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Structural and transport properties of FeO-TiO_2 system through molecular dynamics simulations

Helin Fan, Dengfu Chen*, Peng Liu, Huamei Duan*, Yunwei Huang, Mujun Long, Tao Liu

College of Materials Science and Engineering, Chongqing University, Chongqing 400044, People's Republic of China

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ABSTRACT

The viscosity of titanium slag has a crucial effect on the separation efficiency from metallic iron, the foaming extent of slag, and the kinetics of smelting reactions. Properties of slag depend on its microstructures essentially. Molten FeO-TiO_2 system was investigated through molecular dynamics simulations to characterize its structural and transport properties at 1973 K. With FeO content increasing from 5 to 50%, $CN_{Ti\text{-}O}$ decreases from 6.02 to 5.87, $CN_{O\text{-}Ti}$ decreases from 2.95 to 1.89, and the structural strength of the FeO-TiO_2 system is hence reduced. [TiO_6] octahedron is only one stable structural unit and is distorted in molten FeO-TiO_2 system. [TiO_6] octahedrons are connected by two ways: edge-sharing Ti-Ti and corner-sharing Ti-Ti. The edge-sharing Ti-Ti has stronger combining capacity than the corner-sharing Ti-Ti. The structural strength and viscosity of FeO-TiO_2 system will be reduced by the transformation from Ti-O-Ti to Fe-O-Ti, which is resulted from the addition of FeO. Furthermore, the self-diffusion coefficients of Fe^{2+}, Ti^{4+}, and O^{2-} follow the order: $Fe^{2+} > Ti^{4+} > O^{2-}$. With FeO content increasing from 5 to 50%, the viscosity of molten FeO-TiO_2 system decreases from 0.1272 to 0.0232 Pa·s. The results will contribute to understand and predict the macroscopic properties of high-temperature titanium slag.

1. Introduction

Titanium white and titanium metal are the main products of titanium industry. Titanium white is widely applied in the fields of coating, painting, paper, plastics, rubber, and ceramic due to its non-toxicity, opacity, whiteness and brightness [1,2]. Titanium metal has various applications such as aviation, aerospace, biomedical, marine, and nuclear waste storage because of its high corrosion resistance, high specific strength, light weight, high melting point, and high chemical/heat stability [3,4]. Both titanium white and titanium metal are produced from titanium-bearing materials. Titanium-bearing materials are eagerly and largely required due to the increasing demands of titanium white and titanium metal. Currently, the valued titanium-bearing materials are natural rutile and ilmenite. With the declining resource of natural rutile, ilmenite has become the main raw material in titanium industry [5]. Panzhihua, located in the southwestern of China, holds ilmenite reserves of 870 million tons, accounting for 35.17% of total reserves in the world [6]. The electric furnace smelting was regarded as the dominating process to dispose ilmenite in China [7].

During the electric furnace smelting, the iron oxide in ilmenite is reduced by a reducing agent to the metallic iron while the titanium oxide in ilmenite is left in the slag. The titanium-bearing slag produced from ilmenite smelting in the electric furnace is called “titanium slag”. Due to their differences in viscosity and density, titanium slag and metallic iron gather in the top and bottom of the molten bath, respectively. In fact, the viscosity of slag has a crucial effect on the separation efficiency from metallic iron, the foaming extent of slag, and the kinetics of smelting reactions [8]. Therefore, it is significant to study the viscosity of titanium slag. Handfield et al. [9] revealed that the viscosity of titanium slag was 30 mPa·s with TiO_2 content varying from 67 to 80%. Gao et al. [10] claimed that FeO, CaO, and MgO would decrease the viscosity of titanium slag. Zhao et al. [11] subsequently discovered that Al_2O_3 would increase the viscosity of titanium slag severely and deteriorate the state of electric furnace smelting. Song et al. [12] reported that CaO had more remarkable influence on the reduction of the viscosity of titanium slag than MgO.

Although there are some research about viscosity of titanium slag, essential explanations are absent for its corresponding flow behavior. In fact, the macroscopic properties (such as viscosity) of slag depend on its microstructures essentially. Therefore, it is essential to investigate the structural properties of slag. In recent decades, the structural properties of titanium-bearing slag were intensively analyzed and acquired through many characterization techniques, such as X-ray diffraction [13–24], Raman spectroscopy [13,15–20,23,24], Fourier transform

* Corresponding authors.
E-mail addresses: chendfu@cqu.edu.cn (D. Chen), duanhuamei@cqu.edu.cn (H. Duan).

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infrared (FTIR) [14,16–18,22,23], X-ray photoelectron spectroscopy (XPS) [21,22], and Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) [15,18]. But almost of all the characterization techniques were employed for the quenching slag, which was obtained by a quenching method from the high-temperature slag. In fact, there are still abroad controversy about the quenching method to keep the structure of high-temperature slag. On the other hand, molecular dynamics (MD) has been widely employed to calculate the structural properties of titanium-bearing slag [25–29]. Taking into consideration the controversy of the quenching method and the high chemical activity of titanium slag, MD simulations are suitable to obtain structural properties of titanium slag. Whereas, there are little work of MD simulations applied for titanium slag. Therefore, it is essential to study the structural properties of the titanium slag though MD simulations.

FeO-TiO_2 binary system accounts for approximately 90% components of titanium slag and represents the system of titanium slag. In this study, the objective is to characterize the structural and transport properties of molten FeO-TiO_2 system. The classical MD simulations were carried out to investigate the particle radical distribution function (RDF), coordinate number (CN), distributions of bond angles, mean square displacement (MSD), self-diffusion coefficient, and viscosity in the molten FeO-TiO_2 system at 1973 K with FeO content increasing from 5 to 50%. The results will contribute to understand and predict the macroscopic properties of high-temperature titanium slag.

