substrate. The substrate quartz was used because it is a material reference for tip calibration.

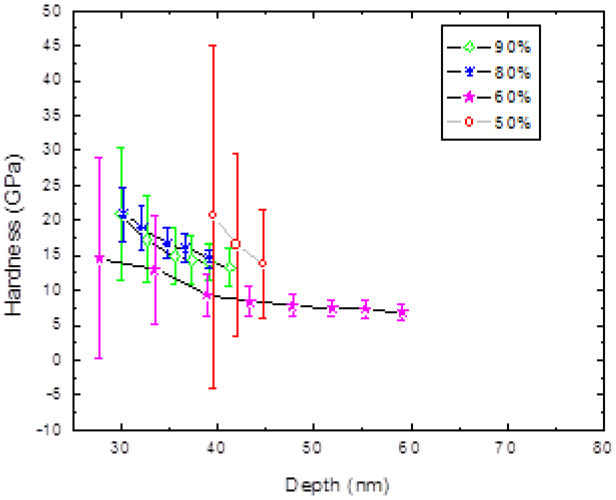

Figure 3: Hardness as function of depth of films deposited in different methane proportion.

The highest hardness values were attained to the samples containing the film deposited with 50 % of methane while the lowest ones were detected in the sample prepared with 60 % of CH_4, that is, only 10 % lower than the first. Huge error bars were observed in both cases owing to spatial inhomogeneity's from film properties. For the condition related to 50% only 3 measures were collected, although the very sensibility from the tip, presenting hard acquisition data in response of tip penetration. Intermediary values were found for the samples prepared using 80 and 90 % of CH_4 in the plasma. In order to minimize the influence of steel substrate on the hardness results, hardness values were determine at regions which correspond to less than 15% of the film thickness. It was observed that, the hardness values between 50% and 60% of methane are non-similar, when compared with measures over 15% of the thickness of the respective films, which was between 13 and 14 GPa. However, it is noted to the same conditions to the films obtained with 80% and 90 % concentration of methane, an increase of hardness, reaching values of 18 GPa up to 20 GPa. The hydrogen tends to connect via σ networks, C-H bonds, which ultimately relieves stress and produces a softer polymer-like-carbon. Graphitization of microstructure can be responsible to decrease hardness [39]. In contrast, sp^3 content is responsible to increase hardness when associated to C-C bonds. For the films produced in this work, this combination is in agreement with a-C:H in the literature because of a non-extreme values founded that reveal good hardness ($10 < H < 20$ GPa), and good low friction coefficients at the same time. It was confirmed bonds type sp^2 and sp^3, characterizing the films as a-C:H as observed by Tamor et al. [40], in which aromatic rings is more resistance against penetration by probe, than the graphites.

4. Discussions and next studies perspectives

It is notice, the good conditions reached by the research group related to this study [28]. It was found for these films, hydrogen content (~ 40 % of H), mixing sp^3 sites and sp^2 sites. The qualitative adherence of coatings was regular It was noted that, the coating deposited in 1800 s, showed the lower friction coefficient ($\mu = 0.2$ for a whole sliding time). This film was deposited with rich methane environment (80%) and poor Argon (20%). Argon is an inert and massive gas. In mechanisms involving great ion bombardment, it is used for induce more sputtering mechanism. In this case, impurities from substrate, or native oxide from substrate, can be promoted to plasma phase, and then, to react with the precursor gases. In fact, Nuclear Reactive Analysis revealed the major contamination (3%) for the films with more argon (at %) than methane (at %). The choose of methane to compose the plasma kinetics with inert plasma was accomplished by some researcher: Grill [29], Donnet [30], Gangopadhyay [31]. Erdemir et al [32, 33], to promote on the surface of the films, lower friction coefficient, in which can explain the purpose application as engine components.

Graphitization of microstructure can be responsible to decrease hardness. In contrast, sp3 content is responsible to increase hardness when associated to C-C bonds. For the films produced in this work, this combination is in agreement with a-C:H in the literature because of a non-extreme values founded that reveal good hardness ($10 < H < 20$ GPa), and good low friction coefficients at the same time [28].

It seems that the films composed by (80 at % of methane) presented the best microstructure, related to Hardness (up 20 GPa), at lower depths (next to 30 nm).

Some questions can be achieved to motivate future studies. Until here, we assume that, the data presented in Figure 3 is inconclusive whether the fluctuations observed among specimens are related to microstructural changed or reflect spatial variabilities of the samples, however the method choosed to extract, μ, presented repeatbitity. There is no information about the pressure generated with the prescribed load, on the other hand, no yielding was observed. The friction coefficient monotonically does not reducing with hydrogen content because some H can link directly with C, to form rings, graphite, DLC or CH_2 clusters. Each microstructure can perform to different friction coefficient of the resulted films as function of sliding time, being inconclusive with we analyze the experimental employed to our studies.

It is valid to notice the point that reveals some limitations of this study. Hence, for further studies, it is possible to give the different thickness values among films the scaling of hardness, in which is best reported as a function of h/t, where h is the indentation depth and t the film thickness. In addition, Hardness tests on coatings start from higher depths compared to the data on substrate. This is counterintuitive as one would expect smaller indentation depths from a harder material. Also, there is no to control the number of data points per sample, they can be different in response of each films, in which can present error bars higher. We assume the material uncertainties, like spatial inhomogeneities, especially for amorphous materials.

The conclusion is consistent, and the present references is in agreement with the films deposited by methane/argon by PIIID.

5. Conclusions

Results demonstrated that the hardness increase 20 times compared to the substrate and friction coefficient reduced in some cases more them 100%, resulting in higher hardness and lower friction coefficient obtained in lower argon concentrations. Raman analysis, friction coefficient, hardness, young modulus and hydrogen content (~ 40 H at %) obtained in this study demonstrated that coating can be classified as a-C:H, mixing sp^3 sites and sp^2 sites. The qualitative adherence of coatings was regular for all substrate surfaces revealing good adhesion. At preceding results, the coating deposited with 80 and 90 at % CH_4 showed the lower friction coefficient and higher hardness, both coatings represent the best combinations of characteristics as coatings to engine parts. In terms of microstructure, Raman analysis was consistent to reveals a non-dispersion of G peak and the FWHM (G) as changed the conditions of films growth. It seems that, in our particular deposition process can induce sp^2 clustering in a a-C:H, even with relatively high H content. In this case, the relation between sp^3 content and sp^2 configuration fails. We suggest further, a multiwavelenght analysis in order to avoid confusion. We assume that, there is no significant change of classification of the films changing the deposition conditions (methane proportion on the gas feed system). In all cases, the study only was possible, owing to the Nuclear Reactive Analysis accomplished in the LAMFI/USP, which a key information confirmed the Carbon percentage from 52% to 57%, while the Hydrogen was found in percentage from 40% to 47% on the a-C:H thin films. More details from the NRA techniques can be found in [41] T.F. Silva et al. 2013.

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Competing Interests:

The authors declare that they have no competing interests.

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