THE TEMPERATURE-INDUCED STRUCTURAL CHANGE IN AMORPHOUS TiO_2

SỰ THAY ĐỔI CẤU TRÚC THEO NHIỆT ĐỘ TRONG TiO_2 VÔ ĐỊNH HÌNH

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ABSTRACT

Molecular dynamic simulation has been conducted to study the temperature-induced structural change in amorphous titanium dioxide. The simulation model consisting of 1200 atoms is prepared at zero pressure and temperature in the range from 315 to 900K. The local microstructure of considered models is analyzed through the partial radial distribution functions, coordination number, bond-angle and void statistics. The simulation reveals a significant change in void and void aggregation at different temperature, but the angle distribution for basic units TiO_x is lightly sensitive to temperature variation; here x=4, 5 and 6. The number of O-voids and Ti-voids strongly depends on temperature. We assume a structural model of amorphous titanium dioxide which constitutes a network of undeformed and identical TiO_x units. The heating or cooling leads only to change in the density and corresponding number of basic units.

TÓM TẮT

Phương pháp mô phỏng động lực học phân tử đã được sử dụng để nghiên cứu sự thay đổi cấu trúc ôxít titan vô định hình. Mô hình gồm 1200 nguyên tử được xây dựng ở áp suất 0 Gpa và vùng nhiệt độ từ 315 đến 900 K. Cấu trúc địa phương của mô hình được phân tích qua hàm phân bố xuyên tâm, phân bố số phối trí, phân bố góc và phân bố lỗ trống. Kết quả mô phỏng đã chỉ ra một sự thay đổi của lỗ trống và đám lỗ trống ở các nhiệt độ khác nhau, nhưng phân bố góc trong các đơn vị cấu trúc TiO_x thay đổi nhẹ với nhiệt độ; với x=4, 5 và 6. Số lượng lỗ trống lớn hơn hoặc bằng nguyên tử Oxy (O-voids) và số lượng lỗ trống lớn hơn hoặc bằng nguyên tử Ti (Ti-voids) phụ thuộc mạnh vào nhiệt độ. Chúng tôi cho rằng mô hình cấu trúc của ôxít titan vô định hình gồm một mạng các đơn vị cấu trúc TiO_x giống nhau và không biến dạng. Quá trình nung nóng hoặc làm nguội chỉ dẫn tới làm thay đổi mật độ và số lượng các đơn vị cấu trúc cơ bản.

I. INTRODUCTION

Titanium dioxide is a very important material with technological application in many fields. In crystalline state TiO_2 has three stable forms: rutile, anatase, and brookite [1-3], all of which have been prepared synthetically [4]. Amorphous TiO_2 is formed at room temperature, when it precipitates from sulfate or chloride solutions. TiO_2 does not form glass by itself, it forms glass when combined with some glass-modifying oxides [7]. So the sol-gel technique is widely employed to produce, for example, glasses in bulk and thin films of TiO_2-SiO_2 mixtures. By analogy to crystalline, amorphous TiO_2 has been investigated intensively by both experiment and the simulation [5-9]. Salama *et al.* [6] uses EXAFS-XANES absorption techniques to study structure of the amorphous state by dispersing TiO_2 microcrystallines on SiO_2. The phase transformation in treatment of bulk gel-derived TiO_2 and the microstructure of bulk amorphous TiO_2 produced by similar method have been studied using Raman spectroscopy and X-ray absorption spectroscopy. It found that titanium atom has a octahedral coordination in all investigated phases [8,9]. More detail information about the microstructure of titanium dioxide can be inferred from simulation. Molecular dynamic simulation of model containing 1200 atoms shows that the Ti-O and O-O nearest distance are 1.77 and 2.65Å, respectively. Moreover, the Ti coordination number is estimated to 5.4 and he concludes that amorphous phase consists mainly of distorted octahedral units [5]. This compares well with experiment. However, as far as we know, the temperature-induced structure change in amorphous titania is not investigated yet. Furthermore, the void and void aggregation in this material is studied very little, although they attract great interest in both liquid and glass science. Therefore, it is worth carrying out the

study that mention problem. The current paper is organized as follows: after brief introduction, in section 2 we describe the calculation technique to prepare model and derive the structural characteristics from it. Result and discussion of simulation data is presented in section 3. Conclusions will be given in section 4

