SUPPORTING INFORMATION

Methionine as friction modifier for tungsten carbide functionalized surfaces via in-situ tribo-chemical reactions

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This supporting information contains 7 figures and 1 table.

1. Ab-initio simulation of L-methionine conformers

In this section four different perspectives of the calculated equilibrium geometries are shown. These equilibrium geometries were obtained by placing the L-methionine on top of the WC slab, and allowing a subsequent atomic relaxation as described in the text. Four variants of the L-methionine were simulated: the equilibrium ground state (Fig. S1a), the corresponding geometry with dissociation of the acid hydrogen (Fig. S1b), and two conformers of this dissociated state, named conformer A (Fig S2) and B (Fig S3) for simplicity, the latter presented only in the main text. The last figures in this section shows a plot of the charge density difference for the equilibrium adsorption configuration of conformer A (Fig. S4), where charge transfer caused by the formation of a S-W bond and the van der Waals interaction between the surfaces slab and the L-methionine atoms is presented (Fig. S5).

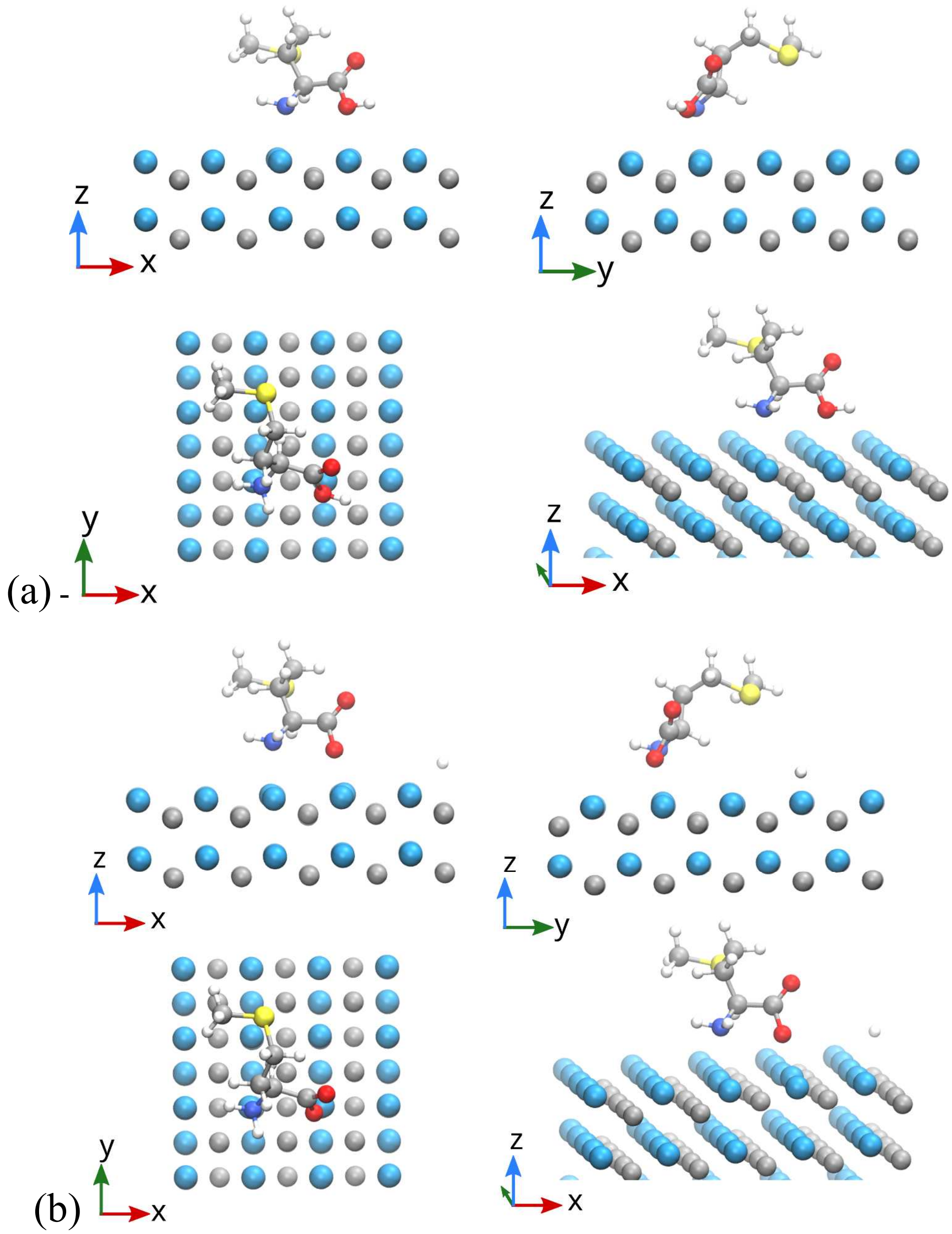

Figure S1. Equilibrium adsorption geometry of L-methionine on a WC (10$\bar{1}$0) surface (a) and equilibrium adsorption geometry of the dissociated L-methionine on a WC (10$\bar{1}$0) surface (b). For simplicity, only part of the simulated metallic slab is shown in both cases. Legend: ● = C, ● = N, ● = O, ● = S, ● = W.

