Molecular dynamic study of the mechanical properties of two-dimensional titanium carbides \( \text{Ti}_{n+1}\text{C}_n \) (MXenes)

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Abstract

Two-dimensional materials beyond graphene are attracting much attention. Recently discovered 2D carbides and nitrides (MXenes) have shown very attractive electrical and electrochemical properties, but their mechanical properties have not been characterized yet. There are neither experimental measurements reported in the literature nor predictions of strength or fracture modes for single-layer MXenes. The mechanical properties of two-dimensional titanium carbides were investigated in this study using classical molecular dynamics. Young’s modulus was calculated from the linear part of strain–stress curves obtained under tensile deformation of the samples. Strain-rate effects were observed for all \( \text{Ti}_{n+1}\text{C}_n \) samples. From the radial distribution function, it is found that the structure of the simulated samples is preserved during the deformation process. Calculated values of the elastic constants are in good agreement with published DFT data.

Keywords: MXenes, 2D materials, molecular dynamics, Young’s modulus

(Some figures may appear in colour only in the online journal)

1. Introduction

A new, large family of two-dimensional transition metal carbides and nitrides, known as MXenes, was recently discovered [1]. Due to their atomically thin structure [2], investigation of the mechanical properties of two-dimensional (2D) materials experimentally is much more challenging compared to 3D materials. Despite that, Lee et al [3] have measured the elastic properties of monolayer graphene by atomic force microscopy (AFM) indentation. Implementation of such technique to MXenes presents an even harder challenge because of the smaller lateral size of sheets that are currently produced [4]. Besides that, basal planes of all MXenes produced so far are terminated by oxygen-containing functional groups, which make the experimental investigation of elastic properties of pure non-terminated MXene sheets impossible, at least for now. Therefore, all current information on elastic properties of pristine MXene sheets was obtained from theoretical (modeling) studies.

Important structural characteristics such as lattice parameters, and interatomic distances, as well as elastic constants, band structure and electronic density of states of the MXenes were obtained using the first principles techniques [5–13]. Although \textit{ab initio} techniques are precise and powerful, usually only a small number of atoms, i.e. a few unit cells, can be modeled. Thus, some important collective effects requiring larger statistics may be overlooked.

The large-scale computer simulation by classical molecular dynamics (MD) is an alternative approach that is widely used in investigating mechanical properties of 2D materials [14–17].

In classical MD, the trajectory of a system is obtained by integration of Newton equations of motion containing interatomic forces for all particles involved in simulation [18].
However, due to the recent discovery of MXenes, the exact expressions for interatomic potentials directly fitted to the interaction energy in two-dimensional Ti$_{n+1}$C$_n$ crystals are not yet established. There are, however, several examples of MD simulations involving Ti and C atoms [19, 20] in other materials. Modified embedded atom method (MEAM) described in [19] was fitted for a 3D NaCl-type Ti-C binary system, but it cannot reproduce a 2D Ti$_{n+1}$C$_n$ structure without major adjustments. Moreover, the MEAM contains a large number of parameters that need to be revised to fit the potential energy of Ti–C interaction in MXene. Empirical potential energy function (PEF) [20] was fitted to a layered-type Ti–C interaction in titanium covered carbon nanotube, which has atomic configuration similar to Ti$_{n+1}$C$_n$ MXene. The analytical expressions for potentials in a PEF approach have only three empirical parameters; therefore it may be easily adjusted to represent Ti–C interaction in 2D Ti$_{n+1}$C$_n$ carbides.

In this paper, we report the first classical MD study of the mechanical properties of 2D Ti$_{n+1}$C$_n$ MXenes. The aim of this work is to calculate the structural and elastic properties of the 2D Ti$_{n+1}$C$_n$ carbides by a large-scale MD simulation and compare them with those obtained from DFT data on single crystal cells [9]. In the absence of a specific force field for MXenes, we seek to develop a simple and accurate approach that can be used in future investigations of the structural and mechanical properties of the MXenes. Using this approach, we also aim to obtain new insights into fracture modes of MXenes.