2. Simulation methods

2.1. Interatomic potential

Because of its successful and general application in MD simulations of melts, the two-body potential function of Born-Mayer-Huggins (BMH) was applied to describe pair interactions of Ti-Ti, Ti-O, Fe-O, and O-O. The BMH function composed of the long-range Coulomb interaction, short-range repulsion interaction, and van der Waals force. On the other hand, a Lennard-Jones (L-J) two-body potential function was applied to describe pair interactions of Fe-Fe and Fe-Ti in this study. Parameters for pair interactions of Ti-Ti, Ti-O, and O-O for BMH potential were referenced from Hirao's work [30]. Parameters for Fe-O were obtained from the calculations performed by Belashchenko [31], while parameters for pair interactions of Fe-Fe and Fe-Ti for L-J potential were collected from Rappe's work [32]. Parameters for BMH and L-J potentials are listed in Tables 1 and 2, respectively. The BMH and L-J potential function are displayed as Eqs. (1) and (2), respectively.

$$U_{ij}(r) = \frac{q_i q_j}{r_{ij}} + A_{ij}\exp(-B_{ij}r) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

$$U_{ij}(r) = D_0\left\{\left(\frac{R_0}{r_{ij}}\right)^{12} - 2\left(\frac{R_0}{r_{ij}}\right)^{6}\right\} \quad (2)$$

where $U_{ij}(r)$ is the interatomic potential between atoms i and j; q_i and q_j are charges of atoms i and j, respectively; r_{ij} is the distance between atoms i and j; A_{ij}, B_{ij}, and C_{ij} are parameters for the BMH potentials; D_0 is the depth of the potential well; R_0 is the distance where potential function reaches its minimum.

The accuracy of such potential sets was evaluated by comparing experimental and calculated lattice parameters of relevant crystals.

Table 1
Parameters for BMH potential.

Atom 1	Atom 2	A_{ij} (eV)	B_{ij} (1/Å)	C_{ij} (eV·Å^6)
Ti	Ti	35,133.15	6.25	0
Ti	O	242,696.25	6.06	0
Fe	O	1900.21	3.45	0
O	O	1,497,693.51	5.88	17.35

Table 2
Parameters for L-J potential.

Atom 1	Atom 2	D_0 (eV)	R_0 (Å)
Fe	Fe	0.00056	2.91
Fe	Ti	0.00064	3.04

Table 3
Comparison between experimental and calculated structure of relevant crystals.

		a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	V(Å^3)
TiO_2(P42/mnm)	Exp [34]	4.594	4.594	2.959	90	90	90	62.449
	Cal	4.546	4.546	3.023	90	90	90	62.474
FeO(Fm-3m)	Exp [35]	4.354	4.354	4.354	90	90	90	82.540
	Cal	4.405	4.404	4.404	90	90	90	85.436
Fe_2TiO_4(Fm-3)	Exp [36]	8.527	8.527	8.527	90	90	90	612.00
	Cal	8.588	8.588	8.588	90	90	90	633.40
$FeTiO_3$(R-3)	Exp [37]	5.141	5.141	14.225	90	90	120	325.60
	Cal	5.19	5.19	14.659	90	90	120	341.96
$FeTi_2O_5$(Cmcn)	Exp [38]	3.756	9.812	10.093	90	90	90	371.97
	Cal	3.777	9.957	10.232	90	90	90	384.80

According to the phase diagram of FeO-TiO_2 system, the complex crystals in FeO-TiO_2 system include ulvospinel, ilmenite, and pseudo-brookite [33]. The experimental lattice parameters of relevant crystals are well reproduced within negligible deviation as shown in Table 3 [34–38]. It can be deduced from Table 3 that such potential sets are accurate and reliable.

2.2. Calculation method and procedure

The Materials Explorer5.0 (FUJITSU LIMITED) was applied for the MD simulations in this work. Now that the number of calculated atoms was always limited, the periodic boundary conditions were performed on all faces of the model box to obtain an infinite atom system with no boundaries. With the periodic boundary conditions, the calculated results were convincible enough to reflect the real system. All MD simulations were performed with NVT ensemble, which implied that the simulations were run with a system with a constant value of atomic number (N), sample volume (V), and temperature (T). Gear's predictor-corrector method was employed to solve the motion equations [39]. The temperature of the system was controlled by a velocity scaling method. The Ewald method was applied for the long-range Coulomb interaction with a precision of 10^{-5}. The cutoff radius was set to 10 Å in term of the short-range forces to balance the calculation accuracy and cost. The density of all samples was set as a constant of 4.00 g/cm^3 to simply the calculation because the effect of density difference on structure and property was small [40]. Composition, atomic number and length of cubic box model for samples at 1973 K are shown in

Table 4
Composition, atomic number and length of cubic box model for samples at 1973 K.

Sample	Mass fraction (%)		Atomic number				Density (g/cm^3)	Length (Å)
	TiO_2	FeO	Ti	Fe	O	Total		
1	95	5	1283	75	2642	4000	4.00	35.5116
2	90	10	1232	152	2616	4000	4.00	35.6692
3	85	15	1179	231	2590	4000	4.00	35.8272
4	80	20	1125	313	2562	4000	4.00	35.9931
5	75	25	1069	396	2535	4000	4.00	36.1550
6	70	30	1012	482	2506	4000	4.00	36.3247
7	65	35	953	571	2476	4000	4.00	36.4986
8	60	40	892	661	2446	3999	4.00	36.6667
9	55	45	830	755	2415	4000	4.00	36.8496
10	50	50	766	851	2383	4000	4.00	37.0307