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First-principles investigation on the corrosion resistance of rare earth disilicates in water vapor

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Abstract

Rare earth disilicates are used as environmental barrier coatings to prevent the non-oxide silicon-based ceramics from water vapor corrosion at high temperatures. However, existing experimental results about the water vapor corrosion behavior of these materials are scarce and sometimes contradictory. In this paper, we report theoretical studies on the water vapor corrosion resistance of rare earth disilicates using Mulliken analysis based on first-principles. The Mulliken populations of Si–O bonds in $Y_2Si_2O_7$, $Sc_2Si_2O_7$, $Yb_2Si_2O_7$, $Lu_2Si_2O_7$, and substituted $Y_2Si_2O_7$ are calculated. The relative water vapor corrosion resistance of these materials is predicted by comparing the values of Mulliken population. The predictions are consistent with the reported experimental data. This work suggests a computational method for design and selection of rare earth disilicate materials for better water vapor corrosion resistance.

Keywords: Corrosion; Silicate; Engine components; Environmental barrier coatings

1. Introduction

Further development of advanced gas turbine engines for low emission and high efficiency needs increasing operating temperatures and reducing the cooling requirements.[1,2] Current superalloys with thermal barrier coatings have reached their limit in high temperature applications. New materials are needed to meet the requirements of the next generation turbine engine systems. Silicon-based non-oxide ceramics, such as SiC, Si_3N_4, and their composites, are promising candidates for such applications because of their high strength, high creep resistance, good thermal shock resistance, and excellent high temperature stability.[2–4]

Applications of silicon-based ceramics have been limited since they are sensitive to water vapor at high temperature. In dry and clean oxygen environments, silicon-based ceramics can be used since the formation of a slow-growing, dense silica layer which protects the further oxidation of the materials.[5] However, in the combustion environments containing water vapor, the protective silica scale will be severely degraded by reacting with water vapor[6,7]:

$$SiO_2(s) + 2H_2O(g) = Si(OH)_4(g) \tag{1}$$

Fast combustion gas flow will cause a quick removal of $Si(OH)_4$, and result in the recession of components. One way to solve this problem is to apply environmental barrier coatings (EBCs) on the top of the silicon-based ceramics to improve their durability at high temperatures.

The earlier EBC system was based on mullite due to the fact that its coefficient of thermal expansion (CTE) matches closely with that of the SiC matrix.[8] However, mullite has a high recession rate in high-velocity combustion gas, which leads to the need of environmental overlay coatings.[8] Yttria-stabilized zirconia (YSZ) was selected as the baseline overlay coating because of its success performance in combustion environments as a thermal barrier coating.[9,10] Although YSZ-mullite EBC systems have greatly improved the resistance to environmental corrosion, the large CTE mismatch between YSZ and mullite layers results in cracks, leading to the enhanced oxidation of SiC, and in turn the recession of matrix. To address these issues, overlay coatings with both low recession rates and crack resistance, such

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as BSAS ($Ba_{1-x}Sr_xO–Al_2O_3–2SiO_2$, $0 \leq x \leq 1$), were developed. BSAS has been applied successfully into aero-engine hot sections,[11] exhibiting long-term durability in combustion environments at temperatures below 1300 °C. However, next-generation advanced turbine engines expect that the EBC coatings can work at the temperature as high as 1500 °C.[2] BSAS-mullite systems cannot be used at such a high temperature due to the limited durability and chemical compatibility of BSAS.[11,12] In order to improve the operation temperatures of EBC systems, rare earth silicates, $RE_2Si_2O_7$ (RE = rare earth element, including Y, Sc, Yb and Lu), have been developed to meet these requirements because of their low recession rates, low CTE mismatch with matrix, and their high chemical compatibility.[2,13–17]

Although rare earth silicates are promising EBC materials for high temperature applications, the available experimental data on wet corrosion behaviors of these materials are scarce, sometimes contradictory.[2,13–19] Possible reasons for the contradictory could be the contamination effects,[14] the variation in the precision of test facility, and the difficulties in test condition control. Overall, predicting the hydro corrosion resistance of these materials beyond trial and error has been a challenge for the researchers in this field.