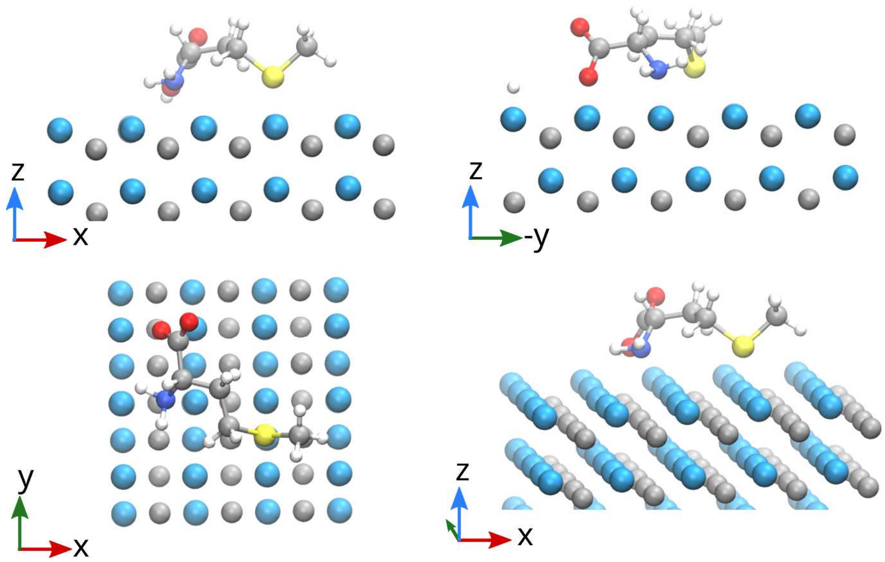

Figure S2. Adsorption geometry of an L-methionine conformer (conformer A) on a WC $(10\overline{1}0)$ surface. For simplicity, only part of the simulated metallic slab is shown. Legend: ● = C, ● = N, ● = O, ● = S, ● = W.

