Molecular dynamics study on creep behavior of montmorillonite

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Abstract. Clay-rich rocks are widely used in high temperature and stress environment in a very long term like disposal of high-level radioactive waste, exploring its creep deformation mechanism is essential. Clay minerals, as the essential components of clayey rocks, have a crucial influence on the creep behavior. However, it is of great challenge to experimentally investigate the mechanical property of a single crystal mineral due to its small size. In recent years, molecular dynamics (MD) simulations are widely used to address a series of scientific issues including creep mechanism from atomic level. In this study, we selected montmorillonite (MMT), a representative clay mineral in clayey rocks, as the principal object to explore the creep behavior in different temperatures and stresses. The temperature varies from 300 K to 1200 K while the stress is applied in the range of 14 GPa to 32 GPa. Meanwhile, the anisotropic creep behavior along the two orthogonal crystal orientations is studied as well. It is found the atomic numerical results show a good agreement with macroscopic data that the deformation increases with the temperature raise and applied stress, the creep curve contains two different phases under low temperature and stress while three phases are observed under high values of temperature and stress. Besides, the creep deformation exhibits an obvious anisotropic trend, due to oriented atomic structures. This study provides a better understanding of the creep mechanism of single crystal of MMT and an atomic insight on macroscopic time-dependent deformation of clayey rocks.

Keywords: molecular dynamics, temperature, applied stress, anisotropy, creep.

1 Introduction

During the last few decades, the macroscopic mechanical behavior of clay-rich rocks has been extensively studied as a potential geological barrier for subterranean radioactive waste disposal[1]. These accomplishments have contributed to the knowledge of the basic mechanical behavior of clayey-rich rocks. According to previous laboratory studies, local deformation mechanisms of clay particles and aggregates at the nanometer and micrometer scales generate macroscopic plastic deformation[2]. However, it is quite challengable to perform direct experimental measurement at such small scales in view of identifying those mechanisms. In recent years, the rapid development of molecular dynamics (MD) and wide application in clay-rich materials provides an effective means for the study at nanoscale. MD was first used to investigate hydration-related swelling behavior, structural distribution, and water molecule or cation ion diffusion between layers[3-4]. Afterward, works on the mechanical property of clay minerals with MD have been reported gradually and obtained a serious valuable results, such as the elastic property and failure mechanism[5-7]. However, in most previous studies, MD simulations were performed on crystal samples subjected to the loading paths like uniaxial compression, tension, triaxial compression with constant confining stress and triaxial compression with constant mean stress. As a matter of fact, due to the demand for the safety of high level radioactive waste disposal for hundreds years, it is crucial to study the
long-term deformation and failure mechanism. To the best of our knowledge, the creep property of clay-rich materials have so far not been investigated at nanoscale by MD while it is widely used in the researches of metal[8]. In this study, we shall perform atomic simulations on Na-montmorillonite with constant uniaxial stress under different temperature, applied stress level and loading orientation to identify the basic deformation and failure features and then to build the links between microscopic and macroscopic behaviors.

2 Computational method

Molecular dynamics (MD) is the computational method applied in this case. As in most prior MD simulation research, atoms are considered as basic particles. Inter-atomic potentials (force fields) that contain bonded and non-bonded interactions generate the forces acting on the atoms, and atomic movement is governed by Newton equations of motion. This section introduces the different steps of MD simulations employed in this study.

2.1 Crystal structure

The crystal structure considered here is based on the natural Wyoming MMT[9], The unit cell formula is as follows:

$$\text{Na}_{0.75}n\text{H}_2\text{O}[\text{Si}_{7.75}\text{Al}_{0.25}][\text{Al}_{3.5}\text{Mg}_{0.5}]\text{O}_{20}(\text{OH})_4$$

The space group of unit cell is C2/M, monoclinic system, with $a = 5.23\,\text{Å}$, $b = 9.06\,\text{Å}$, $c = 9.6\,\text{Å}$, $\alpha = \gamma = 90^\circ$ and $\beta = 99^\circ$. It is distinguished by a TOT (tetrahedron-octahedron-tetrahedron) layer made up of sheets of silica tetrahedra and alumina octahedra. The layer is negatively charged because of the isomorphous substitution which means the Al$^{3+}$ in the octahedral sheet are substituted by Mg$^{2+}$ and Si$^{4+}$ in the tetrahedron sheet are substituted by Al$^{3+}$. Specifically, one of thirty-two Si$^{4+}$ is replaced by an Al$^{3+}$ and one of eight Al$^{3+}$ is replaced by an Mg$^{2+}$. To keep the electrically neutral of model, the negative charge is balanced by the incorporation of Na cations in the inter-layer space. The model used in this study is shown in Fig.1, it is an 8*4*4 super-cell and the total number of atoms in simulation cell is 5216.
2.2 Force field