Reaction (1) indicates that the wet corrosion of silicates originates from the reaction between Si–O bonds and water vapor. Therefore, we can say that the stronger are the Si–O bonds, the more difficult it is for the reaction to take place, thus the better water corrosion resistance. In this paper, we attempt to determine the Si–O strength of different RE silicates based on the first principles calculations. By comparing the Si–O strength, the relative hydro corrosion resistance of RE silicate materials is predicted. The prediction results are compared with the reported experimental data.

2. Procedures

Previous studies[20,21] indicated that Mullikin population analysis can be used to determine the relative strength of chemical bonds in materials. In this paper, Mulliken populations of Si–O bonds in RE silicates are calculated using CASTEP code following the formalism described by Segall et al.[20,21] The values of Mulliken population are then used to express the Si–O strength.

The calculation is based on density functional theory (DFT), the CA-PZ local density approximation (LDA) for exchange correlation, Broyden–Fletcher–Goldfarb–Shanno (BFGS) for optimization algorithm, ultrasoft pseudopotentials, supercells,

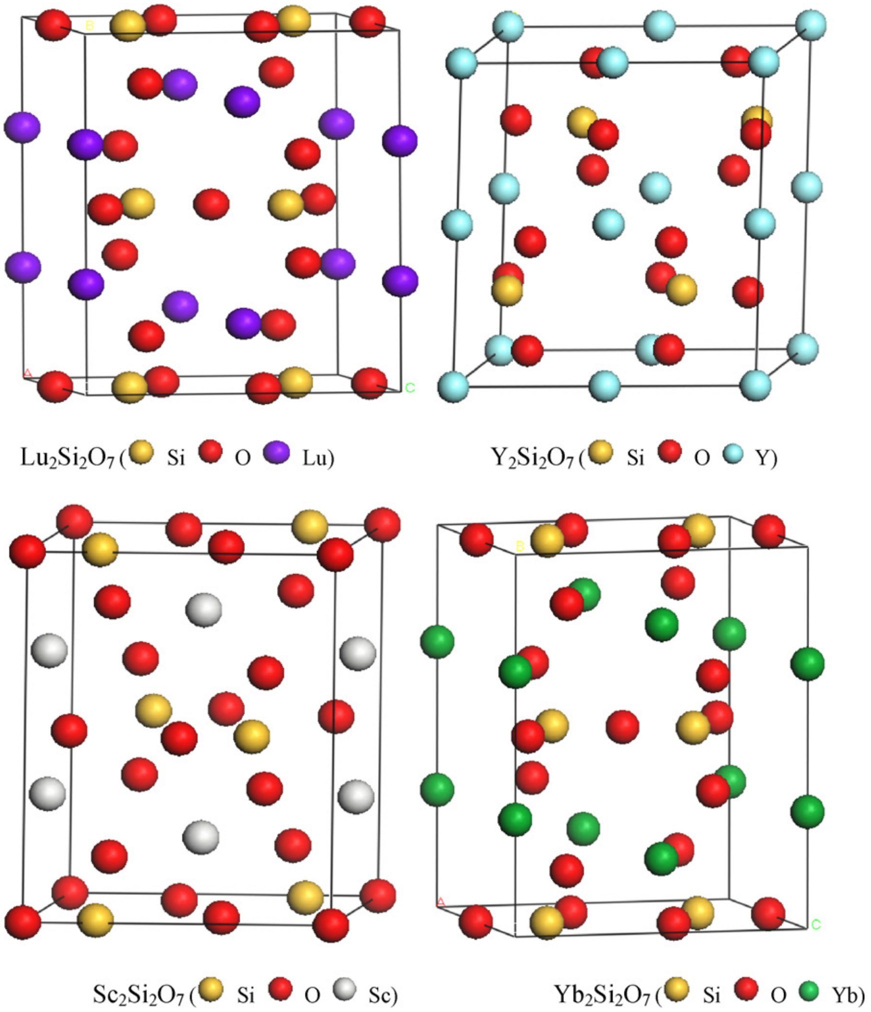
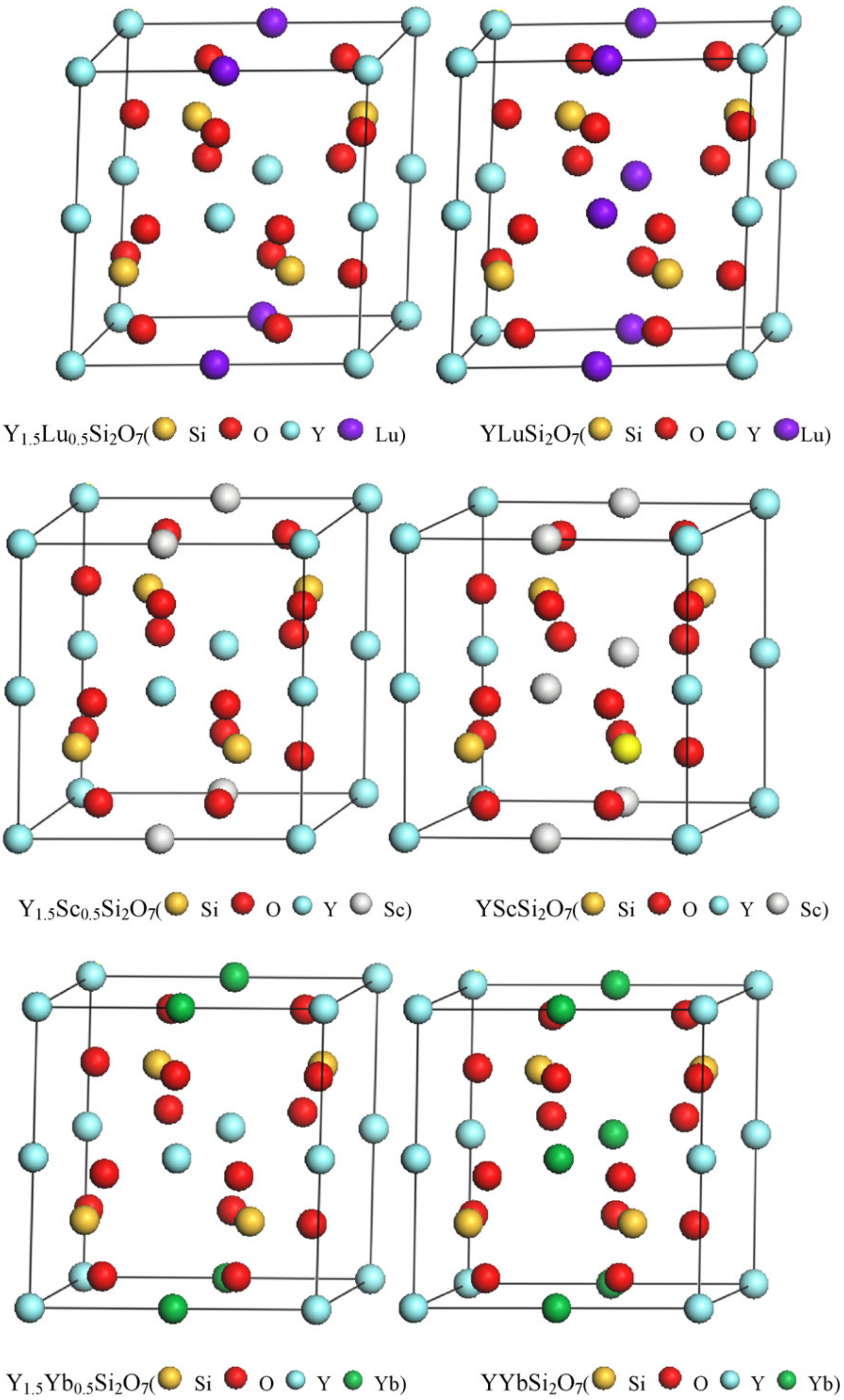