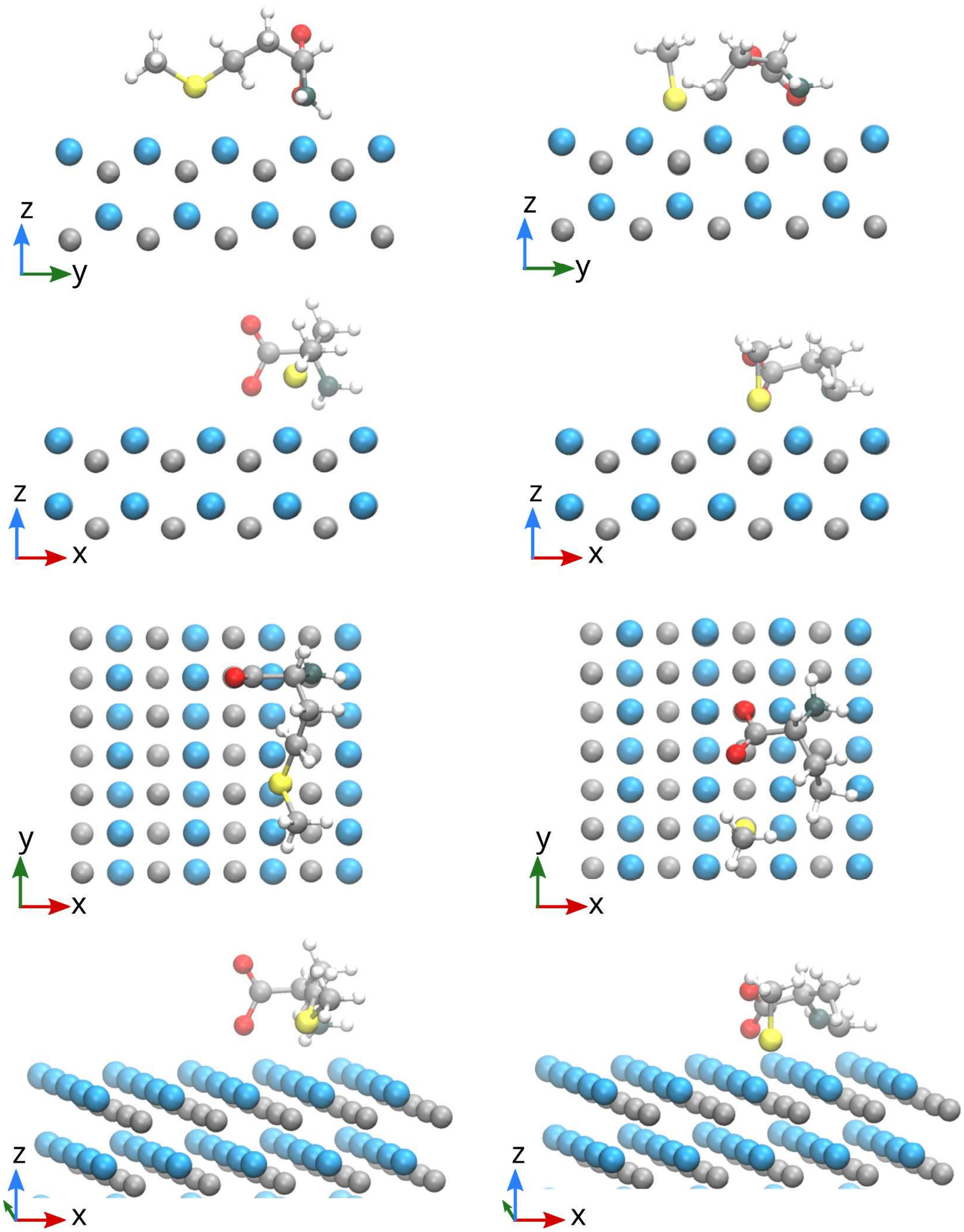

Figure S3. Adsorption geometry of an L-methionine conformer (conformer B) on a WC $(10\overline{1}0)$ surface before (left) and after (right) atomic relaxation. For simplicity, only part of the simulated metallic slab is shown. Legend: ● = C, ● = N, ● = O, ● = S, ● = W.

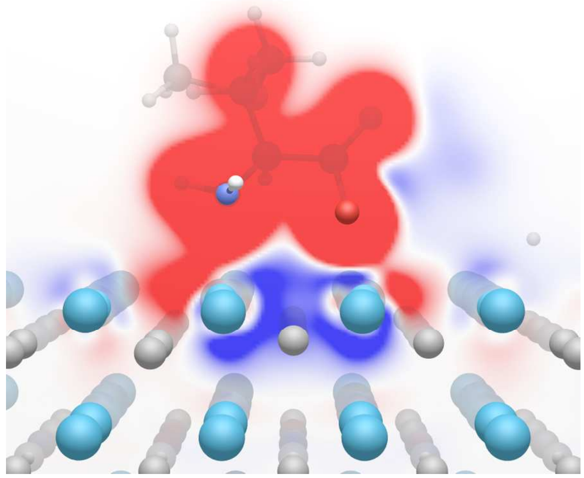

Figure S4. Charge density difference (ρ_{diff}) of dissociated L-methionine on a WC ($10\bar{1}0$) surface. The charge density difference is defined as $\rho_{\mathrm{diff}} = \rho - (\rho_{\mathrm{mol}} + \rho_{\mathrm{WC}})$ where ρ denotes the charge density of the dissociated L-methionine adsorbed on WC($10\bar{1}0$), while ρ_{mol} and ρ_{WC} represent the charge densities of the isolated molecule and clean WC($10\bar{1}0$) surface, respectively. The charge density difference is plotted in a plane perpendicular to the surface, which crosses the vicinity of the reactive nitrogen and oxygen atoms. The values range from -0.07 (solid blue, deficit) to 0.07 (solid red, accumulation) electrons/Å^3.