II. CALCULATION METHOD

The molecular dynamic (MD) simulation has done on systems containing 1200 particles (400 Ti and 800 O) and using Vashishta potential [5]. The model is constructed as follows. The initial configuration is generated by randomly placing all atoms in a cubic box with condition that the distance between i^{th} and j^{th} atom is above 1.0 Å. This configuration is treated by statistic relaxation method within 50,000 steps. Then, the sample is heated to 315K and at zero pressure during 20,000 MD steps. Next, the system is allowed to reach equilibrium for over 50,000 MD steps without any disturbance. From this well-equilibrated TiO_2 we prepared 7 models by heating up at different temperature and at zero pressure by several thousand MD steps. Then the sample is hold at constant pressure and temperature by 100,000 MD steps to reach well equilibrium. After that structural characteristics are computed. To calculate the coordination number and bond-angle we adopt the fixed cutoff radius by 3.58, 2.26 and 3.32 Å for Ti-Ti, Ti-O and O-O pair, respectively. Those cut-off radii are chosen as the position of the minimum after the first peak in the radial distribution function $g_{ij}(r)$. All structural characteristics have been computed for every run and in order to improve statistics they are averaged over last 1000 configurations separated by 5 MD steps.

III. RESULTS AND DISCUSSIONS

The structural characteristics of constructed models are summarized in Table 1 and it can be seen that the model reproduces well experimental data reported in [9]. The first peak of partial radial distribution function (PPDFs) for Ti-O pair is located at 1.76Å closed to simulation data in Ref. 12 (1.77 Å). From the position of the first peak in $g_{O-O}(r)$ we can determine O-O nearest-neighbor distance that is in the range of 2.80-2.84 Å. These values are very likely close to one obtained from the anatase (2.8202 Å) [1], brookite (2.495- 2.993 Å) [3], and rutile (2.959 Å) [2].

Table 1. Structural characteristics of amorphous titania. r_{ij}, g_{ij}- the position and height of the first peak in the RDFs $g_{ij}(r)$; Z_{ij}- the averaged coordination number. Here 1-1 for the Ti-Ti pair; 1-2 for the Ti-O; 2-1 for the O-Ti; and 2-2 for the O-O.

Temperature,	r_{ij}(Å)			g_{ij}			Z_{ij}			
K	1-1	1-2	2-2	1-1	1-2	2-2	1-1	1-2	2-1	2-2
315	3.06	1.76	2.82	2.29	11.23	3.20	7.23	5.16	2.08	13.76
400	3.08	1.76	2.80	2.30	10.59	3.13	7.17	5.16	2.08	13.73
500	3.06	1.76	2.82	2.22	9.88	3.10	7.05	5.15	2.08	13.67
600	3.10	1.76	2.84	2.09	9.59	3.04	6.90	5.14	2.07	13.56
700	3.14	1.76	2.80	2.17	9.20	2.95	6.77	5.15	2.07	13.44
800	3.12	1.76	2.80	2.10	9.01	2.87	6.49	5.13	2.07	13.31
900	3.16	1.76	2.80	2.09	8.80	2.82	6.40	5.12	2.06	13.18

Table 2. The distribution of oxygen-connectivity in amorphous titania. m is number of bridging oxygen that two adjacent TiO_x are bonded to. Next columns show the percentage of connectivity. For example, at 400K there are 6.05% of connectivity by two bridging oxygen.

M	Temperature, K						
	315	400	500	600	700	800	900
1	94.30	93.86	94.31	95.25	95.88	96.50	96.76
2	5.59	6.05	5.68	4.74	4.09	3.49	3.21
3	0.11	0.09	0.00	0.01	0.03	0.01	0.03
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00