The interatomic interactions in crystal systems are described by forces fields which are derived from energy potential functions. In the present study, the CLAYFF force field developed by Cygan et al [10]. is adopted. This force field is widely accepted because it has been shown to be highly effective in modeling the crystal structure with a number of different clay, mobility of interlayer water because of the huge advantage of providing atoms with complete translational freedom. Recently, it has also been frequently utilized to investigate the mechanical behavior of clay and has aided in the understanding of fundamental mechanical mechanisms at the atomic level. The total potential energy (E_{total}) is composed of the Coulomb interactions (E_{Coul}), the van der Waals interactions (E_{VDW}) and the bonded interactions. The bonded terms include the bond stretch energy (E_{bond-stretch}) and the angle bend energy (E_{angle-bend}) that is used in water and metal with hydroxyl. One gets:

\[
E_{total} = E_{Coul} + E_{VDW} + E_{bond-stretch} + E_{angle-bend}
\]

\[
E_{Coul} = \frac{e^2}{4\pi\varepsilon_0} \sum_{ij} \frac{q_i q_j}{r_{ij}}
\]

\[
E_{VDW} = \sum_{ij} D_{0,ij} \left( \frac{R_{0,ij}}{r_{ij}} \right)^{12} - 2 \left( \frac{R_{0,ij}}{r_{ij}} \right)^{6}
\]

\[
E_{bond-stretch} = k_j (r_{ij} - \varepsilon_j)^2
\]

\[
E_{angle-bend} = k_i \left( \theta_{ij} - \theta_0 \right)^2
\]

where \( r_{ij} \) is the distance between the atoms i and j. In the Coulombic energy, \( e \) is the charge of an electron, \( \varepsilon_0 \) is the dielectric permittivity of a vacuum (8.85419 × 10^{-12} F/m) and \( q_i \) and \( q_j \) are the atomic partial charges, which can be derived from quantum mechanics calculations. In the Van der Waals energy, the terms \( D_{0,ij} \) and \( R_{0,ij} \) are calculated by:

\[
\begin{align*}
R_{ij} &= \frac{1}{2} (R_{ij} + R_{ji}) \\
D_{ij} &= \frac{1}{2} (D_{ij} + D_{ji})^{1/2}
\end{align*}
\]

2.3 MD simulation procedure

A parallel molecular dynamics code LAMMPS [11] is used to perform simulations on the crystal structure of Na-Montmorillonite defined above. The samples are first relaxed at the desired temperature for 200 ps using an NVT (number of atoms, volume, and temperature) ensemble, then independently relaxed in three directions for another 200 ps using an NPT (number of atoms, pressure, and temperature to mimic bulk behavior) ensemble with zero pressure in all directions. The goal of these relaxation processes is to evenly distribute the surplus free energy throughout the system. This model is used as a starting point for mechanical loading. In order to study the impact of temperature, applied stress and the anisotropy on the creep deformation of MMT, the sample is subjected to different levels of applied stress along the x direction and z direction respectively while other two directions were exposed to zero pressure at temperature ranging from 300 K to 1200 K for 200ps. Finally, the corresponding creep curves are obtained to explore the creep mechanism at nanoscale.

3 Results and discussion

3.1 Effect of applied stress

With the objective to investigate the effects of applied stress and the possibility of tertiary creep, a series of creep tests at different applied stress level have been calculated. The selection of applied stress is based on the method of macroscopic creep experiments. According to previous researches, the ratio of applied stress in creep to the peak strength of conventional short-term uniaxial compression (\( \sigma / q_{peak} \)) is used to evaluate creep deformation under different stress states [12]. The published compressive strength of Na-MMT calculated by molecular dynamics is 33.74 GPa along z direction and it is 21.26 GPa along x direction [13]. The 60 percent of the peak strength is chosen as the minimum applied stress, then it is gradually increased at intervals of 2 GPa until the
stress exceeds the long-term strength. Therefore, the creep tests along the z direction are under the applied stress level ranging from 20 to 34 GPa and it is from 14 GPa to 22 GPa along x direction. The creep curves are presented in Fig. 3 where Fig. 3(a) represents the results in z direction and Fig. 3(b) is along x direction. It can be concluded that the same positive correlation of creep strain with the development of applied stress for both loading directions. Besides, under high stresses levels, the creep rate is significantly enhanced during the secondary region, especially when the loading direction is along z direction. Moreover, the tertiary creep stage is the key to study creep failure relating to time-dependent under certain specific conditions, while it doesn’t occur within the calculation time of this work. Under the temperature of 300 K, the model deforms unstable to rupture abruptly under \( \sigma_z = 34 \) GP loaded in the z direction while the similar scenario occurs under \( \sigma_x = 22 \) GPa along x loading direction.

