MOLECULAR DYNAMICS SIMULATION OF DEFORMATION BEHAVIOR OF GADOLINIA DOPED CERIA UNDER TENSILE LOADING

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Summary In this paper, molecular dynamics simulations have been carried out on the uniaxial tensile deformation process of GDC. The stress-induced martensitic transformation was observed from fluorite structure to rutile structure, and was illustrated with the evolution of the atomic configurations of the calculation model. It is found the addition of point defects would have a significant influence on GDC's phase-transformation behavior, which limited the further deformation and loading capacity of the materials.

INTRODUCTION

Intermediate-temperature solid oxide fuel cells (SOFCs) received extensive attentions due to the high efficiency and low operating temperature. Gadolinia doped ceria (GDC) is a promising candidate electrolyte material for SOFCs. However, the mechanical properties of GDC are seriously decreased by the point defects introduced in the doping process which is necessary to get a desirable ionic conductivity [1]. The defect concentration increases with the increasing doping concentration. In this paper, the deformation behavior of GDC under uniaxial tensile load is analyzed by means of molecular dynamics simulations, and the effects of defects were explained in a microscopic view.

CALCULATION MODEL AND METHOD

The key of MD simulation is the interatomic potential. In this paper, the potential derived by combining the lattice inversion and quantum chemical calculation was used [2]. The Wolf algorithm was employed to estimate the Coulomb interaction and the cutoff distance was set as 15 Å [3].

Table 1 Potential parameters for GDC

	a(eV)	*b*	*c (Å)*
O^{2-}- O^{2-}	0.77109	7.85216	1.99458
Ce^{4+}- O^{2-}	0.20	8.46211	3.42512
Gd^{3+}- O^{2-}	0.20	7.95857	3.40062

$$\Phi_{++}(r) = \frac{q_+^2}{4\pi\varepsilon_0 r}$$

$$\Phi_{--}(r) = a_{--}\left\{\exp\left[b_{--}\left(1-\frac{r}{c_{--}}\right)\right] - 2\exp\left[\frac{b_{--}}{2}\left(1-\frac{r}{c_{--}}\right)\right]\right\} + \frac{q_-^2}{4\pi\varepsilon_0 r}$$

$$\Phi_{+-}(r) = a_{+-}\exp\left[b_{+-}\left(1-\frac{r}{c_{+-}}\right)\right] + \frac{q_+ q_-}{4\pi\varepsilon_0 r}$$

The ceria lattice is fluorite structure, which consist of Ce^{4+} in face-centered cubic (FCC) sublattice and O^{2-} in simple cubic (SC) sublattice. To create the GDC model, a certain amount Ce^{4+} were replaced with Gd^{3+} and half the amount O^{2-} were deleted to keep the charge neutrality. Gd^{3+} and oxygen vacancies were distributed randomly. $(CeO_2)_{1-x/100}(GdO_{1.5})_{x/100}$ were abbreviated as xGDC in this paper. Periodic boundary conditions were applied in all directions. The dimensions of models are 32.52Å × 151.76Å × 32.52Å before relaxations performed initially. The simulation system includes 12096 atoms for ceria or a fewer atoms for GDC because of the oxygen removal. All simulations are performed using LAMMPS code. The tensile loading method is displacement loading in [0 1 0] direction. The strain rate was $5\times10^8 s^{-1}$. The equations of motion are integrated using velocity Verlet algorithm. The NPT ensemble was adopted, implemented by Nosé-Hoover thermostat and Parinello-Rahaman barostat. Virial formula was used to calculate stress.

SIMULATION RESULTS

Deformation behavior of GDC under tensile load

A stress-induced pre-transformation occurs at a strain of 0.027 for ceria. The whole model turns into transition phase simultaneously. The two adjacent O^{2-} make a relative movement in tensile direction and keep consistent in other directions, as shown in figure 1. Meanwhile, the slope of stress-strain curve decrease, that indicates elastic constant softening, as shown in figure 3. The reason can be inferred that the tensile stress promotes soft modes and causes vibrational instability [4]. Every O^{2-} is in a tetrahedral interstitial site, constrained by four cations, and repulsed by

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neighbor O^{2-}. When the tensile load applied in Y direction, contraction take place in X and Z directions, and intensifies the repulsion of O^{2-}. As a consequence, the restoring force on O^{2-} becomes weaker because of the stronger component on Y direction of repulsion. The lattice instability and transformation occur when the stress exceeds the threshold.