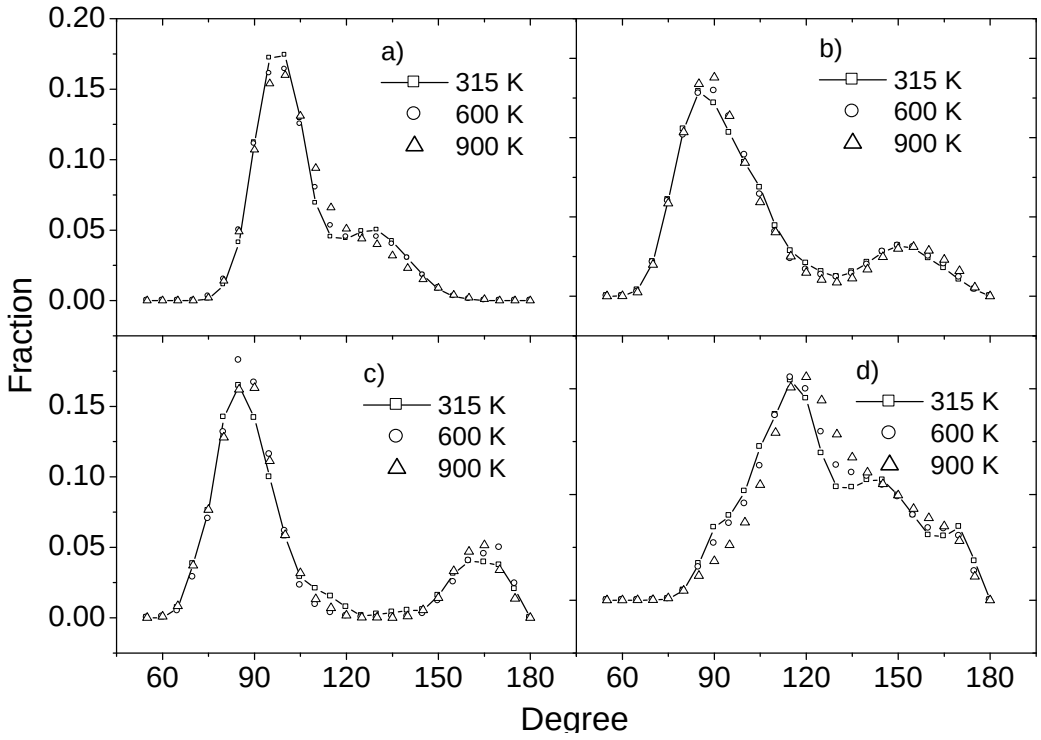

Fig.1 The distribution for O-Ti-O bond-angle in TiO_4 (a), TiO_5 (b), TiO_6 (c) and for Ti-O-Ti angle between two adjacent TiO_x (d)

Useful information about short-range order in network structure can be inferred from the bond-angle distributions. In this work we only calculate the most important angle such as the O–Ti–O and Ti–O–Ti angles. The first angle characterizes the atomic arrangement inside basic unit TiO_x and the second one provides the connectivity between them. In figure 1 we display the angle distribution calculated separately for TiO_4, TiO_5 and TiO_6 units. As shown in Fig. 1, there are several peaks located at 100^o for O-Ti-O and TiO_4; 85^o and 150^o for O-Ti-O and TiO_5, 85^o and 160^o for O-Ti-O and TiO_6, and 115^o for Ti-O-Ti. Note that for TiO_5 and TiO_6 two peaks appear and small shoulder locate at $101\text{-}130^0$ for TiO_4. This shoulder absents for tetrahedral molecular glass

Table 3. The volume void cluster (VC) distribution. First column shows the range of volume: mV_{Ti} - $(m+1)V_{Ti}$. Here V_{Ti} is the volume of Ti atom, m=0, 1,.., 6. Next columns indicate the number of VC detected in the model. For example, at 400K there are 257 VC with the volume in range of 10.54-21.08Å^3.

Temperature	Volume range, (×10.54Å^3)						
K	0-1	1-2	2-3	3-4	4-5	5-6	>6
315	790	257	52	9	2	1	0
400	772	257	54	3	3	3	0
500	841	260	54	4	2	3	1
600	766	261	53	7	1	2	1
700	828	242	68	5	5	3	0
800	793	247	84	10	4	0	0
900	762	241	83	21	2	1	2

such as SiO_2, GeO_2 and Al_2O_3. Regarding temperature variation, we observe a slight change in bond-angle statistic as well as coordination number. Table 2 displays the distribution of oxygen-connectivity. Two adjacent units TiO_x are linked to each other through common oxygen, which is called bridge-oxygen. In accordance to Table 2, most connectivity is one-oxygen and its proportion increases with temperature. The number of two-oxygen connectivity, in contrast decreases. As mention above, void and void aggregation is important characteristic providing a complementary description of amorphous structure. If an atom is considered as a sphere, then there is a part of simulation box in which no atom exits. The void is denoted to a sphere that is in contact with four atoms and does not overlap with any atom. The radii distribution of voids (RDP) is presented in Figure 2. The RDP has a peak at 1 Å and radii of void appears in the range of 0.3-1.9 Å. It is essential to note that the obtained RDP is strongly differ from calculated RDP for Al_2O_3 in ref. [10], which shows two peaks corresponding to voids surrounding Al and O. It means that due to more compacting in comparison with Al_2O_3 a number of large void around cation like Al and Ti is eliminated and it leads to disappearance of second peak in RDP for amorphous TiO_2. We also found a number of large void with radii bigger than radii of Ti and O. Obviously, these voids can freely receive neighboring atoms and participate in diffusion like vacancy diffusion in crystalline materials [11-13]. Void distributes not separately, but they locate together and form a cluster. In this work we examine two kinds of void aggregation: VC and void tube (VT). The VC is a set of voids, which consists of a central void and several another voids overlapped with central void and smaller than one. The void tube (VT) is a series of overlapping voids with radii bigger than radii of oxygen atom. From the view of diffusion mechanism, the VT could be a long diffusion path along which oxygen atom can travel freely. In Table 3 we display the volume VC distributions. The VC volume is determined by generating 5000 points in a cube containing the VC. Then the number of point located in VC, n_{in} is computed. The VC volume is given as $V_{VC} = V_{cube}.n_{in}/5000$. Here V_{cube} is volume of the cube where 5000 points are randomly distributed. Most VC detected in all constructed models have volume less than $V_{Ti} = 10.54$ Å^3. Here $V_{Ti} = 4\pi r_{Ti}^3/3$; r_{Ti} is titanium radii. The number of bigger VC (its volume larger than V_{Ti}) is about 30% of all VCs and we found more 60 VCs (6% of total number of VC) with volume three times bigger than VC. Those VCs are not vacancy, but like a microscopic cavity, which may play an essential role for diffusion in amorphous TiO_2. In order to give additional insight into void and void aggregation we also calculate the number of Ti-void and O-void, which is called void with radii bigger than titanium and oxygen radii. The characteristics of void and void aggregation are summarized in Table 4. We can see that the number of