2. Model

We consider Ti$_{n+1}$C$_n$ sheets with $n = 1, 2, 3$, located in a Cartesian coordinate box as shown in figure 1 (all MD snapshots in this paper were produced using Visual Molecular Dynamics software [21]). Ti$_3$C and Ti$_5$C$_2$ are among the first MXenes reported [1, 4], while Ti$_4$C$_3$ has only been studied computationally [12]. The titanium and carbon atoms were placed at initial positions according to the MXene lattice [4]. It should be noted, however, that at least some bare MXenes are expected to be stable, because the calculated cohesion energy of the appropriate MAX phases Ti$_3$C$_2$ and Ti$_4$C$_3$ is lower than the energy of the appropriate MAX phases Ti$_3$AlC$_2$ and Ti$_4$AlC$_3$, respectively [22]. Just like silicene, germanene or electrides, bare MXenes must be produced in an oxygen-free environment by bottom-up approach. The interatomic distances within the five boundary atomic layers on each side in the $x$–direction are held fixed during the simulation (figure 1), while periodic and free boundary conditions were applied in the $y$– and $z$–directions respectively. The tensile loading in the MD simulations of 2D materials can be implemented in a few ways [23, 24]; in our simulations we used a tensile model as in [23]. During the tensile deformation, the five layers of atoms with fixed interatomic distance on one side of the sample were pulled in the $x$–direction at a constant strain rate of 0.0004 ps$^{-1}$, while the corresponding five layers of atoms on the opposite side of the MXene sheet remained fixed. The lateral ($x$– and $y$–) dimensions of the samples considered in our simulations vary from about 19.50 × 16.84 nm to 38.71 × 33.47 nm, where the total number of atoms involved in simulation varies from 12 288 to 87 808, depending on the MXene and system dimensions.

Interatomic bonding in MAX phases is known to be a combination of metallic, covalent, and ionic [4, 25]. Therefore, various types of potential energy functions were
used to simulate interactions between different types of atoms.

As shown before [26], Ti_{n+1}C_n are metallic conductors, so the metallic type of bonding is supposed to prevail within the Ti layers of the material. With this assumption, the embedded atom method (EAM [27]) was chosen to describe the interactions between titanium atoms in the Ti_{n+1}C_n sheets. The generalized EAM potential is widely used in MD simulations of metal alloys and is well fitted to reproduce the basic material properties [28, 29].

Forces between the titanium and carbon atoms are derived from the empirical potential energy function (PEF) parameterized for C–Ti compounds [20]. Within this approach, the total potential energy of the system can be presented as a truncated sum of two- and three-body potentials, where the two-body term is approximated by the Lennard–Jones (LJ) potential [30]

$$U_{ij} = \varepsilon_0 \left[ \left( \frac{r_{ij}}{r_0} \right)^{12} - 2 \left( \frac{r_{ij}}{r_0} \right)^6 \right], \quad (1)$$

with $r_{ij}$, $r_0$, and $\varepsilon_0$ being the distance between atoms $i$ and $j$, equilibrium distance, and the minimum energy, respectively; and the three-body term by Axilrod–Teller (AT) potential [31]

$$W_{ijk} = \frac{Z \left( 1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k \right)}{(r_{ij} r_{ik} r_{jk})^3}. \quad (2)$$

Figure 2. Evolution of the potential energy (a) and probability distribution of the velocities (b) for the Ti_C sample (inset shows the system temperature during simulations).

Figure 3. Snapshots of the Ti_{n+1}C_n samples after equilibration at 300 K: (a) Ti_2C; (b) Ti_3C_2; (c) Ti_4C_3.

Figure 4. Strain–stress curves obtained for the Ti_{n+1}C_n samples during tensile loading. Dashed lines are extrapolated from the initial linear regions of strain–stress curves.
where $r_{ij}$, $r_{ik}$ and $r_{jk}$ are the distances between atom pairs; $Z$ is a three-body intensity parameter; $\theta_i$, $\theta_j$ and $\theta_k$ are angles of the triangle formed by $r_{ij}$, $r_{jk}$, and $r_{ik}$. Parameters of the LJ + AT model for C–Ti dimer and trimer were estimated from DFT data and used in a simulation of the titanium coating of single-wall carbon nanotubes [20]. However, in our simulations, we adjusted the equilibrium interatomic distance $r_0$ in pair potential (1) according to the Ti$_{n+1}$C$_n$ structure [4].

The carbon atoms in Ti$_{n+1}$C$_n$ MXenes are not chemically bonded with each other, therefore C–C interactions in our simulations are described only by a Lennard–Jones potential as in [32]. The cutoff distance of $r_0^{AT} = 0.25\text{nm}$ was used in AT potential (2), while $r_0^{EAM} = 0.90\ \text{nm}$ was set for long-range EAM and LJ potentials.

In the absence of a force field for MD simulations of Ti$_{n+1}$C$_n$, our approach based on combination of the existing data for Ti and C interactions is the first effort aimed at a qualitatively correct description of the system and may even produce quantitative results.