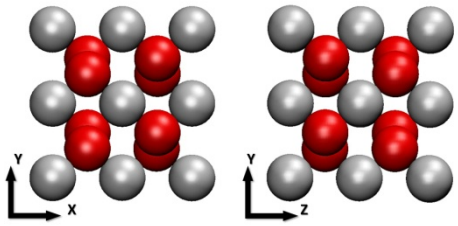

Figure 1. Unit cell structure of transition phase

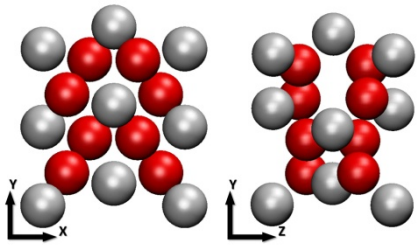

Figure 2. Unit cell structure of martensite

At a strain of 0.06, martensitic nucleation can be observed, which further propagates as the strain increases till the completion of phase transformation. The lattice structure undergoes a fluorite to rutile phase change. The unit cell structure is shown in figure 2. For 12GDC and GDCs with lower doping concentration, fracture occurs in rutile phase after the martensitic transformation; for 16GDC, fracture occurs in the interface of two phases when the rutile phase propagation is blocked; for 20GDC and GDCs with higher doping concentration, fracture occurs in fluorite phase without obvious nucleation and propagation, but regional transformation can still be found in instability zone.

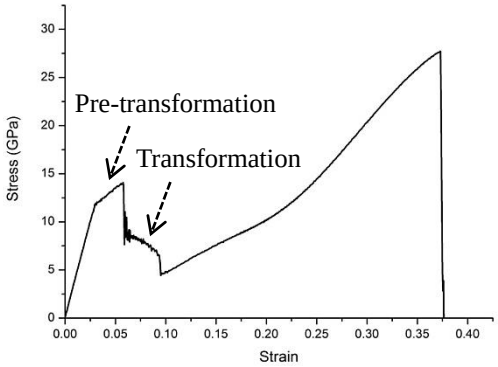

Figure 3. Stress-strain curve of CeO_2

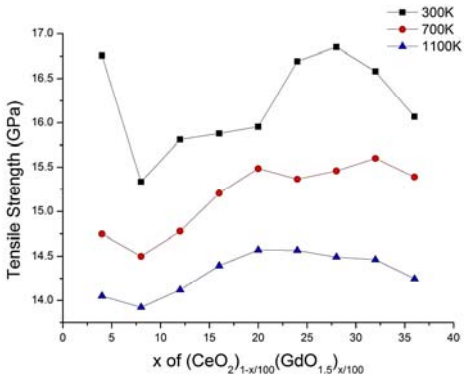

Figure 4. Fracture strength of GDC

Effects of defects on mechanical properties

The process of transformation is blocked by oxygen vacancies because the absences of some O^{2-} weaken the repulsion and break the mechanism of pre-transformation, therefore, the loading capacity of fluorite increases with the increasing defect concentration in an interval. Then it decreases because the oxygen vacancies aggravate the instability of system. The loading capacity of rutile phase is much larger than that of fluorite phase for pure ceria, while it decreases dramatically with the increasing defect concentration because of the aggravated instability too. So, the loading capacity of fluorite phase determines the tensile strength for 8GDC and GDCs with higher doping concentration. As shown in figure 4, the tensile strength shows a fluctuation trend which accords with the trend of experimental fracture strength [1].

CONCLUSIONS

In the work, the stress-induced martensitic transformation of GDC from fluorite structure to rutile structure was illustrated with the evolution of the atomic configurations obtained by using molecular dynamics simulations. A stress-induced pre-transformation caused by vibrational instability occurs before martensitic nucleation. Since the oxygen vacancies break the mechanism of pre-transformation then hinder the transformation, the fluorite phase strength increases with the increasing defect concentration. Meanwhile, the instability is aggravated by oxygen vacancies. Therefore, the tensile strength shows a fluctuation trend, which mostly determined by the fluorite phase strength.

References

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