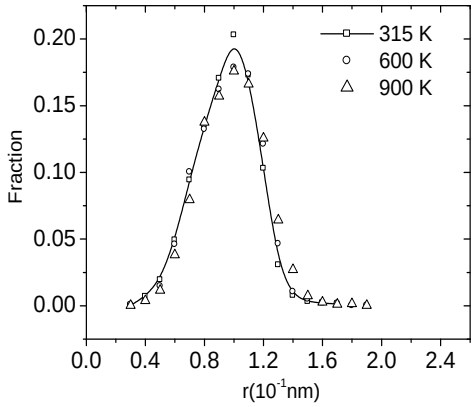

Fig.2 The radii distribution of void

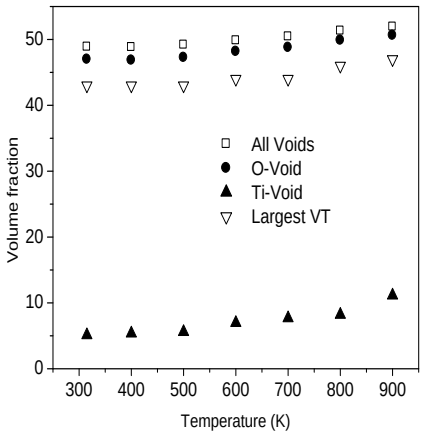

Fig.3 The temperature dependence of volume fraction for different void kinds

Table 4. The characteristics of void aggregations; here N_{void}, $N_{Ti\text{-}void}$, $N_{O\text{-}void}$, N_{VC} , N_{VT} and N_{voidVT} are the number of all voids, number of Ti-void, O-void, VC, VT and the number of voids in largest VT.

Temperature (K)	315	400	500	600	700	800	900
N_{void}	5594	5521	5522	5494	5479	5475	5537
$N_{O\text{-}void}$	5043	4958	4979	5006	5008	5058	5143
$N_{Ti\text{-}void}$	125	139	149	193	202	235	325
N_{VC}	1111	1092	1165	1091	1151	1138	1112
N_{VT}	164	157	186	172	199	184	167
N_{voidVT}	4575	4563	4469	4506	4461	4635	4722

Ti-voids significantly increases with temperature. In particular as temperature increases from 315 to 900 K, it increases about three times (see Table 4). Among detected VTs in each constructed model we found a very large VT which contains most O-voids. The number of O-void in this VT is about 90% of all O-voids and 80% of all voids found in the model. Therefore, the detected largest VT is spread over whole simulation box. Obviously, this VT presents a "diffusion tube" for oxygen atom. Figure 3 displays the volume fraction of various kinds of voids as a function of temperature. We can see that ~49% volume of simulation box is occupied by voids; following 47% by O-voids and ~ 6% by Ti-voids. The largest VT occupy more 43% volume of simulation box. Regarding temperature dependence, the volume fraction of different void kinds monotony increases. For Ti-void we observe the increase in volume fraction by about two times as temperature varies from 315 to 900 K.

IV. CONCLUSIONS

Structures of the amorphous TiO_2 models constructed by molecular Dynamic method and Vashishta potentials are close to experimental data. The simulation reveals that amorphous titania has the octahedral network structure with basic units TiO_4, TiO_5 and TiO_6 linked to each other though one bridging-oxygen atom. We found a number of very large VC with volume three times bigger than volume of titanium. Those VCs like a microscopic cavity and play an essential role for diffusion in amorphous titanium. Furthermore, a large VT is detected in each constructed model and it contains most O-voids that presents a diffusion tube for oxygen. Regarding temperature dependence, the volume fraction of different void kinds increases monotony; especially, the number of Ti-void increases by three times as temperature increases from 315 to 900 K.

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