In order to investigate the elastic properties of the Ti$_{n+1}$C$_n$ carbides, the tensile deformation was applied to the samples and the stress during the deformation was computed according to the virial theorem [33, 34] as

$$\sigma_i = \frac{1}{V} \sum_{\alpha=1}^{N} \left( \frac{1}{2} \sum_{\beta=1}^{N} r_{\alpha\beta} f_{\alpha\beta}^i - m_i v_i^0 v_i^0 \right),$$

where $ij$ are the Cartesian coordinates, $\alpha$ and $\beta$ are atom indexes, $r_{\alpha\beta}^i$ $f_{\alpha\beta}^i$ are corresponding components of the distance and force between atoms $\alpha$ and $\beta$, $m$ is the atom mass and $V$ is the volume of the simulation box. The stress values were estimated from equation (3) with 0.005 Å increments in strain components and averaging over the 2000 simulation steps.

Figure 5. Snapshots of the atomistic configuration of the 2D Ti$_2$C carbide at different strains: (a) 0.025; (b) 0.05; (c) 0.065; (d) 0.08.
Young’s moduli were obtained from the initial slope of the simulated stress–strain curves.

The computational code is implemented using massive parallelism provided by the NVIDIA CUDA [35, 36] platform. Algorithms from the LAMMPS software package [37] were partially used for interatomic forces calculation. Equations of motion were integrated with a time step $dt = 0.2$ fs.

3. Results

In the beginning of the simulation, all atoms were placed in their initial positions to form an ideal Ti$_{n+1}$C$_n$ monolayer and the system was equilibrated over $2 \cdot 10^5$ simulation steps. The temperature was maintained at 300 K, using Berendsen thermostat [38]. During the simulations, the potential energy of the particles, system temperature and the velocities were recorded. Typical evolution charts for potential energy and temperature, as well as velocity distribution for the Ti$_2$C sample, are presented in figure 2.

As seen in figure 2, the potential energy of the system after several major oscillations in the beginning of the run reaches an equilibrium value with anticipated statistical fluctuations around it. The distribution of the velocities has the Maxwell–Boltzmann profile, while the system temperature is maintained at 300 K. The snapshots of the simulated MXenes after equilibration are shown in figure 3.

After the equilibration, the tensile load was applied to the samples, during which the overall stress was calculated by equation (3). Figure 4 shows the stress–strain curves obtained for the Ti$_2$C, Ti$_3$C$_2$, and Ti$_4$C$_3$ samples during their tensile deformation.

All obtained strain–stress curves have a similar shape with an initial linear region, related to elastic deformation. At a higher strain, stress continues to increase up to the threshold point of a yield stress, followed by a sharp drop associated with sample fracture.
The Young’s moduli obtained by linear fit of the strain–stress curves at the strain $\varepsilon < 0.01$ are 597, 502 and 534 GPa for Ti$_2$C, Ti$_3$C$_2$, and Ti$_4$C$_3$, respectively, with an interpolation error within 10%. These results are close to the published data estimated from first principles calculations [9]. As expected, the highest Young’s modulus was observed for Ti$_2$C MXene sheet and decreased with increasing thickness of MXene layer. Ti$_4$C$_3$, which is still to be produced experimentally, showed the highest strain to failure.

Under critical stress all the Ti$_{n+1}$C$_n$ samples exhibit similar behavior during elastic deformation; no significant defects are formed in the structure and the overall strain of the sample is distributed over the interatomic bonds, resulting in their tension. With further increase in stress, the evolution of the Ti$_{n+1}$C$_n$ samples is different.

For the thinnest Ti$_2$C MXene, the bond breakage begins in the outermost regions of the sample at the points of the highest local stress, propagating deeper to the center along the shifting atomic layers. Cracking of the material is accompanied by crumpling and folding of the Ti$_2$C sheet near the growing gap.

After the sample is completely torn apart on its right-side edge, it continues to fold and roll up due to the high surface energy and free boundary conditions in the $z$ direction. However, the radial distribution function (RDF) calculated for the Ti$_2$C sample after its fracture at the end of simulation shows that the atoms locally preserve their Ti$_2$C structure within the crumpled sheet, like in a rolled-up graphene sheet [39]. Snapshots of the simulated Ti$_2$C sample at several strain values are shown in figure 5.

A Ti$_3$C$_2$ sample behaves similarly to a thinner Ti$_2$C, except showing less tendency to wrap up during the fracture under tensile strain, which is probably due to its thickness, i.e. five atomic layers compared to three in Ti$_2$C. As figure 6 shows, only the edges along the crack folded, while the main body of the sample largely retained the initial sheet shape.