Fig. 1. The optimized structures of RE disilicates ($RE_2Si_2O_7$, RE = Lu, Y, Sc, Yb).

and plane waves.[22] The energy cut-off for the basis set is 360 eV, and integrations over the Brillouin zone are done by using the Monkhorst-Pack scheme in the relevant irreducible wedge.[23] The structural optimization is done by relaxing both the internal coordinates and the lattice constants by calculating the *ab initio* forces on the ions, within the Born–Oppenheimer approximation, until the absolute values of the forces were converged to less than 0.05 eV/Å. After geometric optimization, we compute the single point energy of the optimized structure, and analyzed the Mulliken bond populations. The distance cut-off for bond populations is 3.0 Å.

3. Results and discussions

In this paper, four RE disilicates are studied: $Y_2Si_2O_7$, $Sc_2Si_2O_7$, $Yb_2Si_2O_7$, and $Lu_2Si_2O_7$. They all possess the group silicate structure, where the double-tetrahedral (Si_2O_7) groups are connected by the rare earth elements.[24] The structures for



$Y_{1.5}Lu_{0.5}Si_2O_7$(● Si ● O ● Y ● Lu) $YLuSi_2O_7$(● Si ● O ● Y ●Lu)

$Y_{1.5}Sc_{0.5}Si_2O_7$(● Si ● O ● Y ● Sc) $YScSi_2O_7$(● Si ● O ● Y ● Sc)

$Y_{1.5}Yb_{0.5}Si_2O_7$(● Si ● O ● Y ● Yb) $YYbSi_2O_7$(● Si ● O ● Y ● Yb)

Fig. 2. The optimized structures of substituted $Y_2Si_2O_7$ disilicates ($Y_{2-2x}RE_{2x}Si_2O_7$, RE = Lu, Y, Sc, Yb, x = 0.25, 0.5).

Table 1
Mulliken bond populations and bond length of Si–O bonds in RE disilicates ($RE_2Si_2O_7$, RE = Lu, Y, Sc, Yb).

	Si–O bond population	Si–O bond length (Å)
$Lu_2Si_2O_7$	0.5575	1.6103
$Y_2Si_2O_7$	0.5938	1.6046
$Sc_2Si_2O_7$	0.6000	1.6112
$Yb_2Si_2O_7$	0.6125	1.6082

Table 2
Mulliken bond populations and bond length of Si–O bonds in the substituted $Y_2Si_2O_7$ disilicates ($Y_{2-2x}RE_{2x}Si_2O_7$, RE = Lu, Y, Sc, Yb, x = 0.25, 0.5).

	Si–O bond population	Si–O bond length (Å)
$Y_{1.5}Lu_{0.5}Si_2O_7$(Y:Lu = 75:25)	0.5825	1.6023
$Y_{1.5}Sc_{0.5}Si_2O_7$(Y:Sc = 75:25)	0.5975	1.6054
$Y_{1.5}Yb_{0.5}Si_2O_7$(Y:Yb = 75:25)	0.5988	1.6018
$YLuSi_2O_7$ (Y:Lu = 50:50)	0.5700	1.6020
$YScSi_2O_7$ (Y:Sc = 50:50)	0.5950	1.6067
$YYbSi_2O_7$ (Y:Yb = 50:50)	0.6000	1.6023

$Y_2Si_2O_7$, $Sc_2Si_2O_7$, and $Yb_2Si_2O_7$ are constructed using the parameters obtained from references,[25–27] followed by geometric optimization. The structure for $Lu_2Si_2O_7$ is constructed by the substitution of Lu for Yb in $Yb_2Si_2O_7$ because $Lu_2Si_2O_7$ and $Yb_2Si_2O_7$ share the same structure.[24] The optimized structures are shown in Fig. 1.