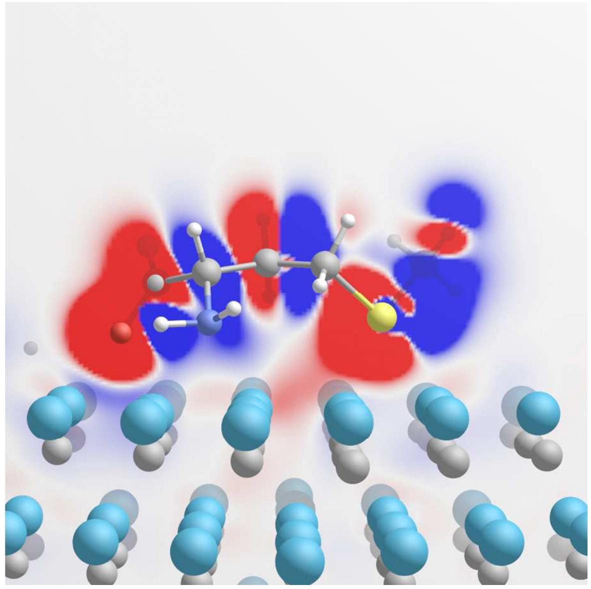

Figure S5. Charge density difference of an isomer of dissociated L-methionine on a WC $(10\bar{1}0)$ surface. The charge density difference is defined and plotted in an analogous way to Fig. S4. The plane here considered is perpendicular to the surface and crosses the vicinity of the main chain of the molecule, including the sulphur atom

2. Morphology of the wear scars obtained under the lack of W or S at the contact interface

The friction performance of the mixture containing 1 wt.% methionine in glycerol was found to be extremely poor, characterised by an initial coefficient of friction with a relatively high value of around 0.3 with friction spike values higher than 0.7. These seizures in friction indicate the welding of asperities and subsequent pull out and breakage due to the incapability of the lubricant to prevent severe metal to metal contact. This friction behaviour led to wear scars with very large dimensions (3.3 x 2.0 mm) as seen in Fig. S6a, with evident signs of scuffing due to local welding of asperities and presence of massive scratches (Fig. S6b). EDX measurements indicated a sulphur concentration on the wear scar of about 0.6 wt.%. The low sulphur concentration on the wear scar is an evident sign that confirms the lack of low friction tribofilm formation, indicating that methionine did not tribo-chemically reacted with the steel substrate under the absence of WC.

The wear scar of the functionalized surface lubricated using pure glycerol shows the presence of scattered black spots across the surface (Fig. S6c). However, opposite to the tests perform using the mixture containing methionine in glycerol, EDX analyses reveal mostly the presence of iron and oxygen (9.0 and 4.8 wt.%, respectively) along with tungsten and carbon from the embedded particles, with a completely lack of sulphur (Fig. S6d). As a consequence, the coefficient of friction remained at a high value throughout the test, confirming that a low friction tribofilm could not be achieved under the lack of methionine at the contact interface.