**Figure 7.** Snapshots of the atomistic configuration of the Ti$_3$C$_2$ 2D carbide at different strains: (a) 0.025; (b) 0.035; (c) 0.06; (d) 0.1.
In a striking contrast to Ti2C and Ti3C2, cracks in the Ti4C3 MXene appear first in the central part of the sheet. At a higher stress, these cracks grow in size, leading to the complete fracture of the sample with formation of several Ti4C3 fragments (Figure 7). It is important to mention that Ti4AlC3 MAX phase or Ti4C3 MXene have not been produced experimentally yet.

To detect the changes in the structure of MXene sheets, the 2D radial distribution functions (RDF) \( g(r) \) were calculated at the end of the strain–stress simulation (Figure 8).

As can be seen from the figure, the short-range order related to the local MXene structure is preserved in the atomic configuration for all samples.

To validate the obtained results, the strain–stress simulations were performed at different strain rates for all three Ti\(_{n+1}C_n\). Three strain rates values of 0.0002 ps\(^{-1}\), 0.0004 ps\(^{-1}\), and 0.001 ps\(^{-1}\) were used in these simulations. The results of

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**Figure 8.** Radial distribution functions (left panels) and corresponding atomistic configurations (right panels) of the 2D Ti\(_{n+1}C_n\) samples after fracture under tensile deformation: (a), (d) Ti2C; (b), (e) Ti3C2; (c), (f) Ti4C3.
these simulations are shown in figure 9. As expected, all the strain–stress curves obtained at different strain rates have a linear region of elastic deformation, with the slope in this region being independent of the strain rate.

The shift of the yield point to larger strain values with increasing strain rate was observed in all Ti\textsubscript{$n+1$}C\textsubscript{$n$} simulations. This phenomenon, known as strain rate effect [40], has been observed experimentally for metals and has several theoretical explanations that have been discussed in the literature [41].

4. Conclusions

Using large-scale classical molecular dynamics simulations we have studied the mechanical properties of the 2D titanium carbides (MXenes) under tensile loading. Calculated strain–stress curves have linear regions at small strains (≤1%). Young’s moduli estimated from these initial regions of strain–stress curves by a linear fit are close to previously published data [9] obtained by DFT. These results were reproduced at different strain rates and were shown to be insensitive to the strain rate in the range 0.0002 ps\textsuperscript{-1}–0.001 ps\textsuperscript{-1}. Mechanical properties and evolution of the atomic structure of 2D Ti\textsubscript{$n+1$}C\textsubscript{$n$} under tensile loading depend on the number of atomic layers $n$ in MXenes. This may indicate different mechanisms of mechanical failure for Ti\textsubscript{$n+1$}C\textsubscript{$n$} with different $n$ (layer thickness). The highest Young’s modulus was obtained for the thinnest Ti$_2$C carbide.

As soon as the free boundary edge appears in the sample, the MXene begins to roll-up onto itself due to a high surface energy in vacuum. However, in the Ti$_4$C$_3$ sample, smaller fragments, which are formed during fracture, largely retain their original flat sheet-like appearance, as the surface tension is not enough to overcome the high rigidity of the thickest of the considered MXenes. The calculated RDFs show that overall, the local Ti\textsubscript{$n+1$}C\textsubscript{$n$} structure remains intact in all the samples after fracture. With increasing rate, a slight growth of yield stress and critical strain was observed, which indicates that Ti\textsubscript{$n+1$}C\textsubscript{$n$} MXenes may possess a mechanism of defect formation and plastic deformation typical for metals [40]. The examined MXenes are almost twice weaker than atomically thin graphene with Young’s modulus of...
$E = 1.0 \pm 0.1$ TPa [3]. At the same time, the elastic constant, obtained for Ti$_2$C is almost twice higher compared to $E = 0.33 \pm 0.07$ TPa [42] of MoS$_2$, another 2D crystal with a similar structure. Thus, as potential materials for nanodevices with high mechanical property requirements or as reinforcement for composites, MXenes can be the preferred choice among other 2D materials beyond graphene.

Although the calculated Young’s moduli are close to those previously obtained by DFT, in the absence of experimental data we cannot claim that other mechanical properties, such as yield stress and related strain, are reproduced correctly by classical MD. Nevertheless, besides the good agreement with DFT data, our simulations have reproduced strain-rate effects that are also observed in experiments on metals and graphene [43]. Overall, we conclude that the employed classical MD approach correctly describes mechanical behavior of the two-dimensional titanium carbides and may be used in further investigations of the structural and mechanical properties of other bare and surface-terminated MXenes. Further efforts in this area should be focused on creating and parameterizing a reliable force field (ReaxFF [44] or similar), which could be used for classical MD simulations of different MXenes.

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