Mulliken analysis is carried out on these optimized structures. The results are shown in Table 1. It is seen that the Mulliken populations of Si–O bonds are in the following order: $Yb_2Si_2O_7 > Sc_2Si_2O_7 > Y_2Si_2O_7 > Lu_2Si_2O_7$. As aforementioned, the Mulliken population reflected the strength of the bonds. The larger is the bond population, the stronger the bonds are. Since the water corrosion behavior of silicates is determined by the strength of Si–O bonds, the water corrosion resistance of these rare earth disilicates should be in the order of $Yb_2Si_2O_7 > Sc_2Si_2O_7 > Y_2Si_2O_7 > Lu_2Si_2O_7$. This seems contradictory to some experimental results, in which $Lu_2Si_2O_7$ showed good water corrosion resistance.[13] However it is found that direct comparison between the existing experimental results and theoretical prediction could be very difficult because of the contamination, the accuracy of test facility, and the uncertain in testing conditions. For example, the aluminum contamination can cause substantial changes in water corrosion behavior of rare earth silicates.[14] In order to compare the experimental results with the theoretical prediction, those data obtained in pure environments without any contaminations should be used. However, the reported experimental results tested in pure environments are very limited. There are only a few literatures[1,13] that reported the corrosion results of $Lu_2Si_2O_7$, $Yb_2Si_2O_7$, and $Y_2Si_2O_7$ in SiC tube (high purity environments). In these papers, the results clearly indicated that the weight loss of $Lu_2Si_2O_7$ was more than those of $Yb_2Si_2O_7$ and $Y_2Si_2O_7$, which are consistent with our calculations, verifying the theoretical model.

Previous studies[2] revealed that the substitution of Sr for Ba in barium aluminosilicates could increase the water corrosion resistance. In this paper, we investigate the substitution effects for RE silicates. We select $Y_2Si_2O_7$ as the basic structure. Different percentages (25%, 50%) of rare earth elements (Sc, Yb, Lu) are used to substitute yttrium in $Y_2Si_2O_7$ symmetrically, followed by the geometric optimization. As can be seen from Fig. 2, all of the optimized structures keep the original structural type. Mulliken analysis is carried out on these structures. The obtained Mulliken populations of Si–O bonds are listed in Table 2. It is seen that the substitution of Yb and Sc caused the increase in Mulliken population of Si–O bonds. The higher contents of substitution elements lead to the larger Si–O bond population. Thus, Yb or Sc substituted $Y_2Si_2O_7$ should have a better water corrosion resistance than pure $Y_2Si_2O_7$. These predictions are consistent with the previous experimental results.[14,15] However, the calculation suggests that the substitution of Lu results in the decrease in the water corrosion resistance of $Y_2Si_2O_7$, which conflicts with the experimental results.[15] The possible reason could be aluminum contamination.[17] These results suggest that the different rare earth elements have different effects on the Si–O strength. The order is Yb > Sc > Y > Lu.

It is worthy of note that Mulliken population is sensitive to the atomic basis set with which they were calculated. For the materials with the same structure, the Mulliken population yields useful information to determine their water corrosion resistance. For the materials with different structures, it is still unclear how to use Mulliken population to determine the relative values of bond strength. This will limit the application of the Mulliken population for comparing the water corrosion resistance of silicates with different structures. Even so, Mulliken analysis can provide a useful guideline for design and selection of materials for achieving better water corrosion resistance.

4. Conclusions

Mulliken analysis based on the first principle theory was used to determine the water corrosion resistance of rare earth disilicates. The Mulliken populations of Si–O bonds in $Yb_2Si_2O_7$, $Sc_2Si_2O_7$, $Y_2Si_2O_7$, $Lu_2Si_2O_7$, and substituted $Y_{2-x}RE_xSi_2O_7$ (RE = Yb, Sc, Lu) were calculated. The following conclusions can be drawn:

1. The calculated water corrosion resistance was in the order of $Yb_2Si_2O_7 > Sc_2Si_2O_7 > Y_2Si_2O_7 > Lu_2Si_2O_7$, which are consistent with the existed experimental results.
2. Different substituted elements have different effects on the water corrosion resistance of Yb and Sc can enhance the water corrosion resistance, while Lu decreases the water corrosion resistance. This was also confirmed by the existed experimental results.
3. Mulliken analysis could provide us a computational method to design and select silicate materials in order to get a better water corrosion resistance.

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