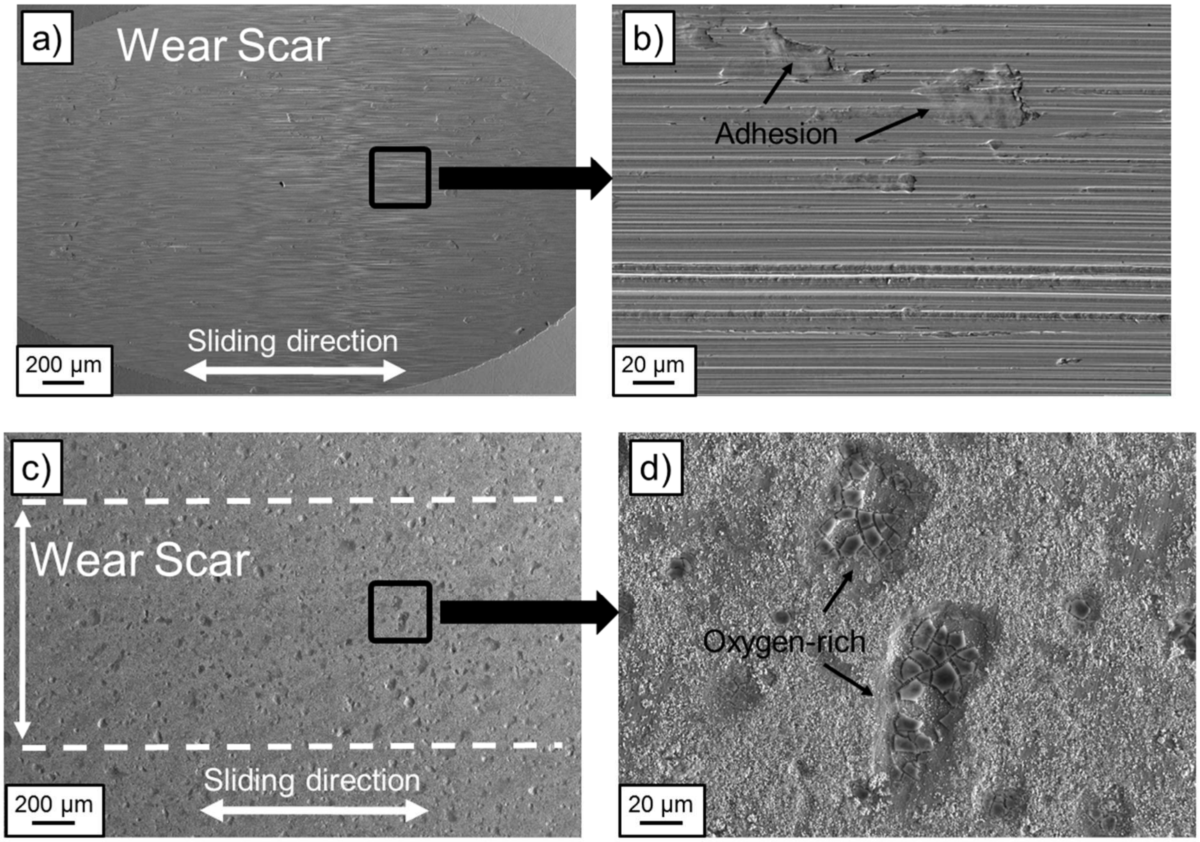

Figure S6. Surface topography using secondary electrons of AISI 304 steel surfaces after being tested using a lubricant mixture of 1 wt.% methionine in glycerol (a and b). Surface topography using secondary electrons of functionalized surfaces after being tested using pure glycerol (c and d).

3. Morphology of the tribofilm and position of the TEM lamella extraction

The morphologies of the wear scars formed on the WC functionalized surfaces after being tested with 1 wt.% methionine in glycerol revealed the presence of a dark-coloured tribofilm under stereo microscopy (Fig. S7). The lamella used for the TEM analyses was extracted at the turning point of the contact, perpendicular to the sliding direction in the position indicated in the figure.

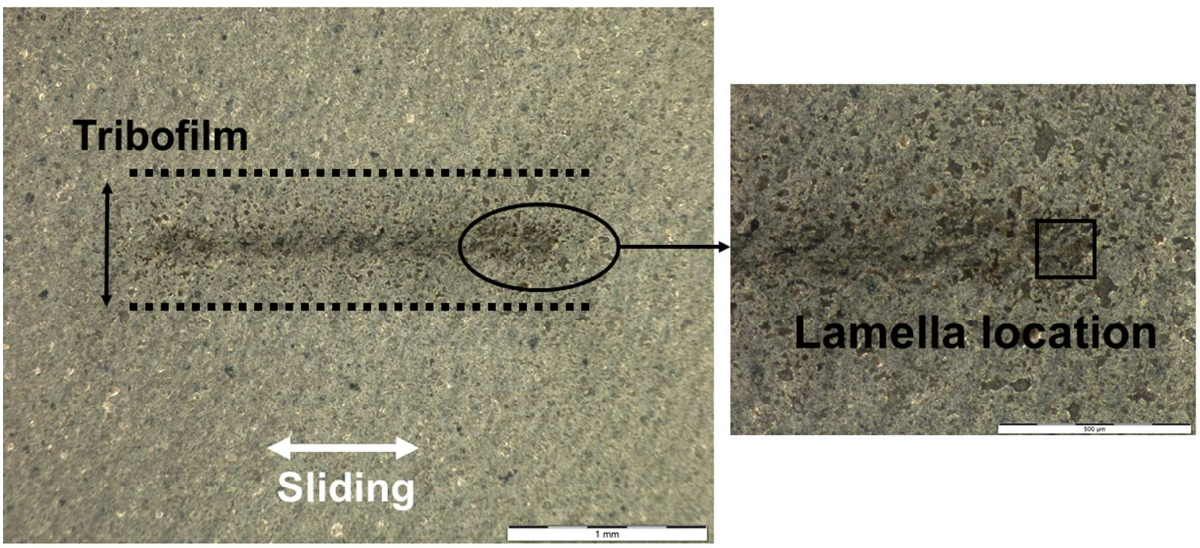

Figure S7 Stereo microscopy picture of a wear track on a WC functionalized surface after being tested with 1 wt% methionine in glycerol.

4. Chemical composition of the low friction tribofilm

Table S1. Relative surface atomic concentrations inside the wear scars as detected by the XPS analysis

Atomic orbital	Atomic concentration (%)
	1 wt% methionine in glycerol
W*4f*	2.9
S*2p*	11.2
C*1s*	60.2
O*1s*	16
Fe*2p*	9.8