![Creep curves](image)

(a) (b)

Fig. 2 Creep stress-strain relationship of MMT under different applied stress level. (a) The loading direction is along the z orientation (b) The loading direction is along the x orientation.

### 3.2 Effect of temperature

![Creep curves](image)

(a) (b)

Fig. 3 Creep stress-strain relationship of MMT under different temperatures. (a) The loading direction is along the z orientation (b) The loading direction is along the x orientation.

Fig. 3(a) shows the creep curve of MMT at different temperatures under the applied of 24 GPa applied along z direction as denoted by \( \sigma_z = 24 \) GPa. A standard creep curve contains three creep regions, including the primary stage, secondary stage, and tertiary stage. However, as presented, only the case loaded in the z direction with T=1200 K shows the tertiary creep zone which means the model is failure after loading for about 50ps, indicat-
ing the applied stress of 24 GPa is over the long-term strength under T=1200 K. The creep failure occurs abruptly which suggests the brittle failure of MMT. Only the first two stages of creep are notably observed under the comparatively low temperatures (e.g., T= 300 K, 600 K, and 900 K). Furthermore, creep strain increases as temperature increases. The reason for this scenario is that high temperatures could accelerate creep deformation and destroy the atomic structure due to intense vibrations. Hence, it becomes easier to deform. The temperature effects on creep characteristics under the stress of 20 GPa applied along the x direction (i.e., $\sigma_x=20$ GPa) can be obtained, as illustrated in Fig2(b).

### 3.3 Anisotropic behavior

In this section, in order to study effects of inherent structural anisotropy on creep deformation, the results that the modes are loaded respectively along the x and z directions with the stress of 20 GPa under different temperatures. As shown in Fig. 4, It can be seen that the creep strain induced by loading along x direction is evidently larger than z direction under the same temperature and applied stress level. Meanwhile, the creep curves are relative parallel, except the case loaded along x direction under 900 K, thus the strain rates are quite similar during secondary region, suggesting that the creep rates are almost independent on the load direction. Therefore, the anisotropic effects of creep behavior are mainly resulted from the rapid loading in the primary stage. In addition, under the temperature of 900 K, the different creep behavior caused by anisotropy are more obvious. There is even no tertiary creep regions loaded along z direction while the creep is accelerated to rapid rupture for x direction, indicating the compressive strength of z direction is much larger than that of x direction, which is consistent with the previous uniaxial and triaxial compression results[7]. The significant differences between these two directions are mainly due to the inherent anisotropy of the structure. The z crystal orientation of montmorillonite consists of negatively charged silicate layers which are bonded together by inter layer cations while the layer is constituted by two tetrahedral sheets sandwiching one octahedral sheet bonded by the covalent bonds along the x crystal orientation. Therefore, the major failure mode along z direction is the decrease of inter layer space causing the decrease of cohesion energy between cations and clay layer. In the case of x loading direction, the clay layer is continuously shortening and even bending, resulting in the sample failure, which is mainly due to the decrease of covalent bond energy.

![Creep stress-strain relationship of MMT in different loading direction](image)

**Fig. 4 Creep stress-strain relationship of MMT in different loading direction**

### 4 Conclusion

In this work, the molecular dynamics is used to identify the impact of applied stress, temperature and anisotropy on the creep property of single crystal montmorillonite. The main conclusions can be given as follows: (1) Creep strain and creep rate of the single crystal montmorillonite are positively correlated with the variation of temperature and the applied stress level. The rapid evolution of creep failure stage shows the brittleness of dry montmorillonite.
The creep deformation and failure strength are strongly influenced by loading direction. The creep strain under the x loading direction is much larger than the z direction while to the contrary, the creep strength is much higher under the z loading direction. The inherent anisotropy of structure is mostly responsible for these differences. In addition, the failure modes are strongly dependent on anisotropy.

This work is an attempt to report the computational investigation of the creep behaviors of MMT by molecular dynamics simulation, the atomic-scale analysis of the creep mechanism will be helpful for the experimental design and understanding. Also, further efforts are required to overcome the limitation of timescale in MD simulations for investigating the creep-related issue.

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